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SOLIDS AND SURFACES: A CHEMIST'S VIEW
OF BONDING IN EXTENDED STRUCTURES

by

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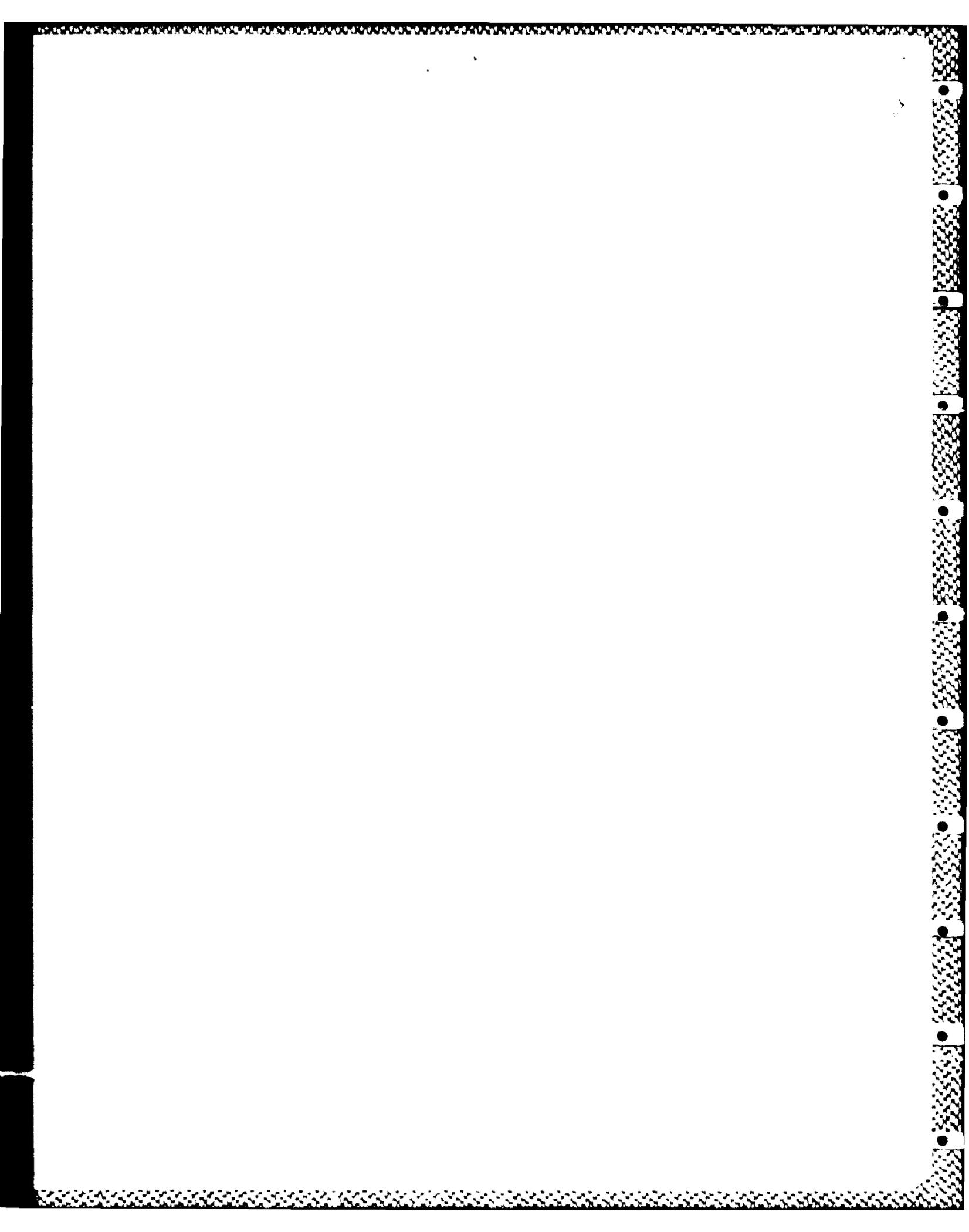
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Roald Hoffmann

for

EARL MUETTERTIES and MIKE SIENKO

Acknowledgement and Preface

The material in this book has been published in two articles in *Angewandte Chemie* and *Reviews of Modern Physics*, and I express my gratitude to the editors of these journals for their encouragement and assistance. The construction of this book from these two articles was suggested by my friend M.V. Basilevsky.

My graduate students, postdoctoral associates and senior visitors to the group are responsible for both teaching me solid state physics and for implementing the algorithms and computer programs that have made this work possible. While in my usual way I've suppressed the computations in favor of explanations, little understanding would have come without those computations. An early contribution to our work was made by Chien-Chuen Wan, but the real computational and interpretational advances came through the work of Myung-Hwan Whangbo, Charles Wilker, Miklos Kertesz, Tim Hughbanks, Sunil Wijeyesekera, and Chong Zheng. This book owes much to their ingenuity and perseverance. Several crucial ideas were borrowed early on from Jeremy Burdett, such as using special k point sets for properties.

Al Anderson was instrumental in getting me started in thinking about applying extended Hückel calculations to surfaces. A coupling of the band approach to an interaction diagram and frontier orbital way of thinking evolved from the study Jean-Yves Saillard carried out of molecular and surface C-H activation. We learned a lot together. A subsequent collaboration with Jérôme Silvestre helped to focus many of the ideas in this paper.



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Important contributions were also made by Christian Minot, Dennis Underwood, Shen-shu Sung, Georges Trinquier, Santiago Alvarez, Joel Bernstein, Yitzhak Apeloig, Daniel Zeroka, Douglas Keszler, Ralph Wheeler, Marja Zonneville, Susan Jansen, Wolfgang Tremel, Dragan Vuckovic and Jing Li.

In the early stages of this work, very important to me was a renewed collaboration with R.B. Woodward, prompted by our joint interest in organic conductors. It was unfortunately cut short by his death in 1979. Thor Rhodin has been mainly responsible for introducing me to the riches of surface chemistry and physics, and I am grateful to him and his students. It was always instructive to try to provoke John Wilkins.

Over the years my research has been steadily supported by the National Science Foundation's Chemistry Division. I owe Bill Cramer and his fellow program directors thanks for their continued support. A special role in my group's research on extended structures has been played by the Materials Research Division of the National Science Foundation. MSC furnished an interdisciplinary setting, a means of interacting with other researchers in the surface science and solid state areas that was very effective in introducing a novice to the important work in the field. I am grateful to Robert E. Hughes, Herbert H. Johnson, and Robert H. Silsbee, the MSC directors, for providing that supporting structure. In the last five years my surface-related research has been generously supported by the Office of Naval Research. That support is in the form of a joint research program with John Wilkins.

One reason it is easy to cross disciplines at Cornell is the existence of the Physical Sciences Library, with its broad coverage of chemistry and physics. I would like to thank Ellen Thomas and her staff for her contributions here. Our drawings, a critical part of the way our research is presented, have been beautifully made over the years by Jane Jorgensen and Elisabeth Fields. I'd like to thank Eleanor Stagg, Linda Kapitany and Lorraine Seager for the typing and secretarial assistance.

This manuscript was written while I held the Tage Erlander Professorship of the Swedish Science Research Council, NFR. The hospitality of Professor Per Siegbahn and the staff of the Institute of Theoretical Physics of the University of Stockholm and of Professor Sten Andersson and his crew at the Department of Inorganic Chemistry at the Technical University of Lund is gratefully acknowledged.

Finally this book is dedicated to two men, two colleagues of mine at Cornell in their time. They are no longer with us. Earl Muetterties played an important role in introducing me to inorganic and organometallic chemistry. Our interest in surfaces grew together. Mike Sienko and his students offered gentle encouragement by showing us the interesting structures they worked on; Mike also taught me something about the relationship of research and teaching. This book is for them - both Earl Muetterties and Mike Sienko were important and dear to me.

Macromolecules extended in one-, two-, three-dimensions, of biological or natural origin, or synthetics, fill the world around us. Metals, alloys, and composites, be they copper or bronze or ceramics, have played a pivotal, shaping role in our culture. Mineral structures form the base of the paint that colors our walls, and the glass through which we look at the outside world. Organic polymers, natural or synthetic, clothe us. New materials - inorganic superconductors, conducting organic polymers - exhibit unusual electric and magnetic properties, promise to shape the technology of the future. Solid state chemistry is important, alive and growing.¹

So is a surface science. A surface - be it of metal, an ionic or covalent solid, a semi conductor - is a form of matter with its own chemistry. In its structure and reactivity, it will bear resemblances to other forms of matter: bulk, discrete molecules in the gas phase and in solution, various aggregated states. And it will have differences. It is important to find the similarities and it is also important to note the differences - the similarities connect the chemistry of surfaces to the rest of chemistry; the differences are what make life interesting (and make surfaces economically useful).

Experimental surface science is a meeting ground of chemistry, physics, and engineering.² New spectroscopies have given us a wealth of information, be it sometimes fragmentary, on the ways that atoms and molecules interact with surfaces. The

tools may come from physics, but the questions that are asked are very chemical - what is the structure and reactivity of surfaces by themselves, and of surfaces with molecules on them?

The special economic role of metal and oxide surfaces in heterogeneous catalysis has provided a lot of the driving force behind current surface chemistry and physics. We always knew that it was at the surface that the chemistry took place. But it is only today that we are discovering the basic mechanistic steps in heterogeneous catalysis. It's an exciting time - how wonderful to learn precisely how Döbereiner's lamp and the Haber process work!

What is most interesting about many of the new solid state materials are their electrical and magnetic properties. Chemists have to learn to measure these properties, not only to make the new materials and determine their structures. The history of the compounds that are at the center of today's exciting developments in high-temperature superconductivity makes this point very well. Chemists must be able to reason intelligently about the electronic structure of the compounds they make, so that they may understand how these properties and structures may be tuned. In a similar way, the study of surfaces must perforce involve a knowledge of the electronic structure of these extended forms of matter. We come here to a problem, that the language which is absolutely necessary for addressing these problems, the language of solid state physics, of band theory, is generally not part of

the education of chemists. It should be, and the primary goal of this book is to teach chemists that language. I will show how it is not only easy, but how in many ways it includes concepts from molecular orbital theory that are very familiar to chemists.

I suspect that physicists don't think that chemists have much to tell them about bonding in the solid state. I would disagree. Chemists have built up a great deal of understanding, in the intuitive language of simple covalent or ionic bonding, of the structure of solids and surfaces. The chemist's viewpoint is often local. Chemists are especially good at seeing bonds or clusters, and their literature and memory are particularly well-developed, so that one can immediately think of a hundred structures or molecules related to the compound under study. From much empirical experience, a little simple theory, chemists have gained much intuitive knowledge of the what, how, and why molecules hold together. To put it as provocatively as I can, our physicist friends sometimes know better than we how to calculate the electronic structure of a molecule or solid, but often they do not understand it as well as we do, with all the epistemological complexity of meaning that "understanding" something involves.

Chemists need not enter a dialogue with physicists with any inferiority feelings at all; the experience of molecular chemistry is tremendously useful in interpreting complex electronic structure (Another reason not to feel inferior: until

you synthesize that molecule, no one can study its properties! The synthetic chemist is quite in control). This is not to say that it will not take some effort to overcome the skepticism of physicists as to the likelihood that chemists can teach them something about bonding. I do want to mention here the work of several individuals in the physics community who have shown an unusual sensitivity to chemistry and chemical ways of thinking: Jacques Friedel, Walter A. Harrison, Volker Heine, James C. Phillips, Ole Krogh Andersen, and David Bullett. Their papers are always worth reading because of their attempt to build bridges between chemistry and physics.

There is one further comment I want to make before we begin. Another important interface is that between solid state chemistry, often inorganic, and molecular chemistry, both organic and inorganic. With one exception, the theoretical concepts that have served solid state chemists well have not been "molecular". At the risk of oversimplification, the most important of these concepts have been the idea that one has ions (electrostatic forces, Madelung energies), and that these ions have a size (ionic radii, packing considerations). The success of these simple notions has led solid state chemists to use these concepts even in cases where there is substantial covalency. What can be wrong with an idea that works, that explains structure and properties? What is wrong, or can be wrong, is that application of such concepts may draw that field, that group of scientists,

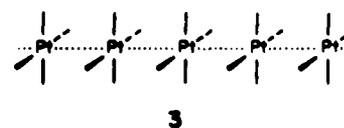
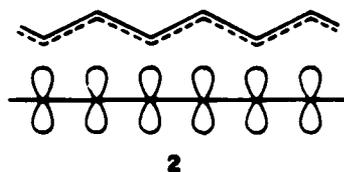
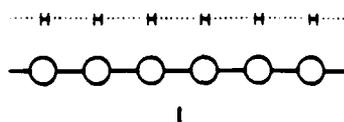
away from the heart of chemistry. At the heart of chemistry, let there be no doubt, is the molecule! My personal feeling is that if there is a choice among explanations in solid state chemistry, one must privilege the explanation which permits a connection between the structure at hand and some discrete molecule, organic or inorganic. Making connections has inherent scientific value. It also makes "political" sense. Again, if I might express myself provocatively, I would say that many solid state chemists have isolated themselves (no wonder that their organic or even inorganic colleagues aren't interested in what they do) by choosing not to see bonds in their materials.

Which, of course, brings me to the exception: the marvelous and useful Zintl concept.³ The simple notion, introduced by Zintl and popularized by Klemm, Busmann, Herbert Schäfer, and others, is that in some compounds A_xB_y , where A is very electropositive relative to a main group element B, that one could just think, that's all, think that the A atoms transfer their electrons to the B atoms, which then use them to form bonds. This very simple idea, in my opinion, is the single most important theoretical concept (and how not very theoretical it is!) in solid state chemistry of this century. And it is important not just because it explains so much chemistry, but especially because it forges a link between solid state chemistry and organic or main group chemistry.

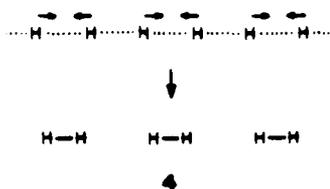
In this book I would like to teach chemists some of the language of bond theory. As many connections as possible will be drawn to traditional ways of thinking about chemical bonding. In particular we will find and describe the tools -- densities of states, their decompositions, crystal orbital overlap populations -- for moving back from the highly delocalized molecular orbitals of the solid to local, chemical actions. The approach will be simple, indeed, oversimplified in part. Where detailed computational results are displayed, they will be of the extended Hückel type,⁴ or of its solid state analogue, the tight binding method with overlap. I will try to show how a frontier orbital and interaction diagram picture may be applied to the solid state or to surface bonding. There will be many effects that are similar to what we know happens for molecules. And there will be some differences.

Orbitals and Bands in One Dimension

It's usually easier to work with small, simple things, and one-dimensional infinite systems are particularly easy to visualize.⁵⁻⁸ Much of the physics of two- and three-dimensional solids is there in one dimension. Let's begin with a chain of equally spaced H atoms, 1, or the isomorphic π -system of a non-bond-alternating, delocalized polyene 2, stretched out for the moment. And we will progress to a stack of Pt(II) square planar complexes, 3, $\text{Pt}(\text{CN})_4^{2-}$ or a model PtH_4^{2-} .

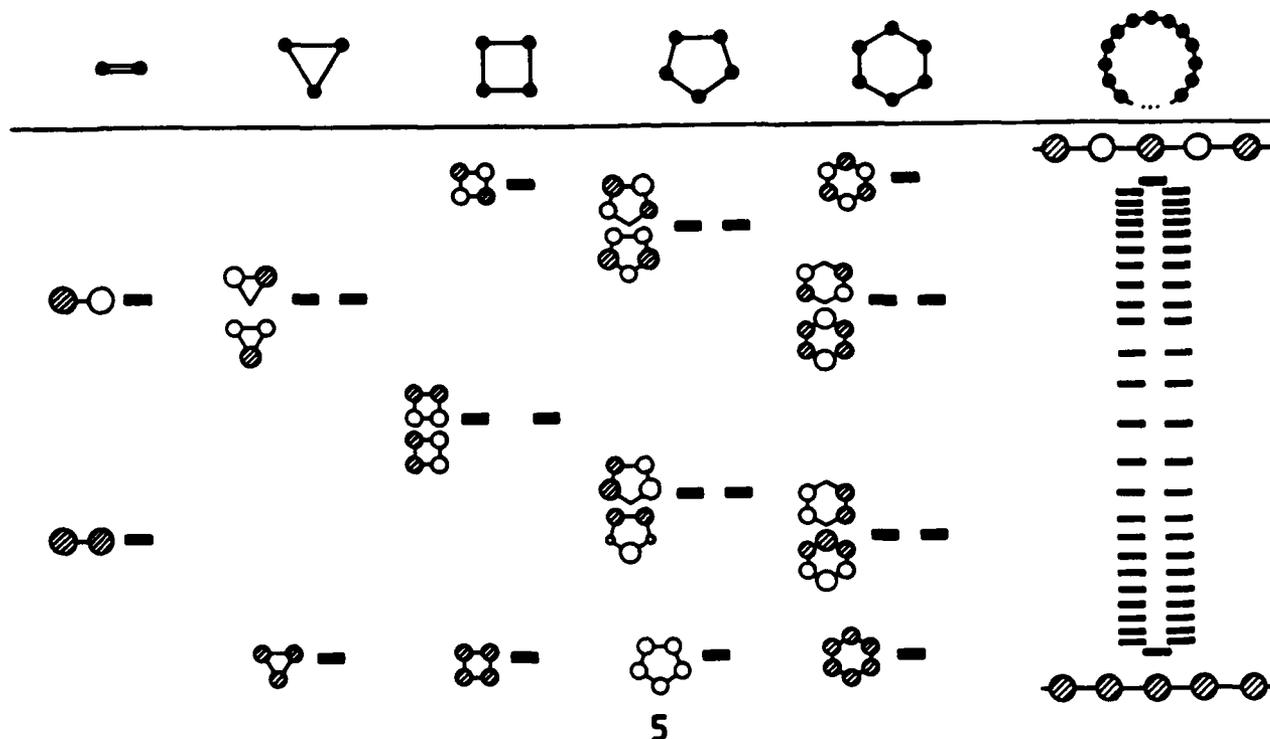


A digression here: every chemist would have an intuitive feeling for what that model chain of hydrogen atoms would do, if we were to release it from the prison of its theoretical construction. At ambient pressure, it would form a chain of hydrogen molecules, 4. This simple bond-forming process would be analyzed by the physicist (we will do it soon) by calculating a



band for the equally spaced polymer, then seeing that it's subject to an instability, called a Peierls distortion. Other words around that characterization would be strong electron-phonon coupling, pairing distortion, or a $2k_F$ instability. And the physicist would come to the conclusion that the initially equally spaced H polymer would form a chain of hydrogen molecules. I mention this thought process here to make the point, which I will do again and again, that the chemist's intuition is really excellent. But we must bring the languages of our sister sciences into correspondence. Incidentally, whether distortion 4 will take place at 2 megabars is not obvious, an open question.

Let's return to our chain of equally spaced H atoms. It turns out to be computationally convenient to think of that chain as an imperceptible bent segment of large ring (this is called applying cyclic boundary conditions). The orbitals of medium-sized rings on the way to that very large one are quite well known. They are shown in 5. For a hydrogen molecule (or ethylene) there is bonding $\sigma_g(\pi)$ below an antibonding $\sigma_u^*(\pi^*)$. For cyclic H_3 or cyclopropenyl we have one orbital below two



degenerate ones; for cyclobutadiene the familiar one below two below one, and so on. Except for the lowest (and occasionally the highest) level, the orbitals come in degenerate pairs. The number of nodes increases as one rises in energy. We'd expect the same for an infinite polymer - the lowest level nodeless, the highest with the maximum number of nodes. In between the levels should come in pairs, with a growing number of nodes. The chemist's representation of the band for the polymer is given at right in 5.

Bloch Functions, k, Band Structures

There is a better way to write out all these orbitals, making use of the translational symmetry. If we have a lattice whose points are labelled by an index $n=0,1,2,3,4$ as shown in 6, and if on each lattice point there is a basis function (a H 1s orbital), χ_0, χ_1, χ_2 etc., then the appropriate symmetry adapted linear combinations (remember translation is just as good a symmetry operation as any other one we know) are given in 6.

$$\begin{array}{cccccc}
 & & \text{---} a \text{---} & & & \\
 n = & 0 & 1 & 2 & 3 & 4 \dots \\
 & \chi_0 & \chi_1 & \chi_2 & \chi_3 & \chi_4
 \end{array}$$

$$\psi_k = \sum_n e^{ikna} \chi_n$$

6

Here a is the lattice spacing, the unit cell in one dimension, and k is an index which labels which irreducible representation of the translation group ψ transforms as. We will see in a moment that k is much more, but for now, k is just an index for an irreducible representation, just like a, e_1, e_2 in C_5 are labels.

The process of symmetry adaptation is called in the solid state physics trade "forming Bloch functions".^{6,8,9-11} To reassure a chemist that one is getting what one expects from 5, let's see what combinations are generated for two specific values of k , $k=0$ and $k=\pi/a$. This is carried out in 7.

$$\begin{aligned}
 k=0 \quad \psi_0 &= \sum_n e^{i0n} \chi_n = \sum_n \chi_n \dots \\
 &= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots \\
 &\quad \text{---} \text{---} \text{---} \text{---} \text{---}
 \end{aligned}$$

$$\begin{aligned}
 k=\frac{\pi}{a} \quad \psi_{\frac{\pi}{a}} &= \sum_n e^{i\pi n} \chi_n = \sum_n (-1)^n \chi_n \\
 &= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots \\
 &\quad \text{---} \text{---} \text{---} \text{---} \text{---}
 \end{aligned}$$

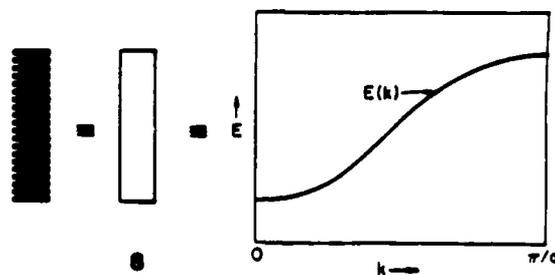
7

Referring back to 5, we see that the wave function corresponding to $k = 0$ is the most bonding one, the one for $k = \pi/a$ the top of the band. For other values of k we get a neat description of the other levels in the band. So k counts nodes as well. The larger the absolute value of k , the more nodes one has in the wave function. But one has to be careful -- there is a range of k and if one goes outside of it, one doesn't get a new wave function, but repeats an old one. The unique values of k are in the interval $-\pi/a \leq k < \pi/a$ or $|k| \leq \pi/a$. This is called the first Brillouin zone, the range of unique k .

How many values of k are there? As many as the number of translations in the crystal, or, alternatively, as many as there are microscopic unit cells in the macroscopic crystal. So let us say Avogadro's number, give or take a few. There is an energy level for each value of k (actually a degenerate pair of levels for each pair of positive and negative k values. There is an

easily proved theorem that $E(k) = E(-k)$. Most representations of $E(k)$ do not give the redundant $E(-k)$, but plot $E(|k|)$ and label it as $E(k)$. Also the allowed values of k are equally spaced in the space of k , which is called reciprocal or momentum space. The relationship between $k = 1/\lambda$ and momentum derives from the de Broglie relationship $\lambda = h/p$. Remarkable k is not only a symmetry label and a node counter, but it is also a wave vector, and so measures momentum.

So what a chemist draws as a band in 5, repeated at left in 8 (and the chemist tires and draws .35 lines or just a block instead of Avogadro's number), the physicist will alternatively draw as an $E(k)$ vs k diagram at right.



Recall that k is quantized, and there is a finite but large number of levels in the diagram at right. The reason it looks continuous is that this is a fine "dot matrix" printer - there are Avogadro's number of points jammed in there, and so it's no wonder we see a line.

Graphs of $E(k)$ vs k are called band structures. You can be sure that they can be much more complicated than this simple one, but no matter how complicated, they can be understood.

Band Width

One very important feature of a band is its dispersion, or band width, the difference in energy between the highest and lowest levels in the band. What determines the width of bands? The same thing that determines the splitting of levels in a dimer, ethylene or H₂, namely the overlap between the interacting orbitals (in the polymer the overlap is that between neighboring unit cells). The greater the overlap between neighbors, the greater the band width. Fig. 1 illustrates this in detail for a chain of H atoms spaced 3, 2 and 1 Å apart. That the bands extend

Figure 1

unsymmetrically around their "origin", the energy of a free H atom at -13.6eV, is a consequence of the inclusion of overlap in the calculations. For two levels, a dimer:

$$E_{\pm} = \frac{H_{AA} \pm H_{AB}}{1 \pm S_{AB}}$$

The bonding E₊ combination is less stabilized than the antibonding one E₋ is destabilized. There are nontrivial consequences in chemistry, for this is the source of 4-electron repulsions and steric effects in one-electron theories.¹¹ A similar effect is responsible for the bands "spreading up" in Fig. 1.

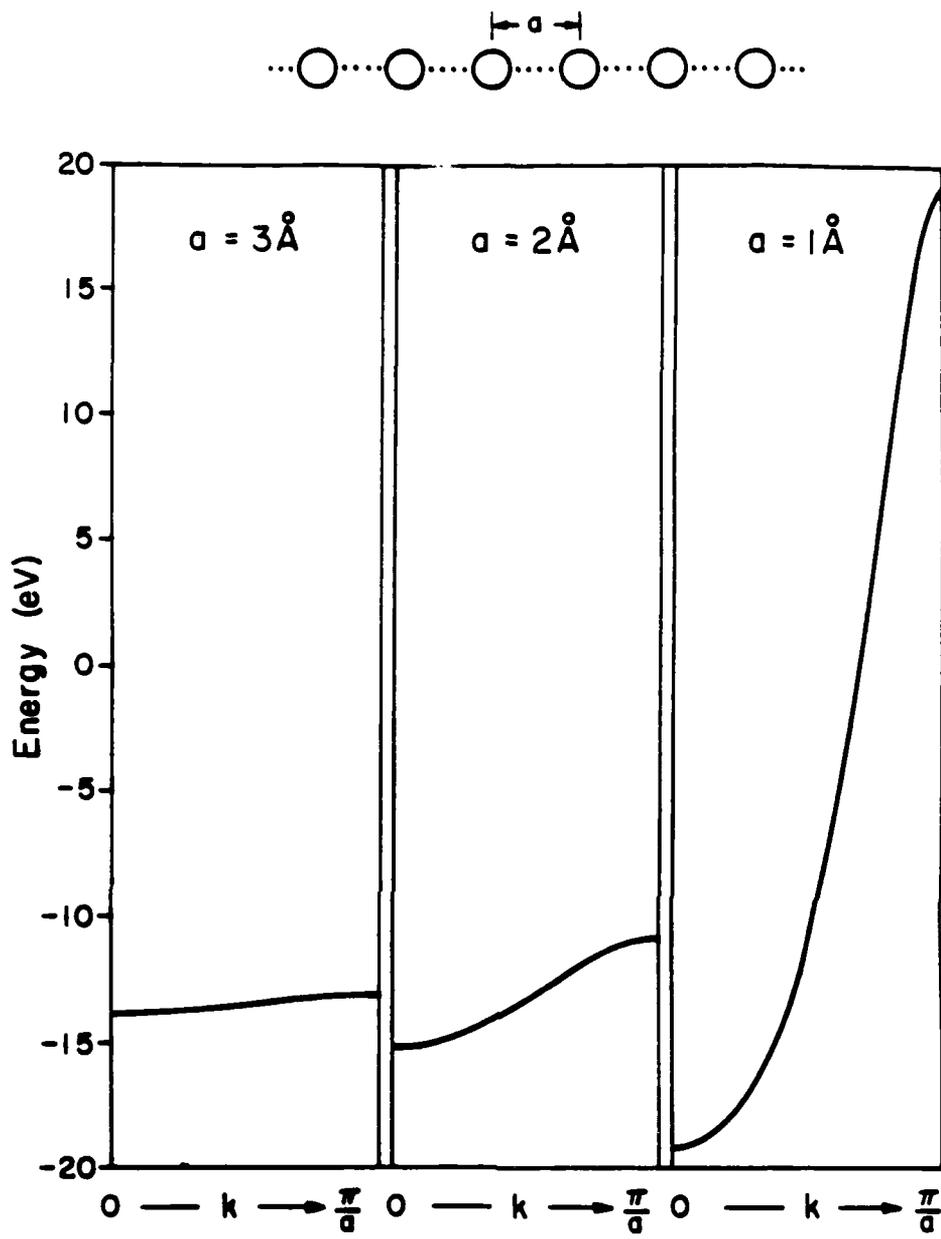
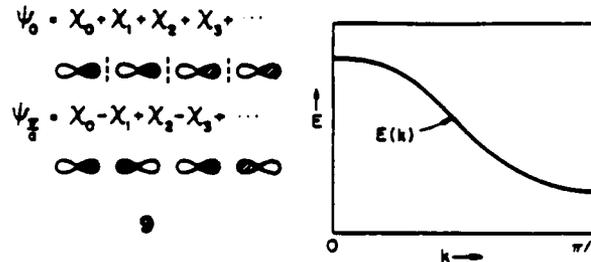


Figure 1. The band structure of a chain of hydrogen atoms spaced 3, 2 and 1 Å apart. The energy of an isolated H atom is -13.6 eV.

See How They Run

Another interesting feature of bands is how they "run". The lovely mathematical algorithm 6 applies in general; it does not say anything about the energy of the orbitals at the center of the zone ($k = 0$) relative to those at the edge ($k = \pi/a$). For a chain of H atoms it is clear that $E(k = 0) < E(k = \pi/a)$. But consider a chain of p functions, 9. The same combinations are given to us by the translational symmetry, but now it is clearly $k = 0$ which is high energy, the most antibonding way to put together a chain of p orbitals.



The band of s functions for the hydrogen chain "runs up", the band of p orbitals "runs down" (from zone center to zone edge). In general, it is the topology of orbital interactions which determines which way bands run.

Let me mention here an organic analogue to make us feel comfortable with this idea. Consider the through-space

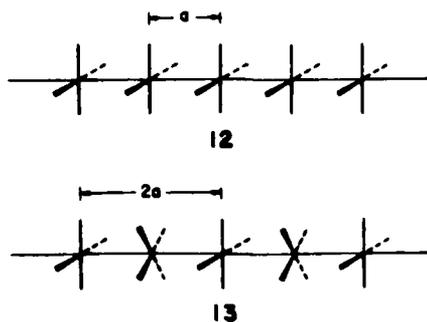


interaction of the three π bonds in 10 and 11. The three-fold symmetry of each molecule says that there must be an a and an e combination of the π bonds. And the theory of group representations gives us the symmetry adapted linear combinations: for a: $x_1 + x_2 + x_3$, for e (one choice of an infinity): $x_1 - 2x_2 + x_3$, $x_1 - x_3$, where x_1 is the π orbital of double bond 1, etc. But there is nothing in the group theory that tells us whether a is lower than e in energy. For that, one needs chemistry or physics. It is easy to conclude from an evaluation of the orbital topologies that a is below e in 10, but the reverse is true in 11.

To summarize: band width is set by inter-unit-cell overlap, and the way bands run is determined by the topology of that overlap.

An Eclipsed Stack of Pt(II) Square Planar Complexes

Let us test the knowledge we have acquired on an example a little more complicated than a chain of hydrogen atoms. This is an eclipsed stack of square planar d^8 PtL_4 complexes, 12. The normal platinocyanides (e.g. $K_2Pt(CN)_4$) indeed show such stacking in the solid state, at the relatively uninteresting $Pt \cdots Pt$ separation of ~ 3.3 Å. More exciting are the partially oxidized materials, such as $K_2Pt(CN)_4Cl_{0.3}$, $K_2Pt(CN)_4(FHF)_{0.25}$. These are also stacked, but staggered, 13, with a much shorter $Pt - Pt$ contact of $2.7 - 3.0$ Å. The $Pt-Pt$ distance had been shown to be inversely related to the degree of oxidation of the material.¹²



The real test of understanding is prediction. So, let's try to predict the approximate band structure of 12 and 13 without a calculation, just using the general principles we have at hand. Let's not worry about the nature of the ligand - it is usually CN^- , but since it is only the square planar feature which is

likely to be essential, let's imagine a theoretician's generic ligand, H^- . And let's begin with 12, because the unit cell in it is the chemical PtL_4 unit, whereas in 13 it is doubled, $(PtL_4)_2$.

One always begins with the monomer. What are its frontier levels? The classical crystal field or molecular orbital picture of a square planar complex (Fig. 2) leads to a 4 below 1 splitting of the d block.¹¹ For 16 electrons we have z^2 , xz , yz , and xy occupied and x^2-y^2 empty. Competing with the ligand-

Figure 2

field-destabilized x^2-y^2 orbital for being the lowest unoccupied molecular orbital (LUMO) of the molecule is the metal z . These two orbitals can be manipulated in understandable ways: π -acceptors push z down, π -donors push it up. Better σ -donors push x^2-y^2 up.

We form the polymer. Each MO of the monomer generates a band. There may (will) be some further symmetry-conditioned mixing between orbitals of the same symmetry in the polymer (e.g. s and z and z^2 are of different symmetry in the monomer, but certain of their polymer MO's are of the same symmetry). But a good start is made by ignoring that secondary mixing, and just developing a band from each monomer level independently.

First a chemist's judgment of the band widths that will develop: the bands that will arise from z^2 and z will be wide, those from xz , yz of medium width, those from x^2-y^2 , xy narrow,

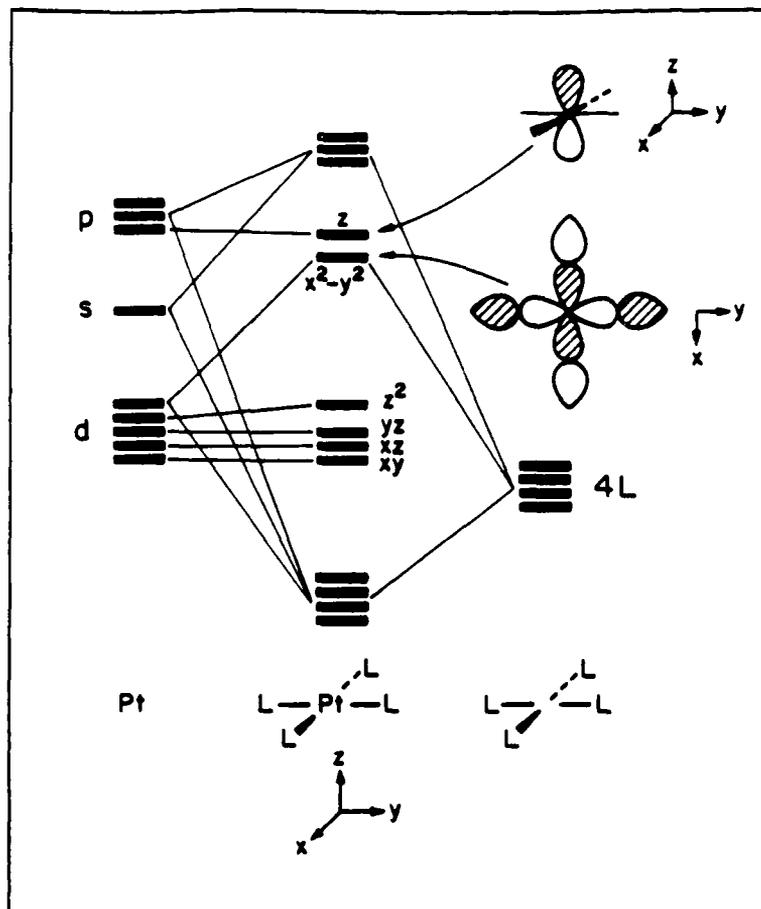
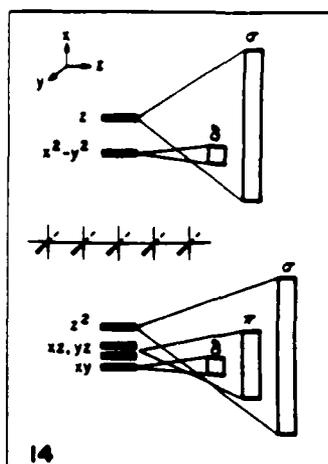
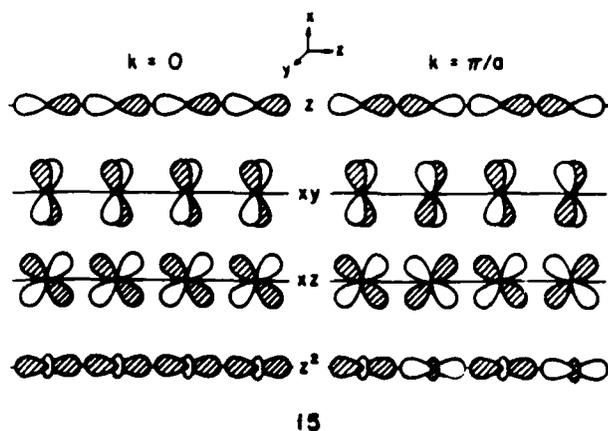


Figure 2. Molecular orbital derivation of the frontier orbitals of a square planar PtL_4 complex.

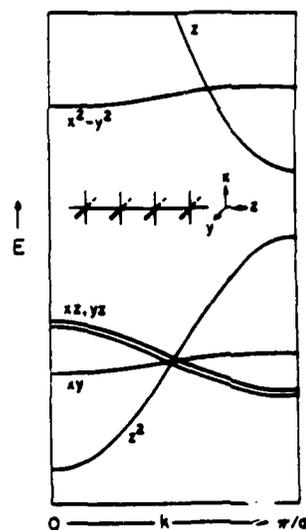


as shown in 14. This characterization follows from the realization that the first set of interactions (z , z^2) is σ type, thus has a large overlap between unit cells. The xz , yz set has a medium π overlap, and the xy and x^2-y^2 orbitals (the latter of course has a ligand admixture, but that doesn't change its symmetry) are δ .

It is also easy to see how the bands run. Let's write out the Bloch functions at the zone center ($k = 0$) and zone edge ($k = \pi/a$). Only one of the π and δ functions is represented in 15. The moment one writes these down, one sees that the z^2 and xy bands will run "up" from the zone center (the $k = 0$ combination is the most bonding) while the z and xz bands will run "down" (the $k = 0$ combination is the most antibonding).



The predicted band structure, merging considerations of band width and orbital topology, is that of 16. To make a real



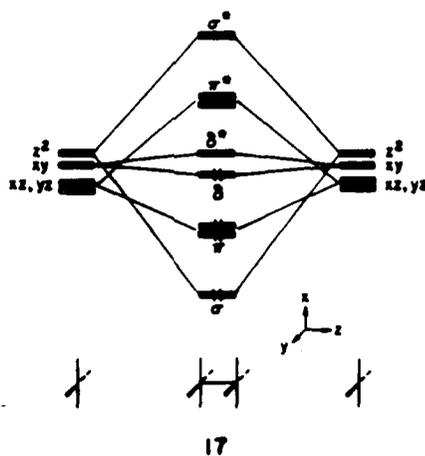
estimate one would need an actual calculation of the various overlaps, and these in turn would depend on the Pt...Pt separation.

The actual band structure, as it emerges from an extended Hückel calculation at Pt-Pt = 3.0 Å, is shown in Fig. 3. It matches our expectations very precisely. There are, of course,

bands below and above the frontier orbitals discussed -- these are Pt-H σ and σ^* orbitals.

Figure 3

To make a connection with molecular chemistry: the construction of 16, an approximate band structure for a platinocyanide stack, involves no new physics, no new chemistry, no new mathematics beyond what every chemist already knows for one of the most beautiful ideas of modern chemistry - Cotton's construct of the metal-metal quadruple bond.¹³ If we are asked to explain quadruple bonding, for instance in $\text{Re}_2\text{Cl}_8^{2-}$, what we do is to draw 17. We form bonding and antibonding combinations



from the $z^2(\sigma)$, xz , $yz(\pi)$ and $x^2-y^2(\delta)$ frontier orbitals of each ReCl_4^- fragment. And we split σ from σ^* by more than π from π^* , which in turn is split more than δ and δ^* . What goes on in the infinite solid is precisely the same thing. True, there are a

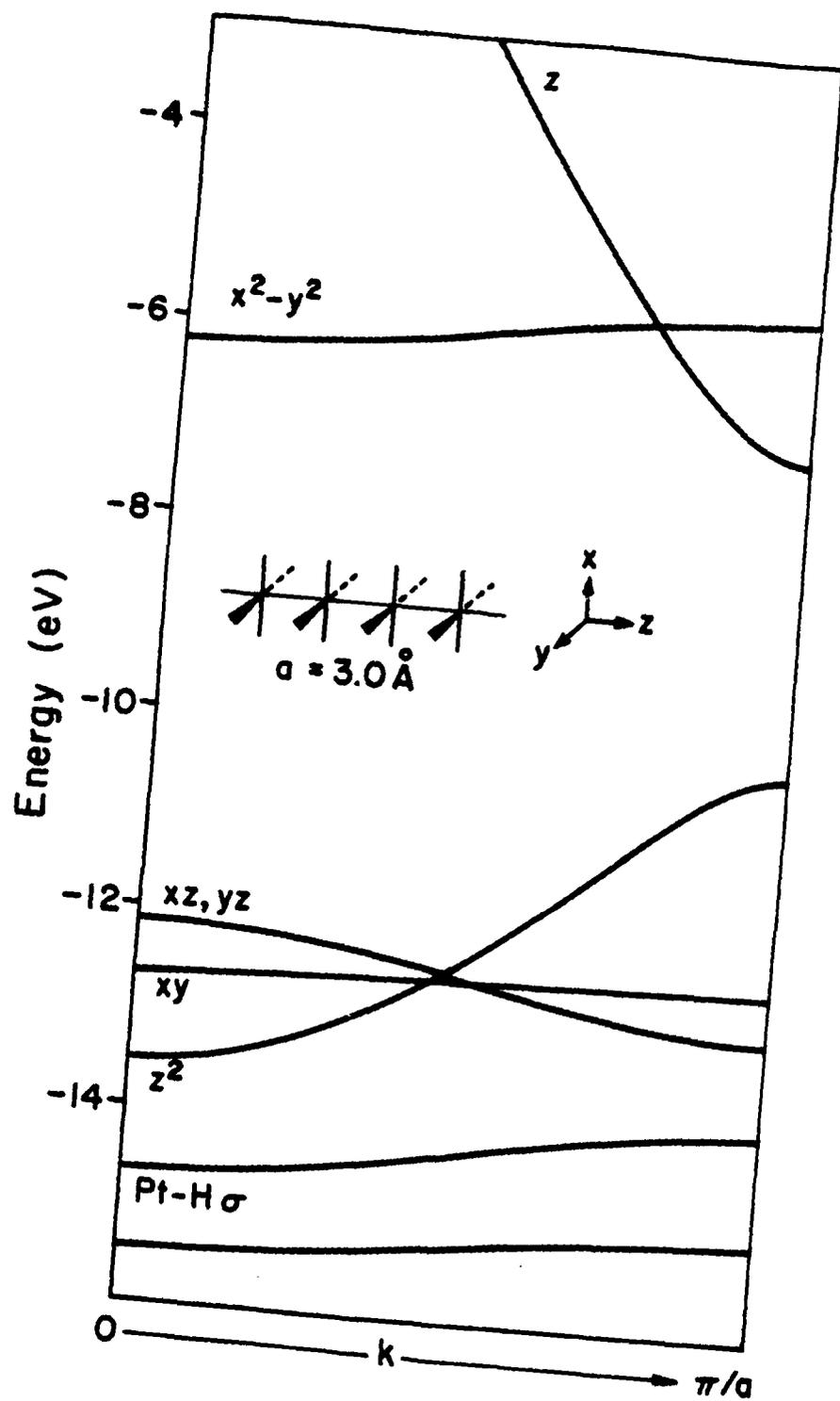


Figure 3. Computed band structure of an eclipsed PtH_4^{2-} stack, spaced at 3 \AA . The orbital marked xz, yz is doubly degenerate.

few more levels, but the translational symmetry helps us out with that. It's really easy to write down the symmetry-adapted linear combinations, the Bloch functions.

The Fermi Level

It's important to know how many electrons one has in one's molecule. Fe(II) has a different chemistry from Fe(III), and CR_3^+ carbocations are different from CR_3 radicals and CR_3^- anions. In the case of $\text{Re}_2\text{Cl}_8^{2-}$, the archetypical quadruple bond, we have formally Re(III), d^4 , i.e. a total of eight electrons to put into the frontier orbitals of the dimer level scheme, 17. They fill the σ , two π and the δ level for the explicit quadruple bond. What about the $[\text{PtH}_4^{2-}]_\infty$ polymer 12? Each monomer is d^8 . If there be Avogadro's number of unit cells, there will be Avogadro's number of levels in each bond. And each level has a place for two electrons. So the first four bands are filled, the xy , xz , yz , z^2 bands. The Fermi level, the highest occupied molecular orbital (HOMO), is at the very top of the z^2 band. (Strictly speaking, there is another thermodynamic definition of the Fermi level, appropriate both to metals and semiconductors⁹, but here we will use the simple equivalence of the Fermi level with the HOMO.)

Is there a bond between platinum in this $[\text{PtH}_4^{2-}]_\infty$ polymer? We haven't introduced, yet, a formal description of the bonding properties of an orbital or a band, but a glance at 15 and 16 will show that the bottom of each band, be it made up of z^2 , xz , yz or xy , is bonding, and the top antibonding. Filling a band completely, just like filling bonding and antibonding orbitals in a dimer (think of He_2 , think of the sequence N_2 , O_2 , F_2 , Ne_2)

provides no net bonding. In fact, it gives net antibonding. So why does the unoxidized PtL_4 chain stack? It could be van der Waals attractions, not in our quantum chemistry at this primitive level. I think there is also a contribution of orbital interaction, i.e. real bonding, involving the mixing of the z^2 and z bands.¹⁴ We will return to this soon.

The band structure gives a ready explanation for why the Pt-Pt separation decreases on oxidation. A typical degree of oxidation is 0.3 electrons per Pt.¹² These electrons must come from the top of the z^2 band. The degree of oxidation specifies that 15% of that band is empty. The states vacated are not innocent of bonding. They are strongly Pt-Pt σ antibonding. So it's no wonder that removing these electrons results in the formation of a partial Pt-Pt bond.

The oxidized material also has its Fermi level in a band, i.e. there is a zero band gap between filled and empty levels. The unoxidized platinocyanides have a substantial gap -- they are semiconductors or insulators. The oxidized materials are good low-dimensional conductors, which is a substantial part of what makes them interesting to physicists.¹⁴

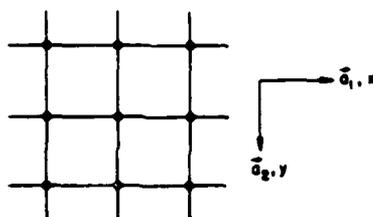
In general, conductivity is not a simple phenomenon to explain, and there may be several mechanisms impeding the motion of electrons in a material.⁹ A prerequisite for having a good electronic conductor is to have the Fermi level cut one or more bands (soon we will use the language of density of states to say

this more precisely). One has to beware, however, 1) of distortions which open up gaps at the Fermi level and 2) of very narrow bands cut by the Fermi level, for these will lead to localized states and not to good conductivity.⁹

More Dimensions, At Least Two

Most materials are two- or three-dimensional, and while one dimension is fun, we must eventually leave it for higher dimensionality. Nothing much new happens, except that we must treat \vec{k} as a vector, with components in reciprocal space, and the Brillouin zone is now a two- or three-dimensional area or volume.^{9,15}

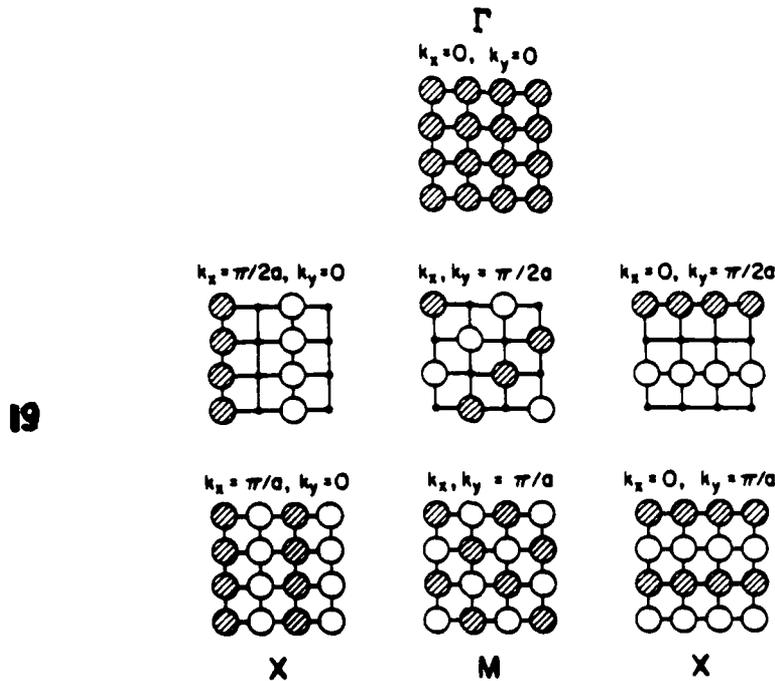
To introduce some of these ideas, let's begin with a square lattice, 18, defined by the translation vectors \vec{a}_1 and \vec{a}_2 .



18

Suppose there is an H 1s orbital on each lattice site. It turns out that the Schrödinger equation in the crystal factors into separate wave equations along the x and y axes, each of them identical to the one-dimensional equation for a linear chain. There is a k_x and a k_y , the range of each is $0 \leq |k_x|, |k_y| \leq \pi/a$ ($a = |\vec{a}_1| = |\vec{a}_2|$). Some typical solutions are shown below, in 19.

The construction of these is obvious. What the construction also shows, very clearly, is the vector nature of k . Consider the $(k_x, k_y) = (\pi/2a, \pi/2a)$ and $(\pi/a, \pi/a)$ solutions. A look at them reveals that they are waves running along a direction which

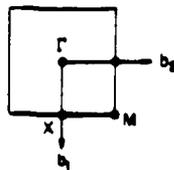


19

is the vector sum of k_x and k_y , i.e. on a diagonal. The wave length is inversely proportional to the magnitude of that vector.

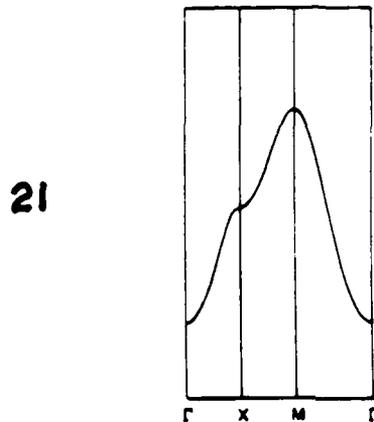
The space of k here is defined by two vectors \vec{b}_1 and \vec{b}_2 , and the range of allowed k , the Brillouin zone, is a square. Certain special values of k are given names: $\Gamma = (0, 0)$ is the zone center, $X = (\pi/a, 0) = (0, \pi/a)$, $M = (\pi/a, \pi/a)$. These are shown in 20, and the specific solutions for Γ , X , M were so labeled in 19.

20



It is difficult to show the energy levels, $E(\vec{k})$ for all \vec{k} . So what one typically does is to illustrate the evolution of E along certain lines in the Brillouin zone. Some obvious ones are

$\Gamma \rightarrow X$, $\Gamma \rightarrow M$, $X \rightarrow M$. From 19 it is clear that M is the highest energy wave function, and that X is pretty much nonbonding, since it has as many bonding interactions (along y) as it does antibonding ones (along x). So we would expect the band structure to look like 21.



A computed band structure and DOS for a hydrogen lattice with $a = 2.0 \text{ \AA}$, Fig. 4, confirms our expectations.

Figure 4

The chemist would expect the chessboard of H atoms to distort into one of H_2 molecules (An interesting problem is how many different ways there are to accomplish this). The large peak in the DOS for the half-filled H square lattice band would make the physicist think of a lattice vibration that would create a gap at ϵ_F . Any pairwise deformation will do that.

Let's now put some p orbitals on the square lattice, with the direction perpendicular to the lattice taken as z. The p_z orbitals will be separated from p_y and p_x by their symmetry.

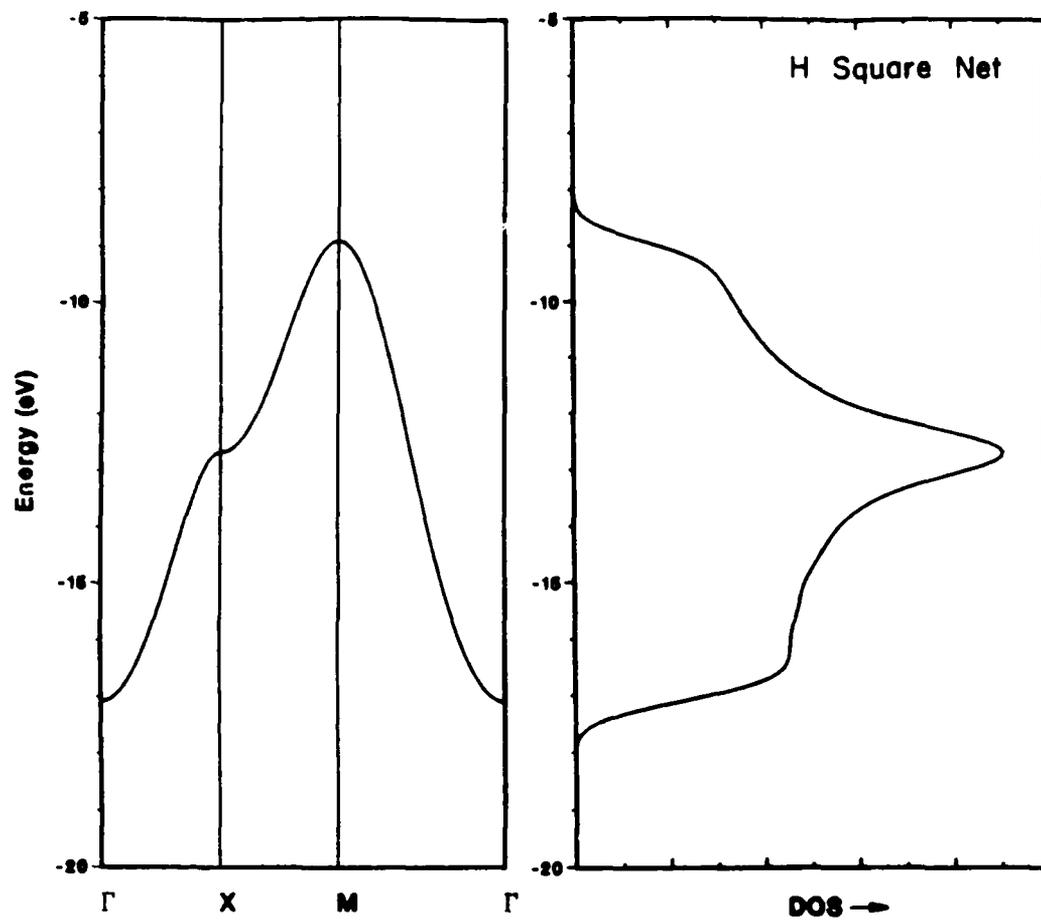
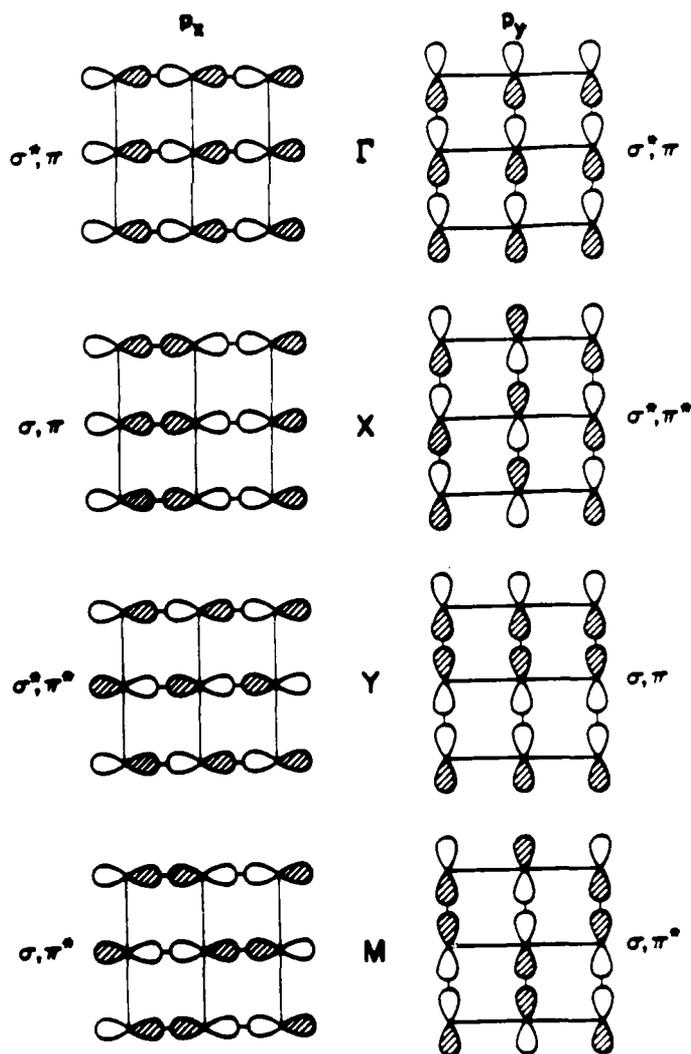


Figure 4. The band structure and DOS of a square lattice of H atoms, H-H separation 2.0 \AA .

Reflection in the plane of the lattice remains a good symmetry operation at all k . The $p_z(z)$ orbitals will give a band structure similar to that of the s orbital, for the topology of the interaction of these orbitals is similar. This is why in the one-dimensional case we could talk at one and the same time about chains of H atoms and polyenes.

The p_x, p_y (x, y) orbitals present a somewhat different problem. Shown below in 22 are the symmetry-adapted combinations



of each at Γ , X, Y, and M. (Y is by symmetry equivalent to X; the difference is just in the propagation along x or y.) Each crystal orbital can be characterized by the p,p σ or π bonding present. Thus at Γ the x and y combinations are σ antibonding and π bonding; at X they are σ and π bonding (one of them), and σ and π antibonding (the other). At M they are both σ bonding, π antibonding. It is also clear that the x, y combinations are degenerate at Γ and M (and it turns out along the line $\Gamma \rightarrow M$, but for that one needs a little group theory¹⁵) and non-degenerate at X and Y (and everywhere else in the Brillouin zone).

Putting in the estimate that σ bonding is more important than π bonding, one can order these special symmetry points of the Brillouin zone in energy and draw a qualitative band structure. This is Fig. 5. The actual appearance of any real band structure will depend on the lattice spacing. Band

Figure 5

dispersions will increase with short contacts, and complications due to s, p mixing will arise. Roughly, however, any square lattice, be it the P net in GdPS¹⁶, a square overlayer of S atoms

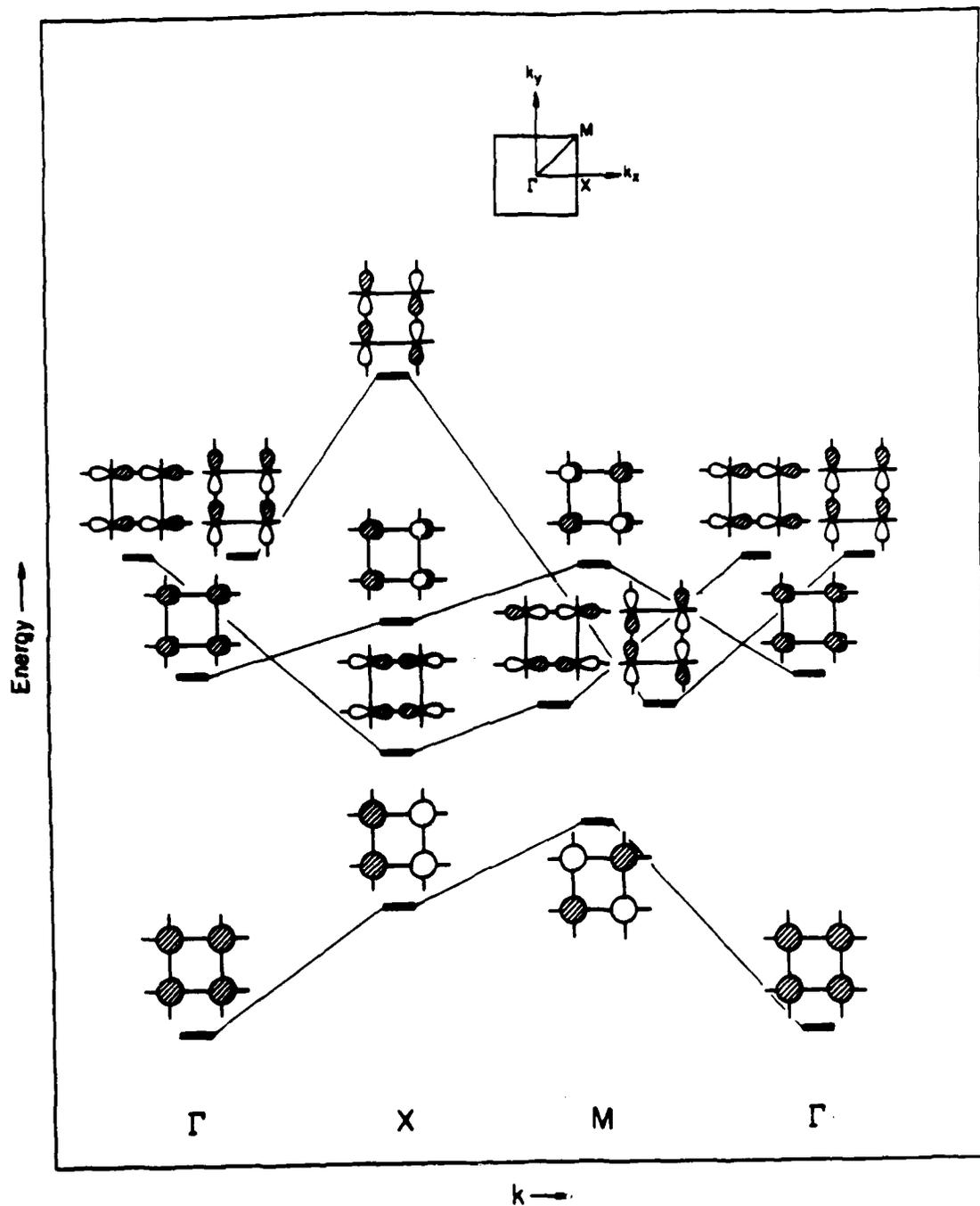


Figure 5. Schematic band structure of a planar square lattice of atoms bearing ns and np orbitals. The s and p levels have a large enough separation that the s and p band do not overlap.

absorbed on Ni(100)¹⁷, the oxygen and lead nets in litharge¹⁸, a Si layer in BaPdSi₃¹⁹, any square lattice will have these orbitals.

Setting Up a Surface Problem

The strong incentive for moving to at least two dimensions is that one obviously needs this for studying surface bonding problems. Let's begin to set these up. The kind of problem that we want to investigate is how CO chemisorbs on Ni, how H₂ dissociates on a metal surface, how acetylene bonds to Pt(111) and then rearranges to vinylidene or ethylidyne, how surface carbide or sulfide affects the chemistry of CO, how CH₃ and CH₂ bind, migrate, and react on an iron surface. It makes sense to look first at structure and bonding in the stable or metastable waypoints, the chemisorbed species. Then one could proceed to construct potential energy surfaces for motion of chemisorbed species on the surface, and eventually for reactions.

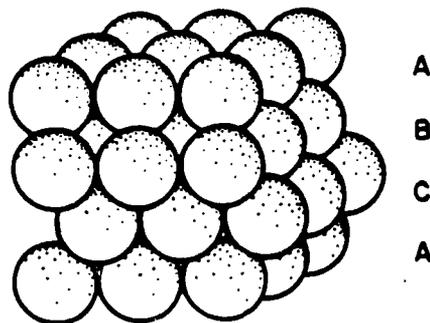
The very language I have used here conceals a trap. It puts the burden of motion and reactive power on the chemisorbed molecules, and not on the surface, which might be thought passive, untouched. Of course, this can't be so. We know that exposed surfaces reconstruct, i.e. make adjustments in structure driven by their unsaturation.²⁰ They do so first by themselves, without any adsorbate. And they do it again, in a different way, in the presence of adsorbed molecules. The extent of reconstruction is great in semiconductors and extended molecules, in general small in molecular crystals and metals. It can also vary from crystal face to face. The calculations I will discuss deal with metal surfaces. One is then reasonably safe (we hope)

if one assumes minimal reconstruction. It will turn out, however, that the signs of eventual reconstruction are to be seen even in these calculations.

It might be mentioned here that reconstruction is not a phenomenon reserved for surfaces. In the most important development in theoretical inorganic chemistry in the seventies, Wade^{21a} and Mingos^{21b} have provided us with a set of skeletal electron pair counting rules. These rationalize the related geometries of borane and transition metal clusters. One aspect of their theory is that if the electron count increases or decreases from the appropriate one for the given polyhedral geometry, that the cluster will adjust geometry -- open a bond here, close one there -- to compensate for the different electron count. Discrete molecular transition metal clusters and polyhedral boranes also reconstruct.

Returning to the surface, let's assume a specific surface plane cleaved out, frozen in geometry, from the bulk. That piece of solid is periodic in two dimensions, semi-infinite, and aperiodic in the direction perpendicular to the surface. Half of infinity is much more painful to deal with than all of infinity, because translational symmetry is lost in that third dimension. And that symmetry is essential in simplifying the problem -- one doesn't want to be diagonalizing matrices of the degree of Avogadro's number; with translational symmetry and the apparatus of the theory of group representations one can reduce the problem to the size of the number of orbitals in the unit cell.

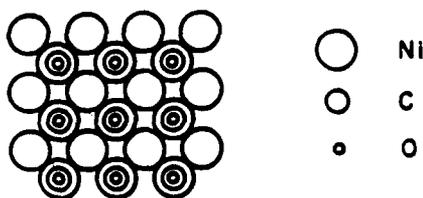
So one chooses a slab of finite depth. 23 shows a four-layer slab model of a (111) surface of an fcc metal, a typical close-packed hexagonal face. How thick should the slab be?



23

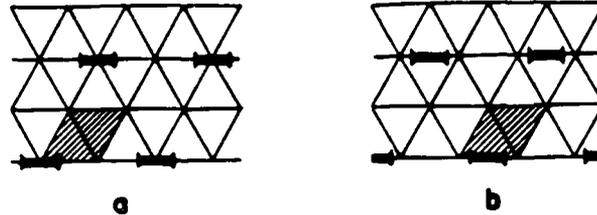
Thick enough so that its inner layers approach the electronic properties of the bulk, the outer layers those of the true surface. In practice, it is more often economics which dictates the typical choice of three or four layers.

Molecules are then brought up to this slab. Not one molecule, for that would ruin the desirable two-dimensional symmetry, but an entire array or layer of molecules maintaining translational symmetry.²² This immediately introduces two of the basic questions of surface chemistry: coverage and site preference. 24 shows a $c(2 \times 2)$ CO array on Ni(100), on-top

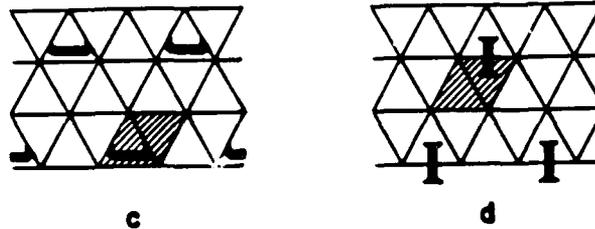


24

adsorption, coverage = $\frac{1}{2}$. 25 shows four possible ways of adsorbing acetylene in a coverage of $\frac{1}{2}$ on top of Pt(111). The



25



hatched area is the unit cell. The experimentally preferred mode is the three-fold bridging one, 25c. Many surface reactions are coverage dependent.² And the position where a molecule sits on a surface, its orientation relative to the surface, is one of the things one wants to know.

So: a slab, three or four atoms thick, of a metal, and a monolayer of adsorbed molecules. Here's what the band structure looks like for some CO monolayers (Fig. 6) and a four layer Ni(100) slab (Fig. 7). The phenomenology of these band structures should be clear by now:

Figures 6 and 7

1) What is being plotted: E vs. \vec{k} . The lattice is two-dimensional. k is now a vector, varying within a two-

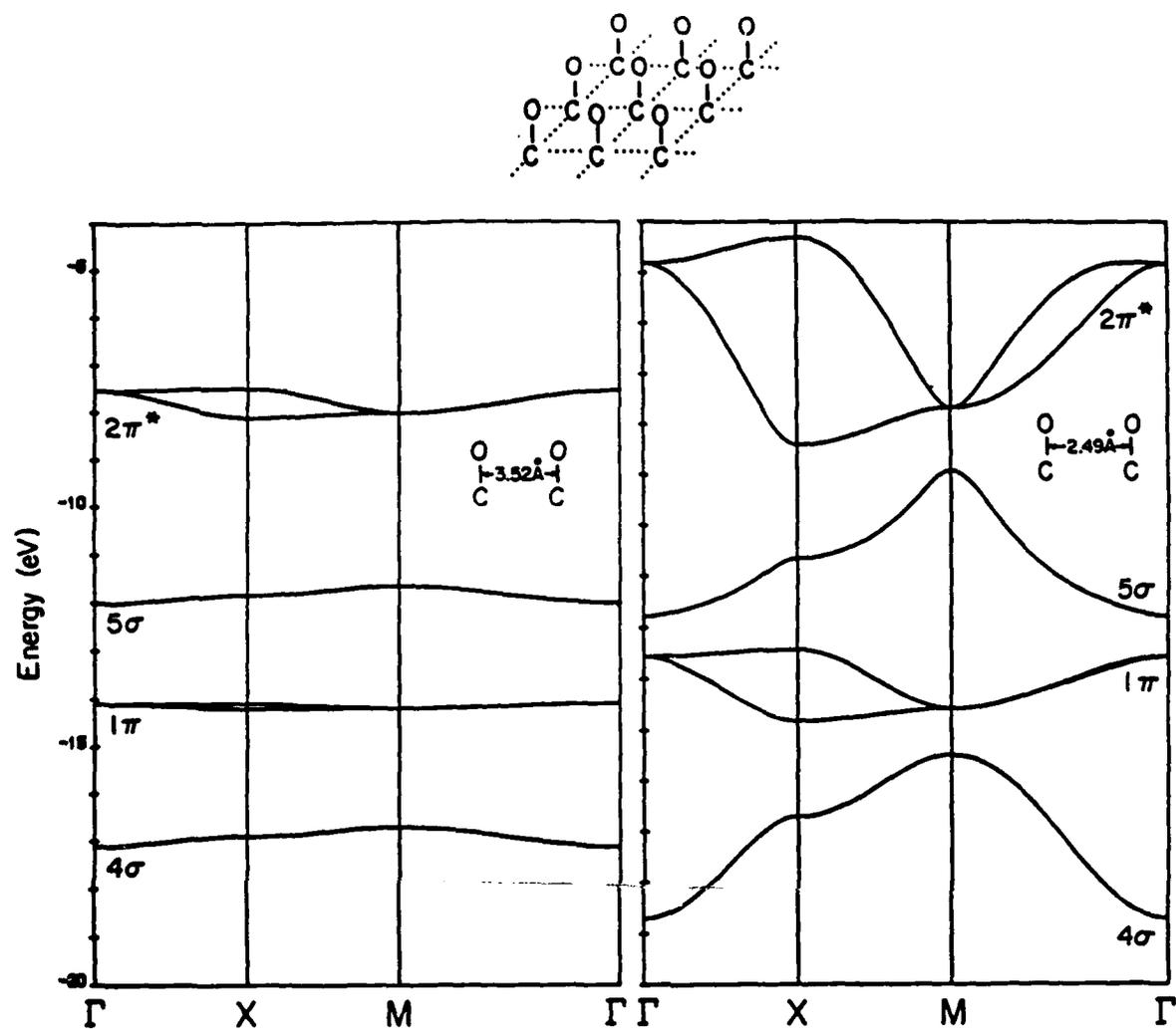


Figure 6. Band structures of square monolayers of CO at two separations: (a) left, 3.52 Å, (b) right, 2.49 Å. These would correspond to $\frac{1}{2}$ and full coverage of a Ni(100) surface.

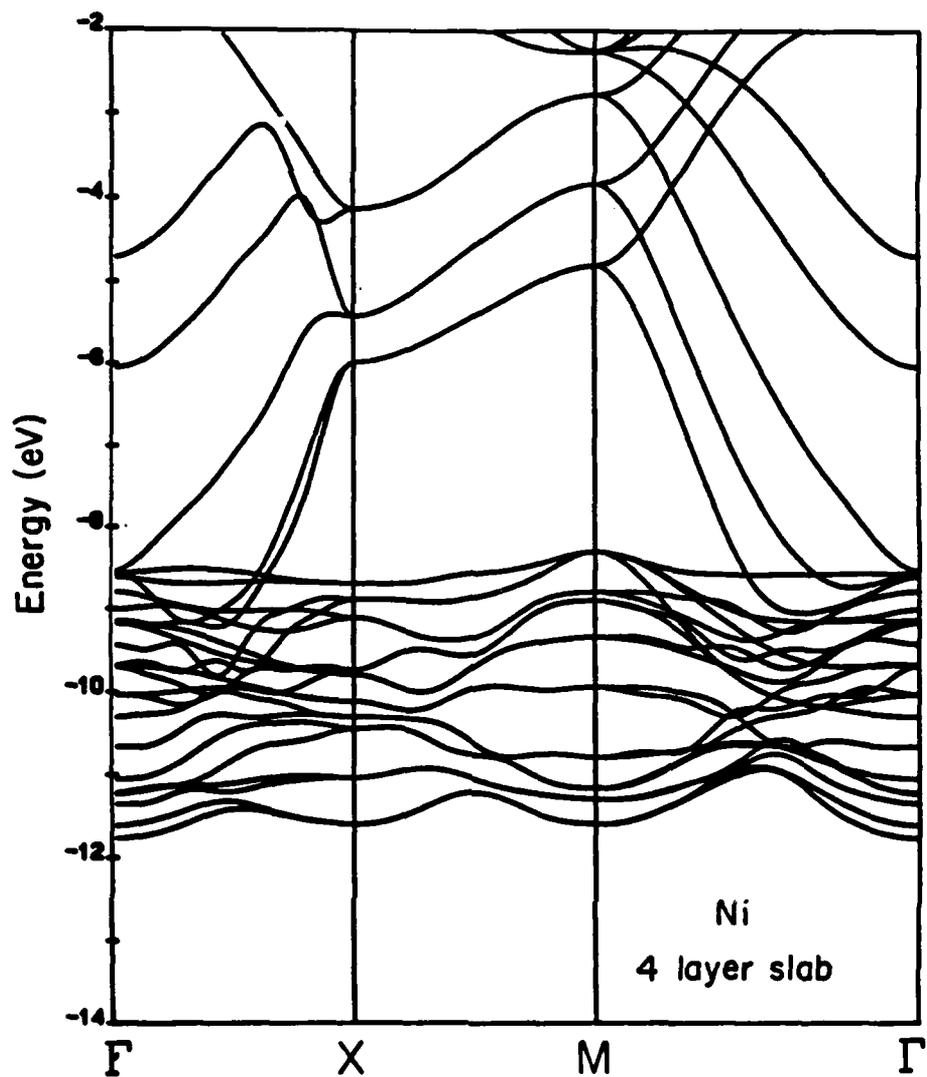


Figure 7. The band structure of a four-layer Ni slab that serves as a model for a Ni(100) surface. The flat bands are derived from Ni 3d, the more highly dispersed ones above these are 4s, 4p.

dimensional Brillouin zone, $\vec{k} = (k_x, k_y)$. Some of the special points in this zone are given canonical names: Γ (the zone center) = $(0, 0)$; $X = (\pi/a, 0)$, $M = (\pi/a, \pi/a)$. What is being plotted is the variation of the energy along certain specific directions in reciprocal space connecting these points.

2) How many lines there are: as many as there are orbitals in the unit cell. Each line is a band, generated by a single orbital in the unit cell. In the case of CO, there is one molecule per unit cell, and that molecule has well-known 4σ , 1π , 5σ , $2\pi^*$ MO's. Each generates a band. In the case of the four-layer Ni slab, the unit cell has 4 Ni atoms. Each has five 3d, one 4s and three 4p basis functions. We see some, but not all, of the many bands these orbitals generate in the energy window shown in Fig. 7.

3) Where (in energy) the bands are: The bands spread out, more or less dispersed, around a "center of gravity". This is the energy of that orbital in the unit cell which gives rise to the band. Therefore, 3d bands lie below 4s and 4p for Ni, and 5σ below $2\pi^*$ for CO.

4) Why some bands are steep, others flat: because there is much inter-unit-cell overlap in one case, little in another. The CO monolayer bands in Fig. 6 are calculated at two different CO-CO spacings, corresponding to different coverages. It's no surprise that the bands are more dispersed when the CO's are closer together. In the case of the Ni slab, the s, p bands are

wider than the d bands, because the 3d orbitals are more contracted, less diffuse than the s, p.

5) How come the bands are the way they are: They run up or down along certain directions in the Brillouin zone as a consequence of symmetry and the topology of orbital interaction. Note the phenomenological similarity of the behavior of the σ and π bands of CO in Fig. 6 to the schematic, anticipated course of the s and p bands of Fig. 5.

There are more details to be understood, to be sure. But, in general, these diagrams are complicated, not because of any mysterious phenomenon, but because of richness, the natural accumulation of understandable and understood components.

We still have the problem of how to talk about all these highly delocalized orbitals, how to retrieve a local, chemical, or frontier orbital language in the solid state. There is a way.

Density of States

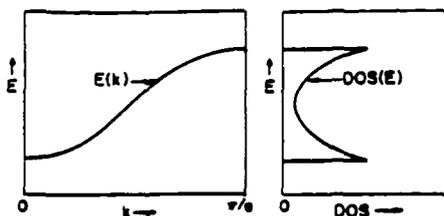
In the solid, or on a surface, both of which are just very large molecules, one has to deal with a very large number of levels or states. If there are n atomic orbitals (basis functions) in the unit cell, generating n molecular orbitals, and if in our macroscopic crystal there are N unit cells (N is a number that approaches Avogadro's number), then we will have Nn crystal levels. Many of these are occupied and, roughly speaking, they are jammed into the same energy interval in which we find the molecular or unit cell levels. In a discrete molecule we are able to single out one orbital or a small subgroup of orbitals (HOMO, LUMO) as being the frontier, or valence orbitals of the molecules, responsible for its geometry, reactivity, etc. There is no way in the world that a single level among the myriad Nn orbitals of the crystal will have the power to direct a geometry or reactivity.

There is, however, a way to retrieve a frontier orbital language in the solid state. We cannot think about a single level, but perhaps we can talk about bunches of levels. There are many ways to group levels, but one pretty obvious one is to look at all the levels in a given energy interval. The density of states (DOS) is defined as follows:

$$\text{DOS}(E)dE = \text{number of levels between } E \text{ and } E+dE$$

For a simple band of a chain of hydrogen atoms, the DOS curve takes on the shape of 26. Note that because the levels are equally spaced along the k axis, and because the $E(k)$ curve, the band structure, has a simple cosine curve shape, there are more

26



states in a given energy interval at the top and bottom of this band. In general, $DOS(E)$ is proportional to the inverse of the slope of $E(k)$ vs. k , or to put it into plain English, the flatter the band, the greater the density of states at that energy.

The shapes of DOS curves are predictable from the band structures. Fig. 8 shows the DOS curve for the PtH_2^+ chain, Fig. 9 for a two-dimensional monolayer of CO. These could have been sketched from their respective band structures. In general, the detailed construction of these is a job best left for computers.

Figures 8 and 9

The density of states curve counts levels. The integral of DOS up to the Fermi level is the total number of occupied MO's. Multiplied by two, it's the total number of electrons. So, the DOS curves plot the distribution of electrons in energy.

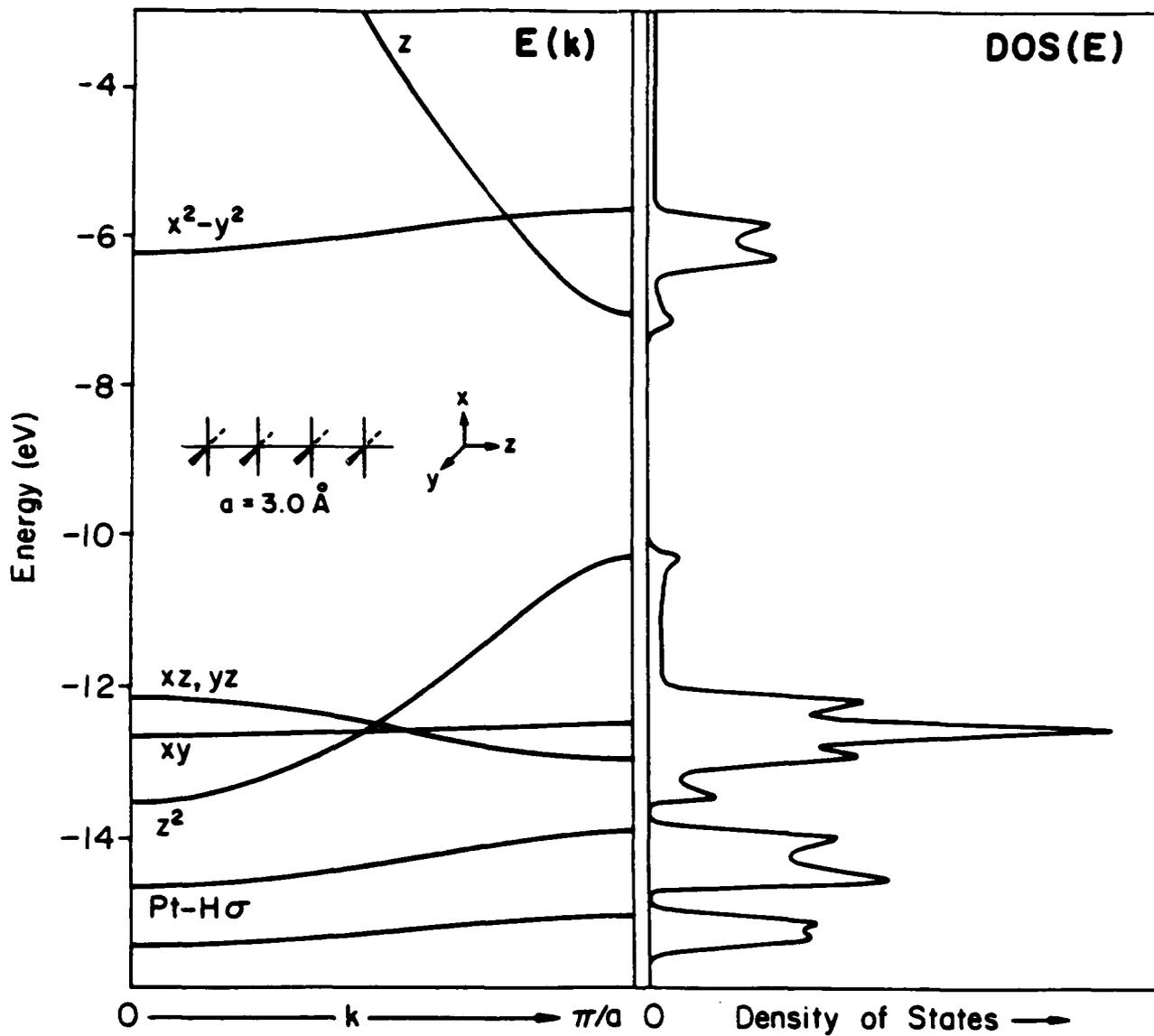


Figure . . . Band structure and density of states for an eclipsed PtH_4^{2-} stack. The DOS curves are broadened so that the two-peaked shape of the xy peak in the DOS is not resolved.

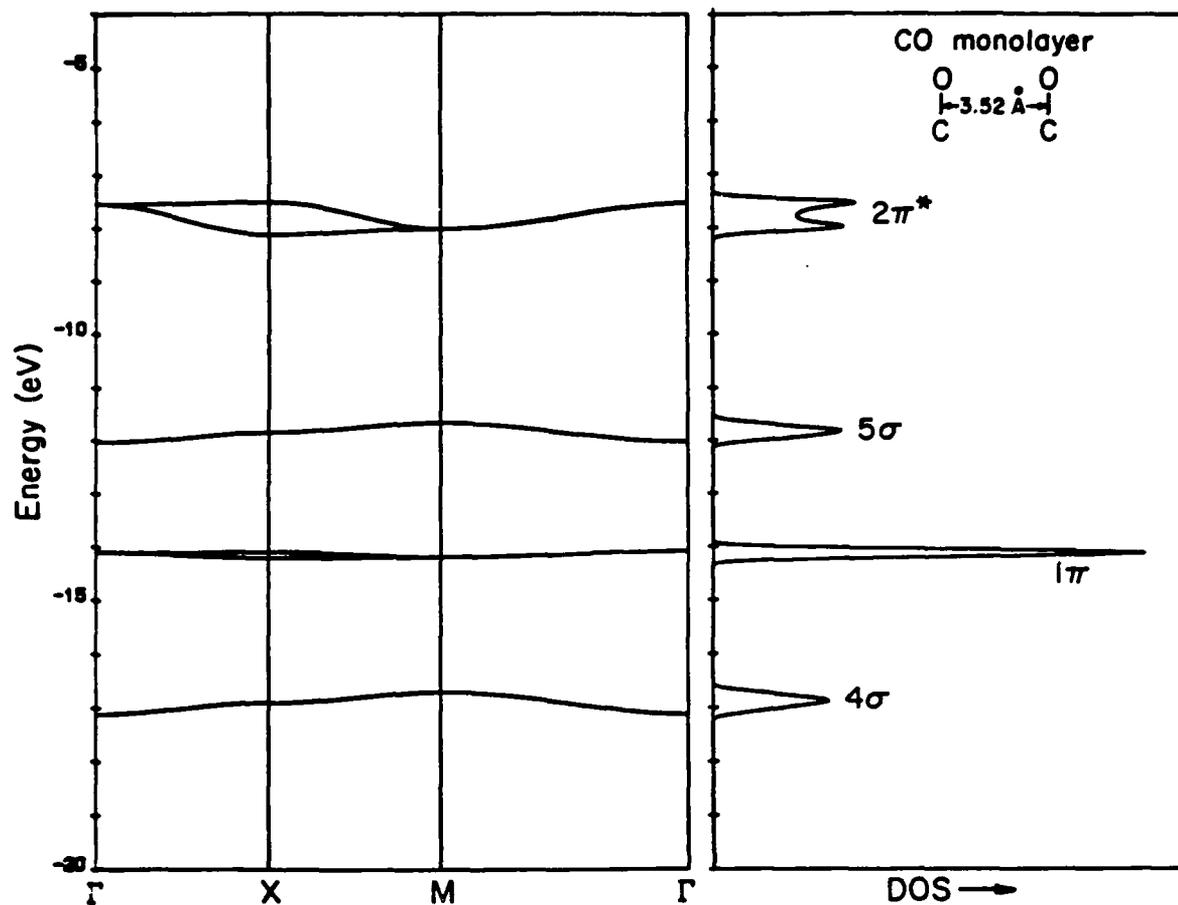
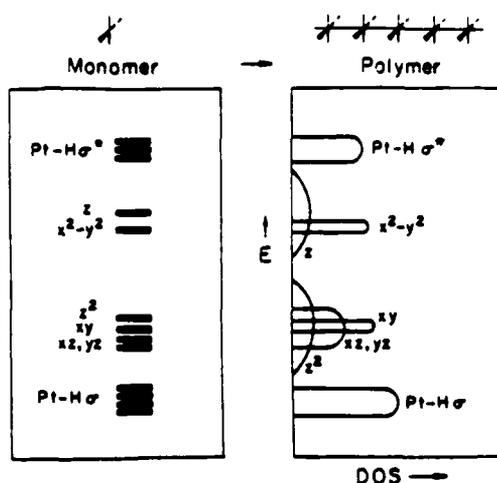


Figure 9. The density of states (right) corresponding to the band structure (left) of a square monolayer of CO's, 3.52 Å apart.

One important aspect of the DOS curves is that they represent a return from reciprocal space, the space of k , to real space. The DOS is an average over the Brillouin zone, over all k that might give molecular orbitals at the specified energy. The advantage here is largely psychological. If I may be permitted to generalize, I think chemists (with the exception of crystallographers) by and large feel themselves uncomfortable in reciprocal space. They'd rather return to, and think in, real space.

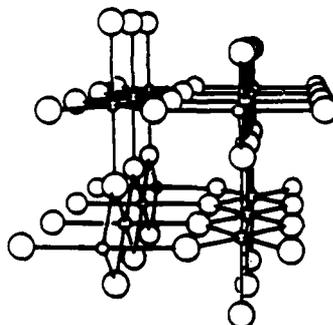
There is another aspect of the return to real space that is significant: chemists can sketch the DOS of any material, approximately, intuitively. All that's involved is a knowledge of the atoms, their approximate ionization potentials and electronegativities, and some judgment as to the extent of inter-unit-cell overlap (usually apparent from the structure).

Let's take the PtH_2^- polymer as an example. The monomer units are clearly intact in the polymer. At intermediate monomer-monomer separations (e.g. 3 Å) the major inter-unit-cell overlap is between z^2 and z orbitals. Next is the xz, yz π -type overlap; all other interactions are likely to be small. 27 is a sketch of what we would expect. In 27 I haven't been careful in drawing the integrated areas commensurate to the actual total number of states, nor have I put in the two-peaked nature of the DOS each level generates -- all I want to do is to convey the rough spread of each band. Compare 27 to Fig. 8.



27

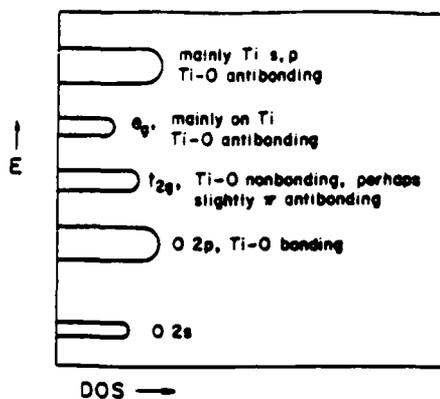
This was easy, because the polymer was built up of molecular monomer units. Let's try something inherently three-dimensional. The rutile structure is a relatively common type. As 28 shows,



28

the rutile structure has a nice octahedral environment of each metal center, each ligand (e.g. O) bound to three metals. There are infinite chains of edge-sharing MO_6 octahedra running in one direction in the crystal, but the metal-metal separation is always relatively long.²³ There are no monomer units here, just an infinite assembly. Yet there are quite identifiable octahedral sites. At each, the metal d block must split into t_{2g}

and e_g combinations, the classic three below two crystal field splitting. The only other thing we need is to realize that O has quite distinct 2s and 2p levels, and that there is no effective $O \cdots O$ or $Ti \cdots Ti$ interaction in this crystal. We expect something like 29.



29

Note that the writing down of the approximate DOS curve is done by-passing the band structure calculation per se. Not that that band structure is very complicated. But it is three-dimensional, and our exercises so far have been easy, in one dimension. So the computed band structure in Fig. 10 will seem complex. The number is doubled (i.e. twelve O 2p, six t_{2g}

 Figure 10

bands), simply because the unit cell contains two formula units, $(TiO_2)_2$. There is not one reciprocal space variable, but several lines ($\Gamma \rightarrow X$, $X \rightarrow M$, etc.) which refer to directions in the

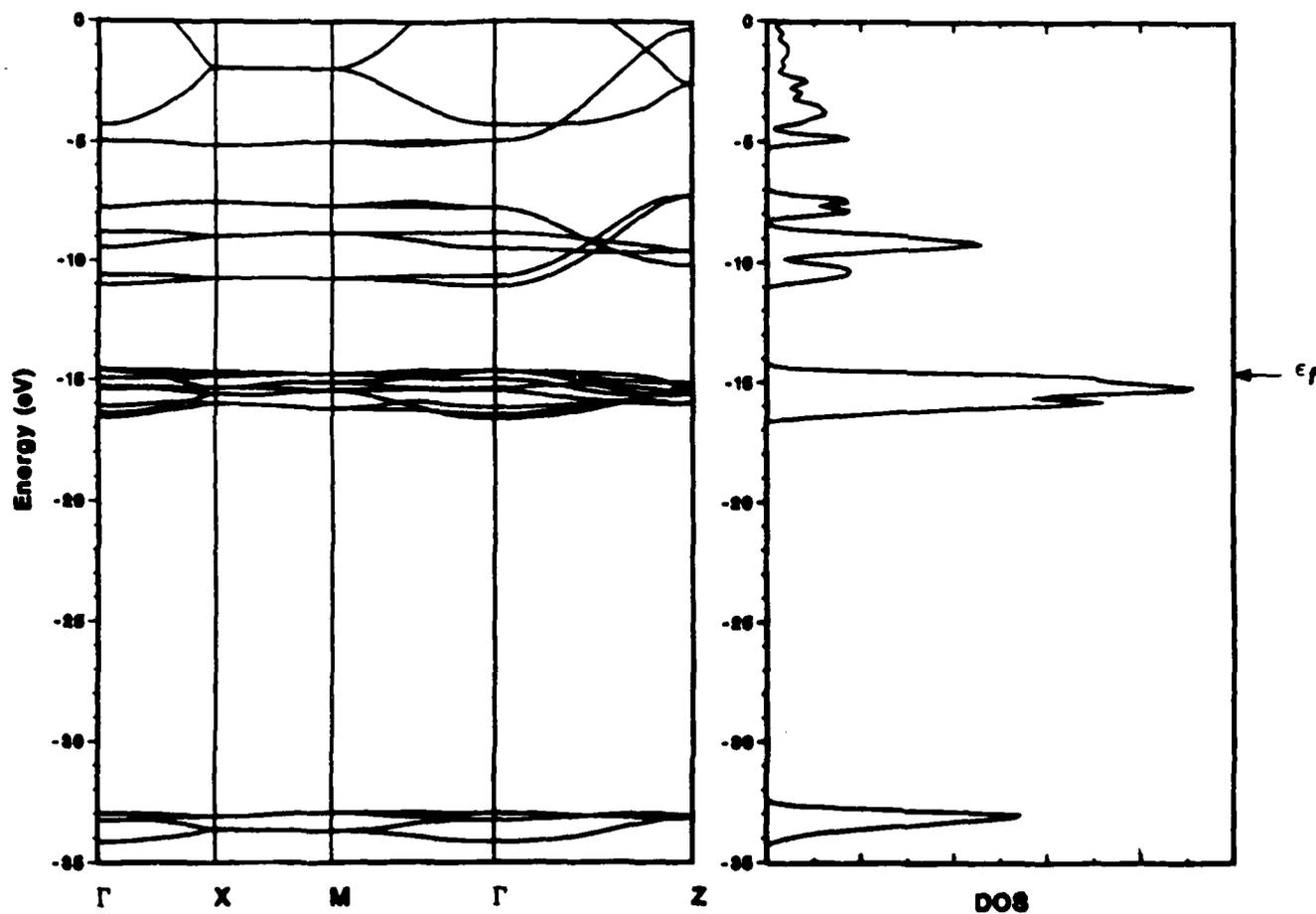


Figure 10. Band structure and density of states for rutile, TiO_2 . The two TiO distances are $2.04(2x)$, $2.07(4x)$ Å in the assumed structure.

three-dimensional Brillouin zone. These complications of moving from one dimension to three we will soon approach. If we glance at the DOS, we see that it does resemble the expectations of 21. There are well-separated O 2s, O 2p, Ti t_{2g} and e_g bands.²³

Would you like to try something a little (but not much) more challenging? Attempt to construct the DOS of the new superconductors based on the La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_7$ structures. And when you have done so and found that these should be conductors, reflect on how that doesn't allow you yet, did not allow anyone, to predict that compounds slightly off these stoichiometries would be remarkable superconductors.²⁴

The chemists' ability to write down approximate density of states curves should not be slighted. It gives us tremendous power, and qualitative understanding, an obvious connection to local, chemical viewpoints such as the crystal or ligand field model. I want to mention here one solid state chemist, John B. Goodenough, who has shown over the years, and especially in his prescient book on "Magnetism and Chemical Bonding", just how good the chemist's approximate construction of band structures can be.²⁵

In 27 and 29, the qualitative DOS diagrams for PtH_4^{2-} and TiO_2 , there is, however, much more than a guess at a DOS. There is a chemical characterization of the localization in real space of the states (are they on Pt, on H; on Ti, on O) and a specification of their bonding properties (Pt-H bonding,

antibonding, nonbonding, etc.). The chemist sees right away, or asks -- where in space are the electrons? Where are the bonds? There must be a way that these inherently chemical, local questions can be answered, even if the crystal molecular orbitals, the Bloch functions, delocalize the electrons over the entire crystal.

Where are the Electrons?

One of the interesting tensions in chemistry is between the desire to assign electrons to specific centers, deriving from an atomic, electrostatic view of atoms in a molecule, and the knowledge that electrons are not as localized as we would like them to be. Let's take a two-center molecular orbital

$$\psi = c_1x_1 + c_2x_2$$

where x_1 is on center 1, x_2 on center 2 and let's assume centers 1 and 2 are not identical, and that x_1 and x_2 are normalized, but not orthogonal.

The distribution of an electron in this MO is given by ψ^2 .

ψ should be normalized, so

$$1 = \int |\psi|^2 dr = \int |c_1x_1 + c_2x_2|^2 dr = c_1^2 + c_2^2 + 2c_1c_2S_{12}$$

where S_{12} is the overlap integral between x_1 and x_2 . This is how one electron in ψ is distributed. Now it's obvious that c_1^2 of it is to be assigned to center 1, c_2^2 to center 2. $2c_1c_2S_{12}$ is clearly a quantity that is associated with interaction. It's called the overlap population, and we will soon relate it to the bond order. But what are we to do if we persist in wanting to divide up the electron density between centers 1 and 2? We want all the parts to add up to 1 and $c_1^2 + c_2^2$ won't do. We must assign, somehow, the "overlap density" $2c_1c_2S_{12}$ to the two centers. Mulliken suggested (and that's why we call this a Mulliken population analysis²⁰) a democratic solution, splitting $2c_1c_2S_{12}$ equally between centers 1 and 2. Thus center 1 is

assigned $c_1^2+c_1c_2S_{12}$, center 2 $c_2^2+c_1c_2S_{12}$ and the sum is guaranteed to add up to 1. It should be realized that the Mulliken prescription for partitioning the overlap density, while uniquely defined, is quite arbitrary.

What a computer does is just a little more involved, for it sums these contributions for each atomic orbital on a given center (there are several), over each occupied MO (there may be many). And in the crystal, it does that sum for several k points in the Brillouin zone, and then returns to real space by averaging over these. The net result is a partitioning of the total DOS into contributions to it by either atoms or orbitals. We have also found very useful a decomposition of the DOS into contributions of fragment molecular orbitals (FMO's) of MO's of specified molecular fragments of the composite molecule. In the solid state trade these are often called "projections of the DOS" or "local DOS". Whatever they're called, they divide up the DOS among the atoms. The integral of these projections up to the Fermi level then gives the total electron density on a given atom or in a specific orbital. Then, by reference to some standard density, a charge can be assigned.

Fig. 11 and 12 give the partitioning of the electron density between Pt and H in the PtH_4^{2-} stack, and between Ti and O in rutile. Everything is as 27 and 29 predict, as the chemist knows it should be -- the lower orbitals are localized in the more electronegative ligands (H or O), the higher ones on the metal.

 Figures 11 and 12

Do we want more specific information? In TiO_2 we might want to see the crystal field argument upheld. So we ask for the contributions of the three orbitals that make up the t_{2g} (xz , yz , xy in a local coordinate system) and e_g (z^2 , x^2-y^2) sets. This is also shown in Fig. 12. Note the very clear separation of the t_{2g} and e_g orbitals. The e_g has a small amount of density in the O 2s and 2p bands (σ bonding) and t_{2g} in the O 2p band (π bonding). Each metal orbital type (t_{2g} or e_g) is spread out into a band, but the memory of the near-octahedral local crystal field is very clear.

In PtH_4^{2-} we could ask the computer to give us the z^2 contribution to the DOS, or the z part. If we look at the z component of the DOS in PtH_4^{2-} , we see a small contribution in the top of the z^2 band. This is easiest picked up by the integral in Fig. 13. The dotted line is a simple integration, like an NMR integration. It counts, on a scale of 0 of 100% at the top, what % of the specified orbital is filled at a given energy. At the Fermi level in unoxidized PtH_4^{2-} 4% of the states are filled.

 Figure 13

How does this come about? There are two ways to talk about this. Locally, the donor function of one monomer (z^2) can

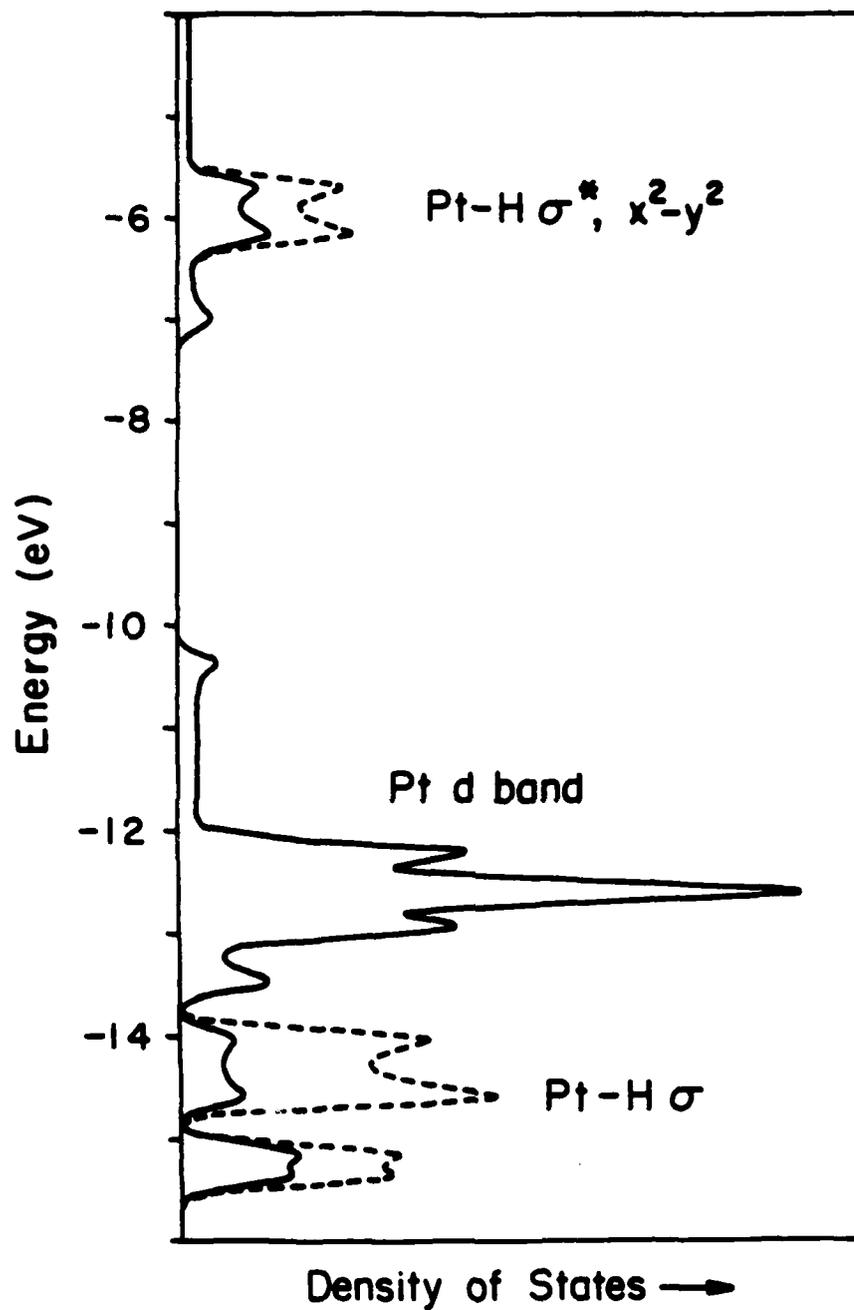


Figure II. The solid line is the Pt contribution to the total DOS (dashed line) of an eclipsed PtH_4^{2-} stack. What is not on Pt is on the four H's.

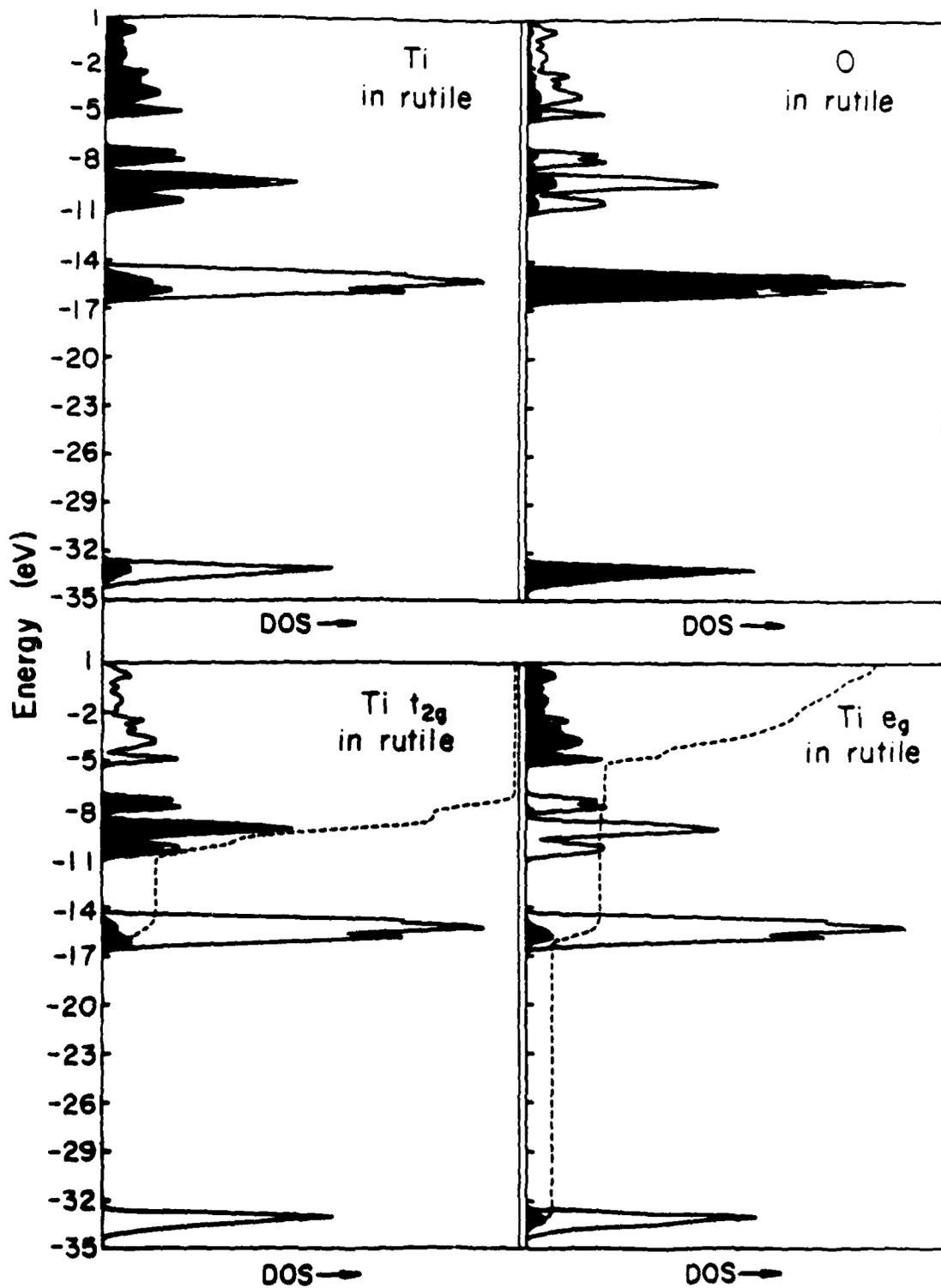


Figure 12. Contributions of Ti and O to the total DOS of rutile, TiO₂ are shown at top. At bottom, the t_{2g} and e_g Ti contributions are shown; their integration (on a scale of 0 to 100%) is given by the dashed line.

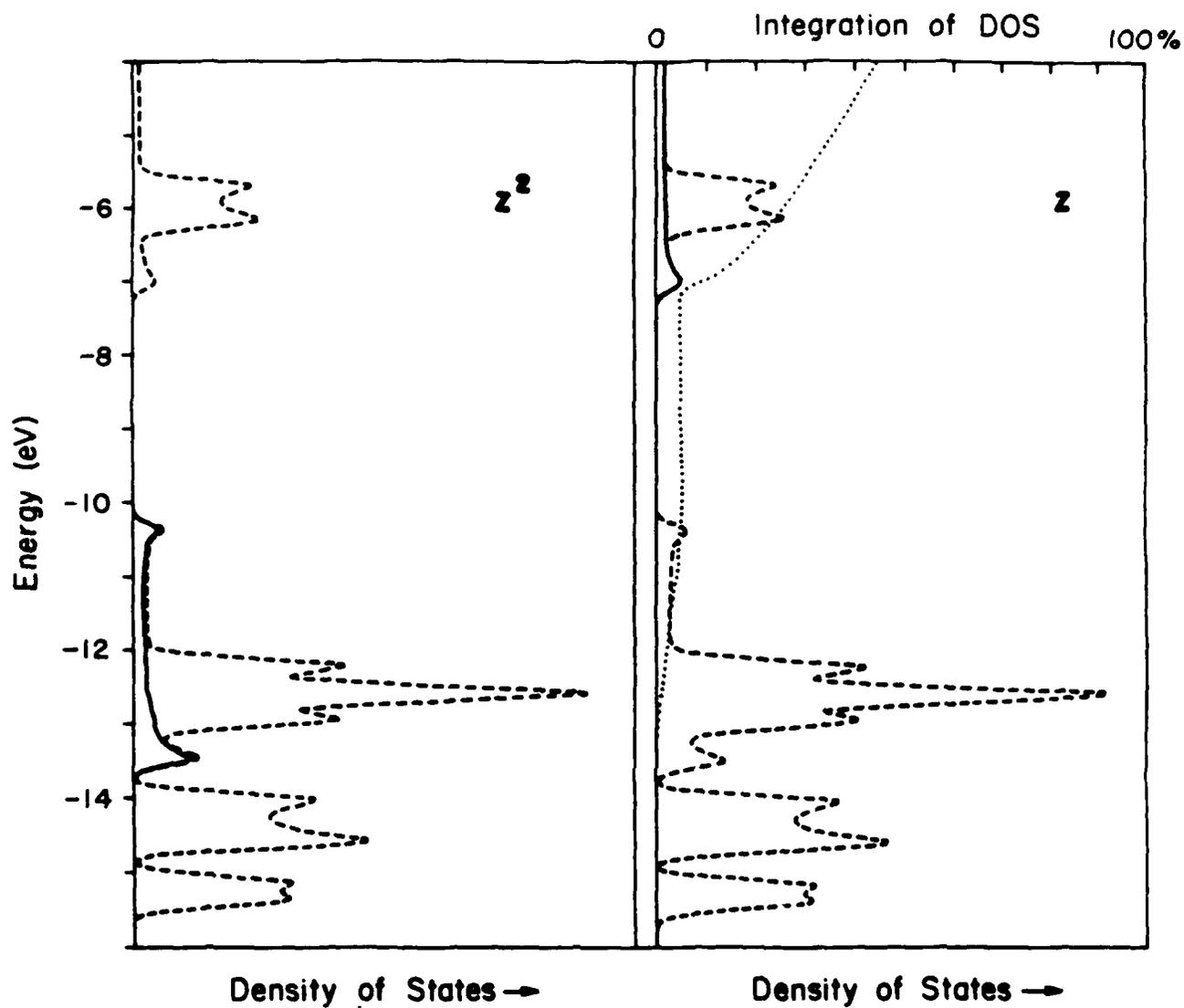


Figure 13. z^2 and z contributions to the total DOS of an eclipsed PtH_4^{2-} stack. The dotted line is an integration of the z orbital contribution

interact with the acceptor function (z) of its neighbor. This is shown in 30. The overlap is good, but the energy match is



30

poor.¹¹ So the interaction is small, but it's there. Alternatively, one could think about interaction of the Bloch functions, or symmetry-adapted z and z^2 crystal orbitals. At $k = 0$ and $k = \pi/a$, they don't mix. But at every interior point in the Brillouin zone, the symmetry group of ψ is isomorphic to C_{4v} ,¹⁵ and both z and z^2 Bloch functions transform as a_1 . So they mix. Some small bonding is provided by this mixing. But it is really small. When the stack is oxidized, the loss of this bonding (which would lengthen the Pt-Pt contact) is overcome by the loss of Pt-Pt antibonding that is a consequence of the vacated orbitals being at the top of the z^2 band.

The Detective Work of Tracing Molecule-Surface Interactions:
Decomposition of the DOS

For another illustration of the utility of DOS decompositions let's turn to a surface problem. We saw in a previous section the band structures and DOS of the CO overlayer and the Ni slab separately (Fig. 6, 7, 9). Now let's put them together in Fig. 14. The adsorption geometry is that shown earlier in 24, with Ni-C 1.8 Å. Only the densities of states are shown, based on the band structures of Fig. 7 and 9.²⁷ Some of the wiggles in the DOS curves also are not real, they're a result of insufficient k-point sampling in the computation.

Figure 14

It's clear that the composite system $c(2 \times 2)\text{CO-Ni}(100)$ is roughly a superposition of the slab and CO layers. Yet things have happened. Some of them are clear -- the 5σ peak in the DOS has moved down. Some are less clear -- where is the $2\pi^*$, and which orbitals on the metal are active in the interaction?

Let's see how the partitioning of the total DOS helps us to trace down the bonding in the chemisorbed CO system. Figure 15

Figure 15

shows the 5σ and $2\pi^*$ contributions to the DOS. The dotted line is a simple integration of the DOS of the fragment of contributing orbital. The relevant scale, 0 to 100%, is to be read at top. The integration shows the total percent of the

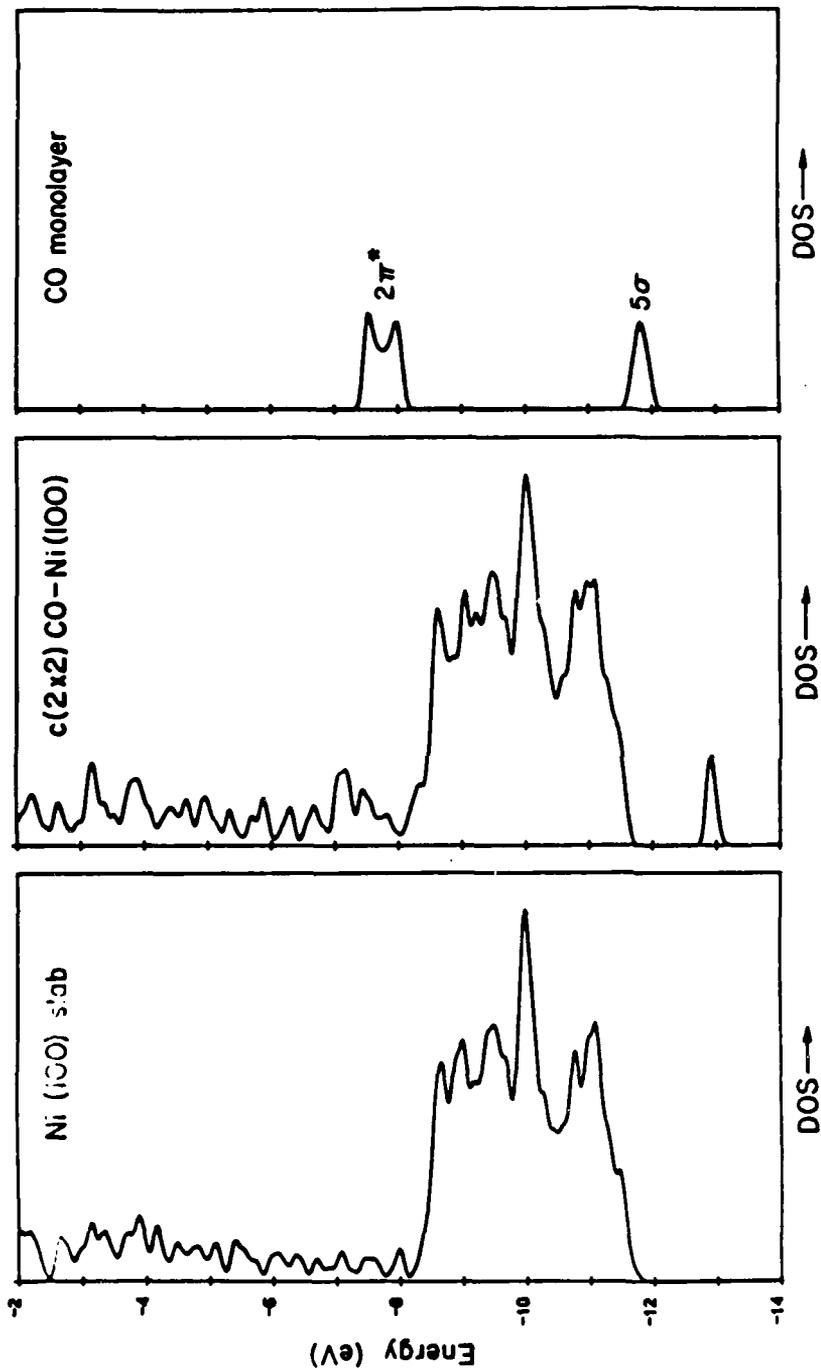


Figure 14. The total density of states of a model $c(2 \times 2)$ CO-Ni(100) system (center), compared to its isolated 4-layer Ni slab (left) and CO monolayer components.

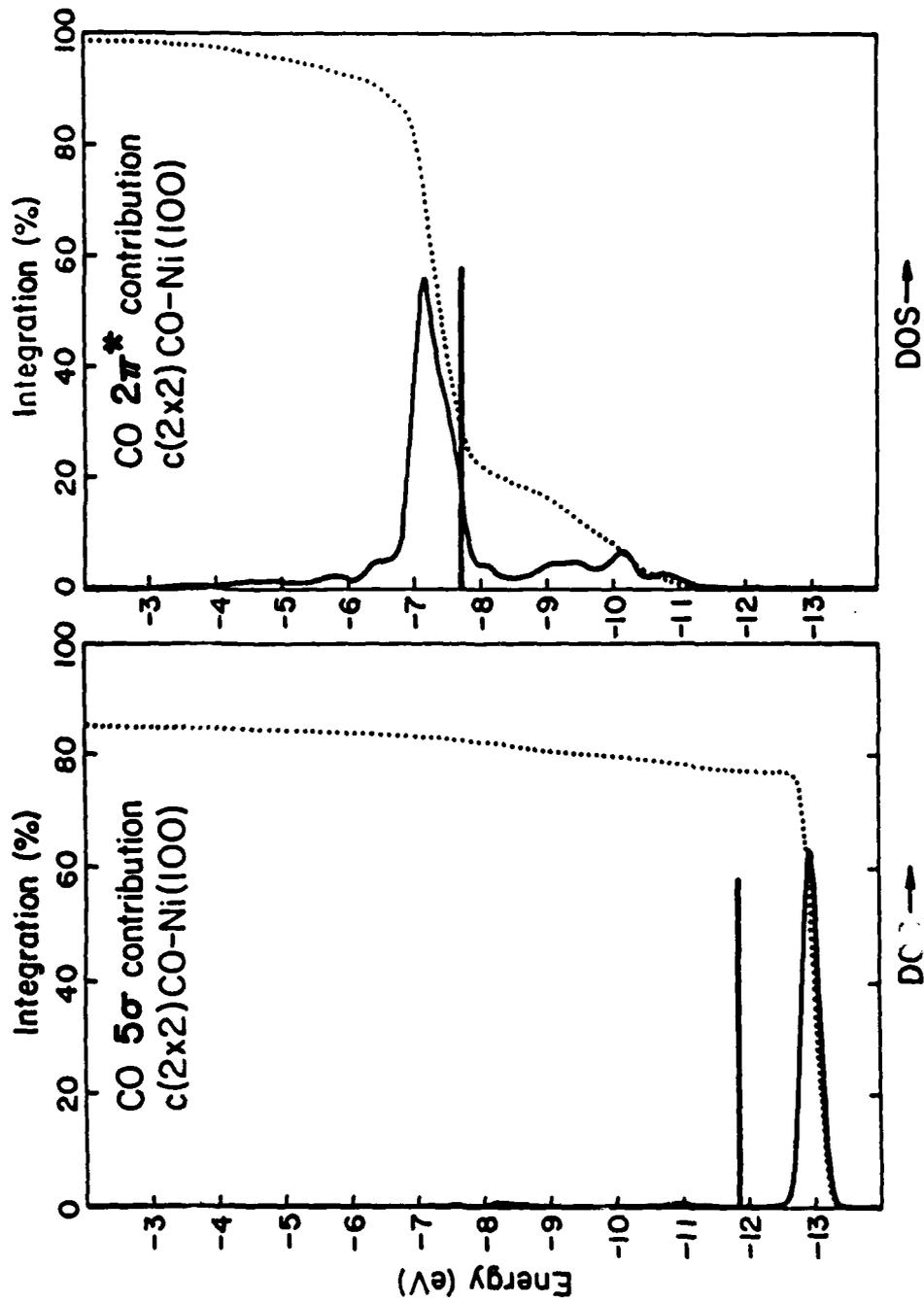
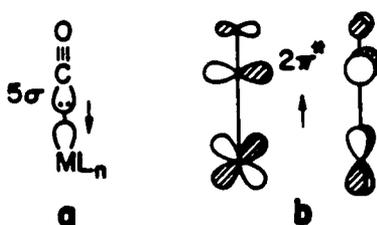


Figure 15. For the $c(2 \times 2)CO-Ni(100)$ model this shows the 5σ and $2\pi^*$ contributions to the total DOS. Each contribution is magnified. The position of each level in isolated CO is marked by a line. The integration of the DOS contribution is given by the dotted line.

given orbital that's occupied at a specified energy. It is clear that the 5σ orbital, though pushed down in energy, remains quite localized. Its occupation (the integral of this DOS contribution up to the Fermi level) is 1.62 electrons. The $2\pi^*$ orbital obviously is much more delocalized. It is mixing with the metal d band, and, as a result, there is a total of 0.74 electrons in the $2\pi^*$ levels together.

Which levels on the metal surface are responsible for these interactions? In discrete molecular systems we know that the important contributions to bonding are forward donation, 31a, from the carbonyl lone pair, 5σ , to some appropriate hybrid on a partner metal fragment, and back donation, 31b, involving the $2\pi^*$



31

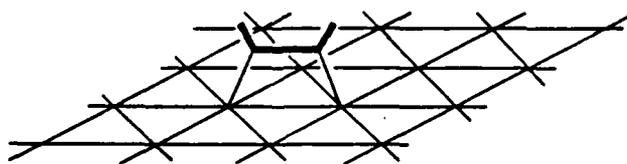
of CO and a d_π orbital, xz , yz , of the metal. We would suspect that similar interactions are operative on the surface.

These can be looked for by setting side by side the d_σ (z^2) and 5σ contributions to the DOS, and d_π (xz , yz) and $2\pi^*$ contributions. In Fig. 16 the π interaction is clearest: note

 Figure 16

how $2\pi^*$ picks up density where the d_π states are, and vice versa, the d_π states have a "resonance" in the $2\pi^*$ density. I haven't shown the DOS of other metal levels, but were I to do so, it would be seen that such resonances are not found between those metal levels and 5σ and $2\pi^*$. The reader can confirm at least that 5σ does not pick up density where d_π states are, nor $2\pi^*$ where d_σ states are mainly found.²⁷ There is also some minor interaction of CO $2\pi^*$ with metal p_π states, a phenomenon not analyzed here.²⁸

Let's consider another system in order to reinforce our comfort with these fragment analyses. In 25 we drew several acetylene-Pt(111) structures with coverage = $\frac{1}{2}$. Consider one of these, the dibridged adsorption site alternative 25b redrawn in 32. The acetylene brings to the adsorption process a degenerate



32

set of high-lying occupied π orbitals, and also an important unoccupied π^* set. These are shown at the top of 33. In all known molecular and surface complexes, the acetylene is bent. This breaks the degeneracy of π and π^* , some s character mixing

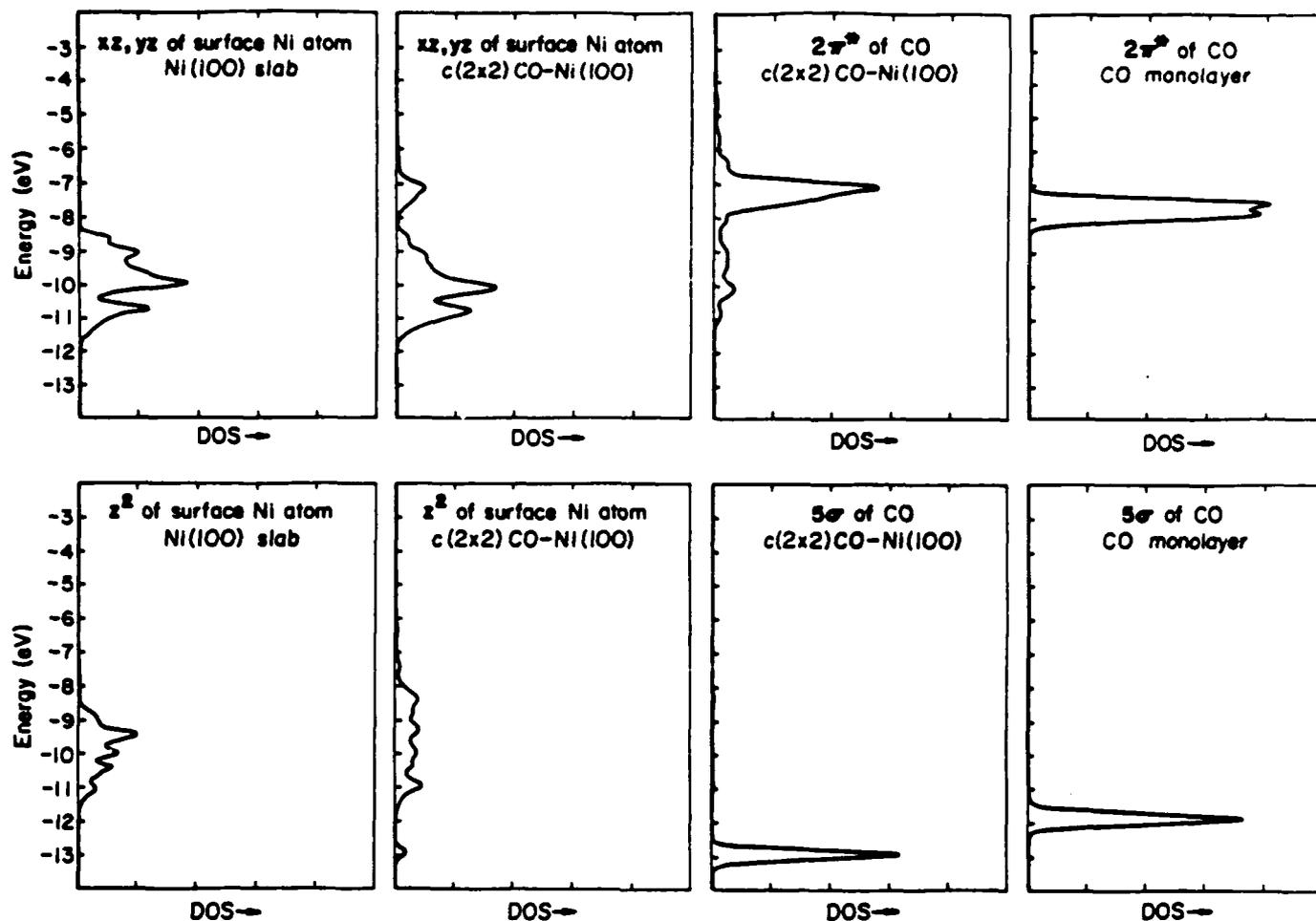
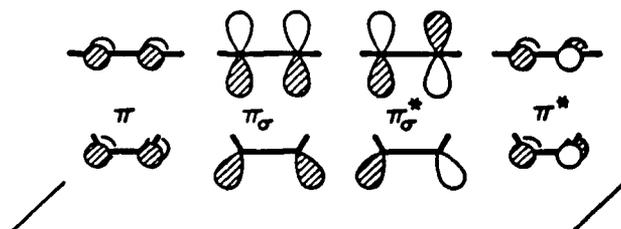


Figure 16. "Interaction Diagrams" for 5σ and $2\pi^*$ of $c(2 \times 2)$ CO-Ni(100). The extreme left and right panels in each case show the contributions of the appropriate orbitals (z^2 for 5σ , xz, yz for $2\pi^*$) of a surface metal atom (left), and of the corresponding isolated CO monolayer MO. The middle two panels then show the contributions of the same fragment MO's to the DOS of the composite chemisorption system.

into the π_σ and π_σ^* components which lie in the bending plane and point to the surface. The valence orbitals are shown at the bottom of 33. In fig. 17 we show the contributions of these

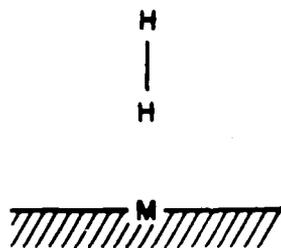


33

valence orbitals to the total DOS of 33. The sticks mark the positions of the acetylene orbitals in the isolated molecule. It is clear that π and π^* interact less than π_σ and π_σ^* of CO.²⁹

Figure 17

A third system: in the early stages of dissociative H₂ chemisorption, it is thought that H₂ approaches perpendicular to the surface, as in 34. Consider Ni(111), related to the Pt(111)



34

surface we have discussed earlier. Fig. 18 shows a series of three snapshots of the total DOS and its $\sigma_u^*(H_2)$ projection.³⁰ These are computed at separations of 3.0, 2.5 and 2.0 Å from the

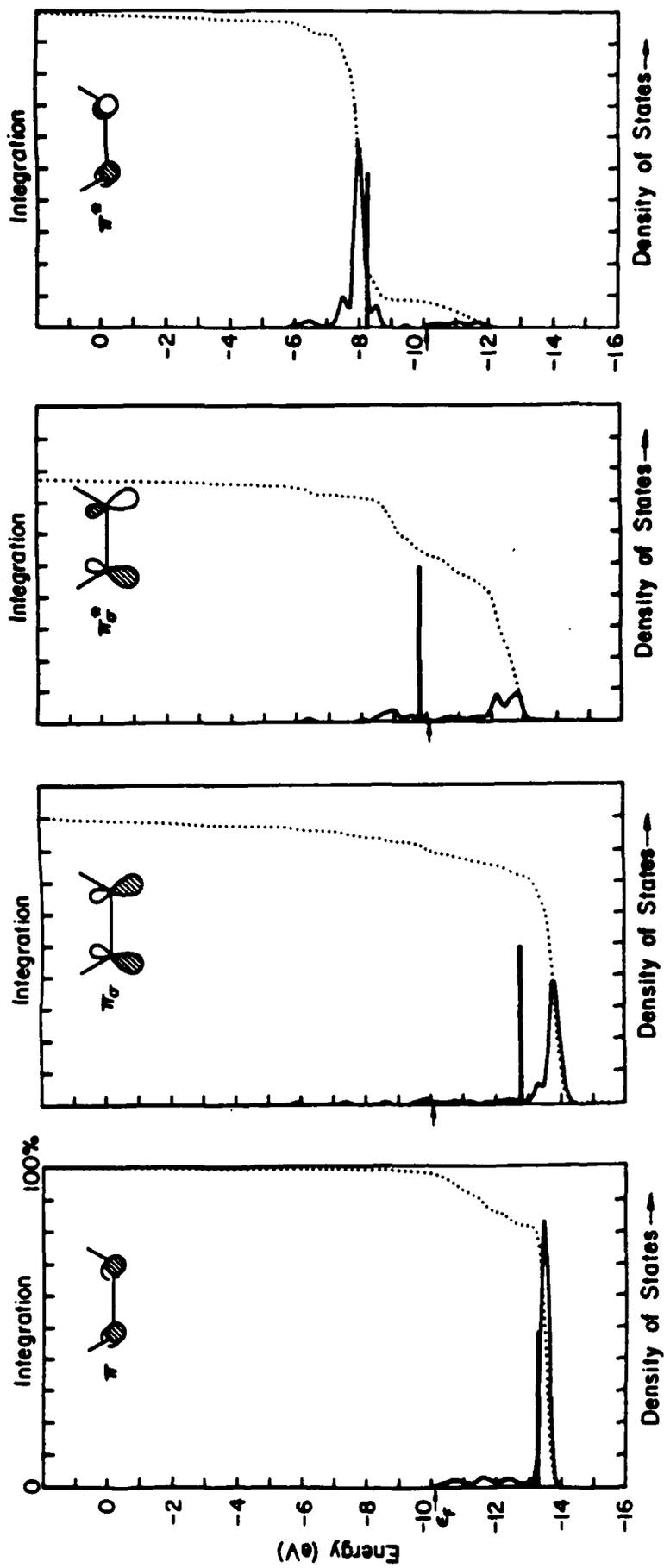


Figure 17. From left to right: contributions of π , π_G , π_G^* and π^* to the DOS of C_2H_2 in a two-fold geometry on Pt(111). The lines mark the positions of these levels in a free bent acetylene. The integrations of the DOS contributions are indicated by the dotted line.

 Figure 18

nearest H of H₂ to the Ni atom directly below it. The σ_g orbital of H₂ (the lowest peak in the DOS in Fig. 18) remains quite localized. But the σ_u^* interacts, is strongly delocalized, with its main density pushed up. The primary mixing is with the Ni s, p band. As the H₂ approaches some σ_u^* density comes below the Fermi level.

Why does σ_u^* interact more than σ_g ? The classical perturbation theoretic measure of interaction

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

helps one to understand this. σ_u^* is more in resonance in energy, at least with the metal s, p band. In addition, its interaction with an appropriate symmetry metal orbital is greater than that of σ_g , at any given energy. This is the consequence of including overlap in the normalization:

$$\psi_{\pm} = \frac{1}{\sqrt{2(1 \pm S_{12})}} (\phi_1 \pm \phi_2)$$

The σ_u^* coefficients are substantially greater than those in σ_g . This has been pointed out by many people, but in the present context importantly emphasized by Shustorovich and Baetzold.³¹⁻³³

We have seen that we can locate the electrons in the crystal. But...

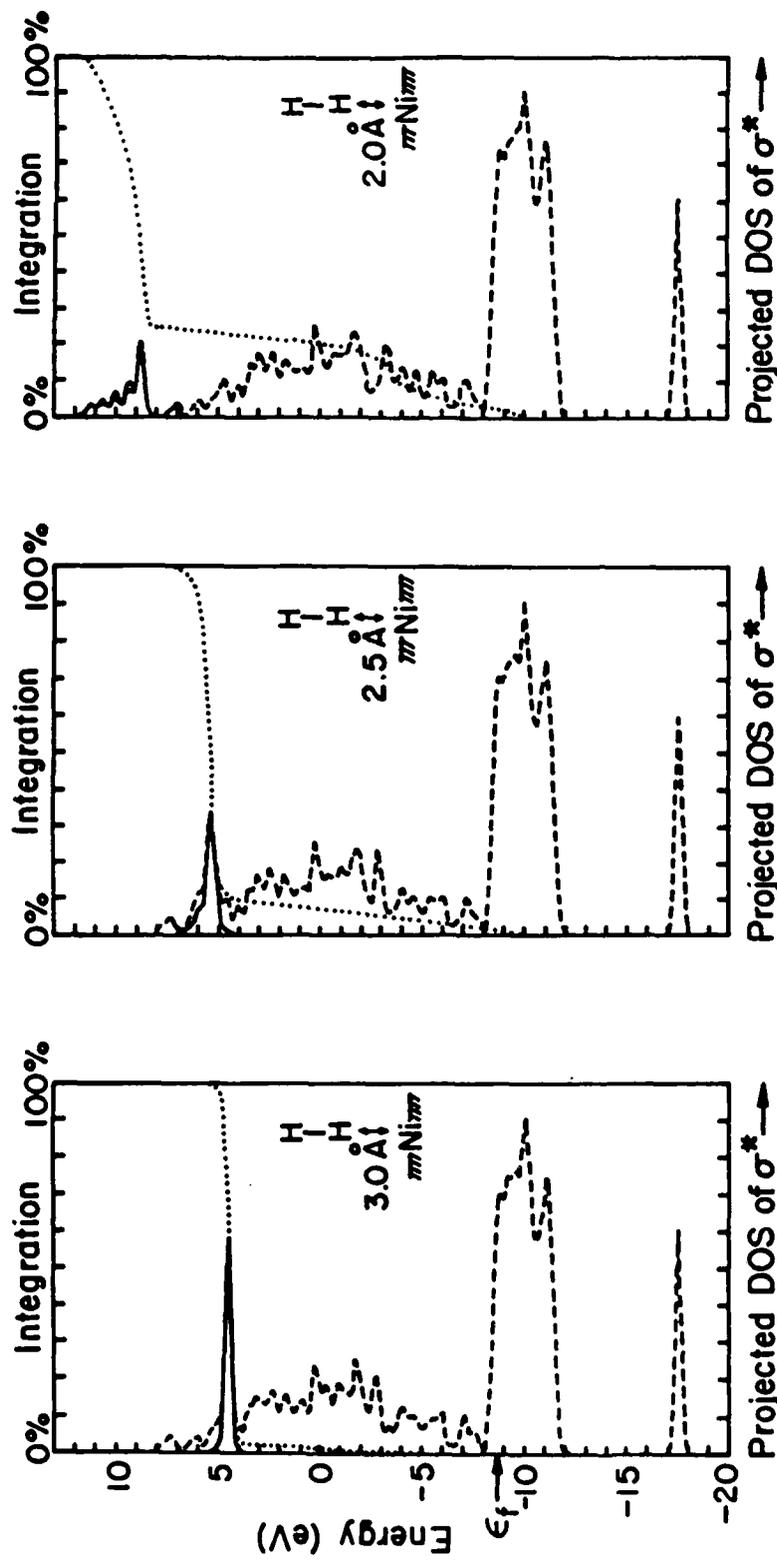


Figure 18. That part of the total DOS (dashed line) which is in the H₂ σ^* (solid line) at various approach distances of a frozen H₂ to a Ni(111) surface model. The dotted line is an integration of the H₂ density.

Where are the Bonds?

Local bonding considerations (see 27, 29) trivially lead us to assign bonding characteristics to certain orbitals and, therefore, bands. There must be a way to find these bonds in the bands that a fully delocalized calculation gives.

It's possible to extend the idea of an overlap population to a crystal. Recall that in the integration of ψ^2 for a two-center orbital, $2c_1c_2S_{12}$ was a characteristic of bonding. If the overlap integral is taken as positive (and it can always be arranged so) then this quantity scales as we expect of a bond order: it is positive (bonding) if c_1 and c_2 are of the same sign, and negative if c_1 and c_2 are of opposite sign. And the magnitude of the "Mulliken overlap population", for that is what $2c_1c_2S_{12}$ (summed overall orbitals on the two atoms, over all occupied MO's) is called, depends on c_i , c_j , S_{ij} .

Before we move into the solid, let's take a look at how these overlap populations might be used in a molecular problem. Fig. 19 shows the familiar energy levels of a diatomic, N_2 , a

Figure 19

"density of states" plot of these (just sticks proportional to the number of levels, of length one for σ , two for π) and the contributions of these levels to the overlap population. $1\sigma_g$ and $1\sigma_u$ (not shown in the figure) contribute little, because S_{ij} is small between tight 1s orbitals. $2\sigma_g$ is strongly bonding, $2\sigma_u$

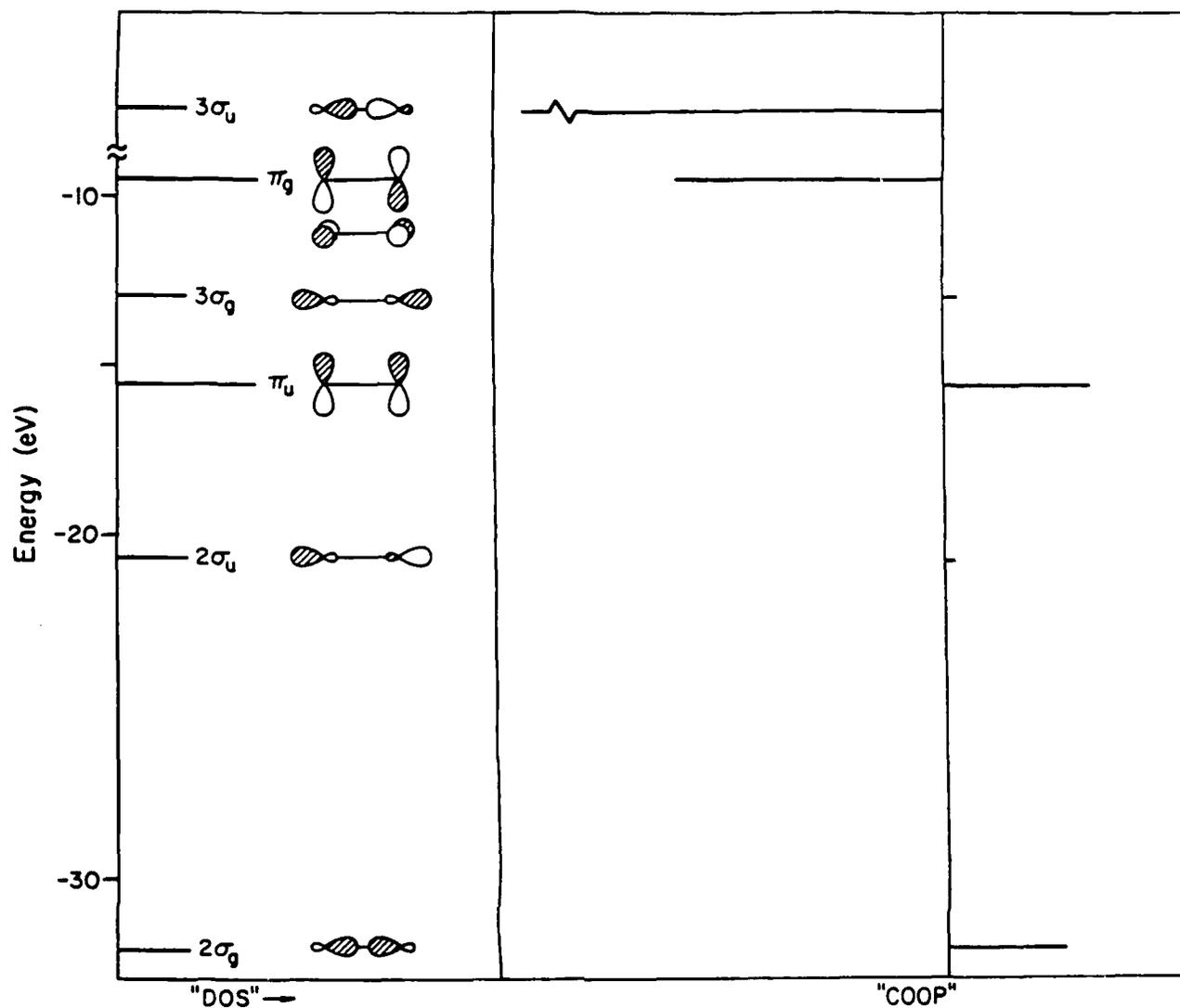


Figure 19. The orbitals of N_2 (left) and a "solid state way" to plot the DOS and COOP curves for this molecule. The $1\sigma_g$ and $1\sigma_u$ orbitals are out of the range of this figure.

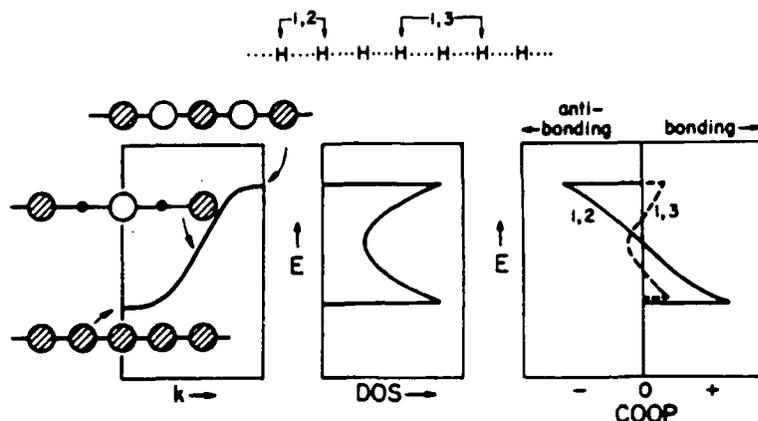
and $3\sigma_g$ are essentially non-bonding. These are best characterized as lone pair combinations. π_u is bonding, σ_g antibonding, $3\sigma_u$ the σ^* level. The right-hand side of Fig. 19 characterizes the bonding in N_2 at a glance. It tells us that maximal bonding is there for 7 electron pairs (counting $1\sigma_g$ and $1\sigma_u$); more or fewer electrons will lower the N-N overlap population. It would be nice to have something like this for extended systems.

A bond indicator is easily constructed for the solid. An obvious procedure is to take all the states in a certain energy interval and interrogate them as to their bonding proclivities, measured by the Mulliken overlap population, $2c_i c_j S_{ij}$. What we are defining is an overlap-population-weighted density of states. The beginning of the obvious acronym (OPWDOS) unfortunately has been preempted by another common usage in solid state physics. For that reason, we have called this quantity COOP, for crystal orbital overlap population.³⁴ It's also nice to think of the suggestion of orbitals working together to make bonds in the crystal, so the word is pronounced "co-op".

To get a feeling for this quantity, let's think what a COOP curve for a hydrogen chain looks like. The simple band structure and DOS were given earlier, 26; they are repeated with the COOP curve in 35.

To calculate a COOP curve, one has to specify a bond. Let's take the nearest neighbor 1,2 interaction. The bottom of the

band is 1,2 bonding, the middle non-bonding, the top antibonding. The COOP curve obviously has the shape shown at



35

right in 35. But not all COOP curves look that way. If we specify the 1,3 next-nearest-neighbor bond (silly for a linear chain, not so silly if the chain is kinked), then the bottom and the top of the band are 1,3 bonding, the middle anti-bonding. That curve, the dotted line in the drawing 35, is different in shape. And, of course, its bonding and antibonding amplitude is much smaller because of the rapid decrease of S_{ij} with distance.

Note the general characteristics of COOP curves -- positive regions which are bonding, negative regions which are antibonding. The amplitudes of these curves depend on the number of states in that energy interval, the magnitude of the coupling overlap, and the size of the coefficients in the MO's.

The integral of the COOP curve up to the Fermi level is the total overlap population of the specified bond. This points us to another way of thinking of the DOS and COOP curves. These are

the differential versions of electronic occupation and bond order indices in the crystal. The integral of the DOS to the Fermi level gives the total number of electrons; the integral of the COOP curve gives the total overlap population, which is not identical to the bond order, but which scales like it. It is the closest a theoretician can get to that ill-defined but fantastically useful simple concept of a bond order.

To move to something a little more complicated than the hydrogen or polyene chain, let's examine the COOP curves for the PtH_4^{2-} chain, Fig. 20 shows both the Pt-H and Pt-Pt COOP curves.

Figure 20

The DOS curve for the polymer is also drawn. The characterization of certain bands as bonding or antibonding is obvious, and matches fully the expectations of the approximate sketch 27. The bands at -14, -15eV are Pt-H σ bonding, the band at -6eV Pt-H antibonding (this is the crystal-field destabilized x^2-y^2 orbital). It is no surprise that the mass of d-block levels between -10 and -13 eV doesn't contribute anything to Pt-H bonding. But of course it is these orbitals which are involved in Pt-Pt bonding. The rather complex structure of the -10 to -13eV region is easily understood by thinking of it as a superposition of σ (z^2-z^2), π (xz, yz)-(xz, yz) and δ ($xy-xy$) bonding and antibonding, as shown in 36. Each type of bonding generates a band, the bottom of which is bonding and the top

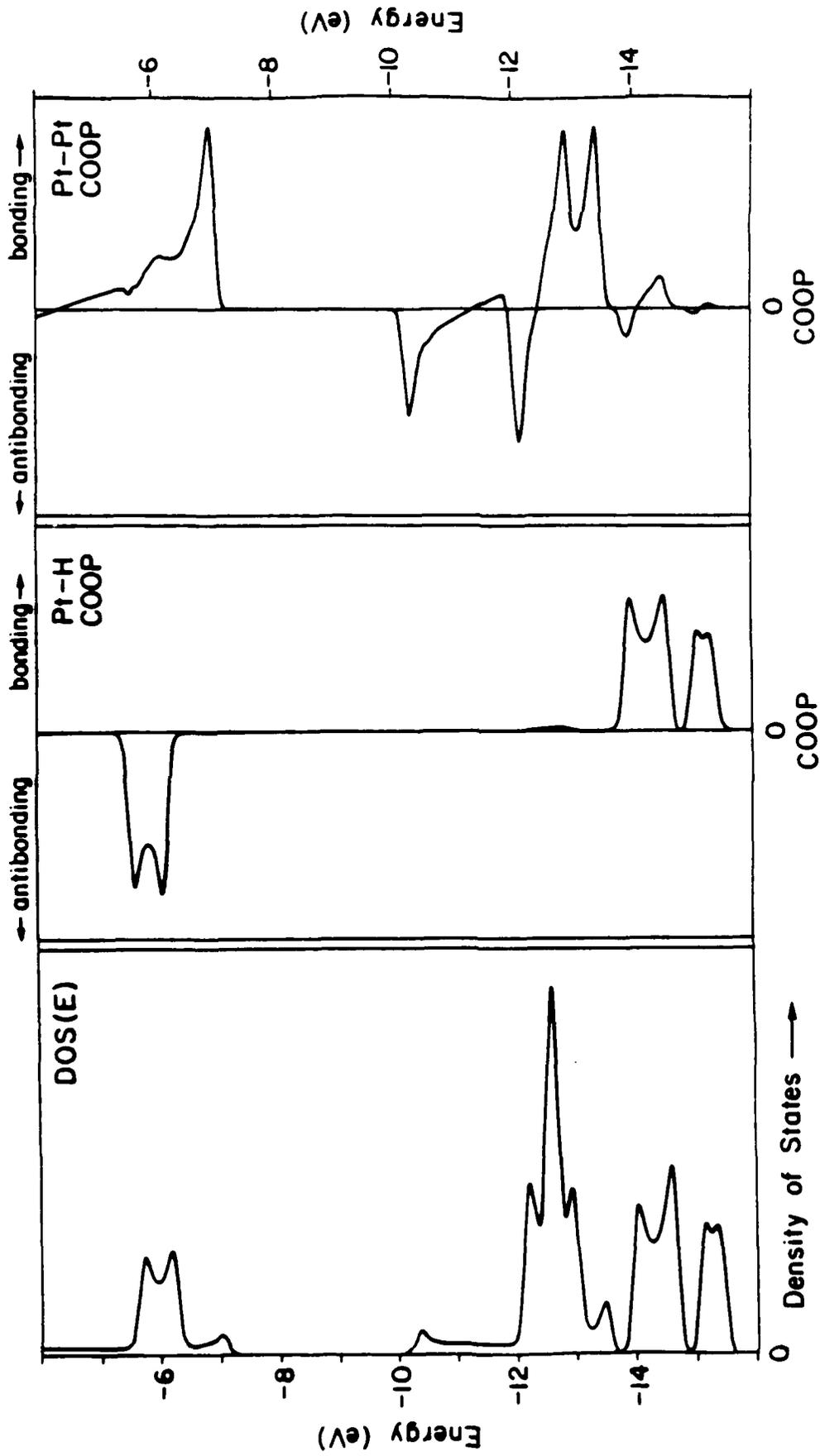
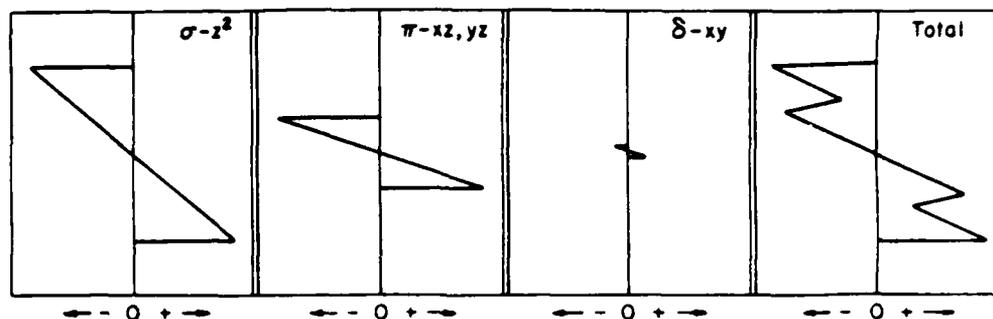


Figure 20. Total density of states (left), and Pt-H (middle) and Pt-Pt (right) crystal orbital overlap population curves for the eclipsed Pth_4^{2-} stack.

Schematic decomposition of the Pt d-block total COOP curve for PtH_4^{2-} 

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antibonding (see 35 and Fig. 3). The δ contribution to the COOP is small, because of the poor overlap involved. The large Pt-Pt bonding region at -7eV is due to the bottom of the Pt z band.

We now have a clear representation of the Pt-H and Pt-Pt bonding properties as a function of energy. If we are presented with an oxidized material, then the consequences of the oxidation on the bonding are crystal clear from Fig. 20. Removing electrons from the top of the z^2 band at -10eV takes them from orbitals that are Pt-Pt antibonding, Pt-H nonbonding. So we expect the Pt-Pt separation, the stacking distance, to decrease, as it does.¹²

The tuning of electron counts is one of the strategies of the solid state chemists. Elements can be substituted, atoms intercalated, non-stoichiometries enhanced. Oxidation and reduction, in solid state chemistry as in ordinary molecular solution chemistry, are about as characteristic (but experimentally not always trivial) chemical activities as one can conceive. The conclusions we reached for the Pt-Pt chain were simple, easily anticipated. Other cases are guaranteed to be

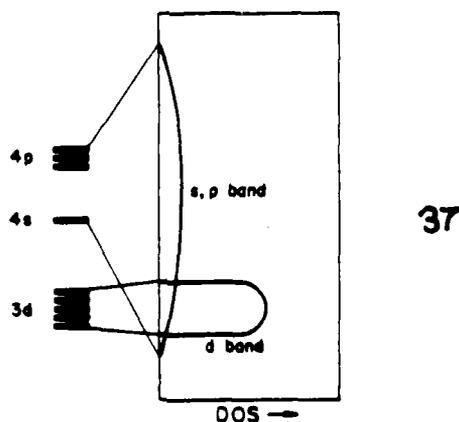
more complicated. The COOP curves allow one, at a glance, to reach conclusions about the local effects on bond length (will bonds be weaker, stronger) upon oxidation or reduction.

We showed earlier a band structure for rutile. The corresponding COOP curve for the Ti-O bond (Fig. 21) is extremely

Figure 21

simple. Note the bonding in the lower, oxygen bands, and antibonding in the e_g crystal-field destabilized orbitals. The t_{2g} band is, as expected, Ti-O nonbonding.

Let's try our hand at predicting the DOS for something quite different from PtH_4^{2-} or TiO_2 , namely a bulk transition metal, the face-centered-cubic Ni structure. Each metal atom has as its valence orbitals 3d, 4s, 4p, ordered in energy approximately as at the left in 37. Each will spread out into a band. We can



make some judgment as to the width of the bands from the overlap. The s, p orbitals are diffuse, their overlap will be large, and a wide band will result. They also mix with each other

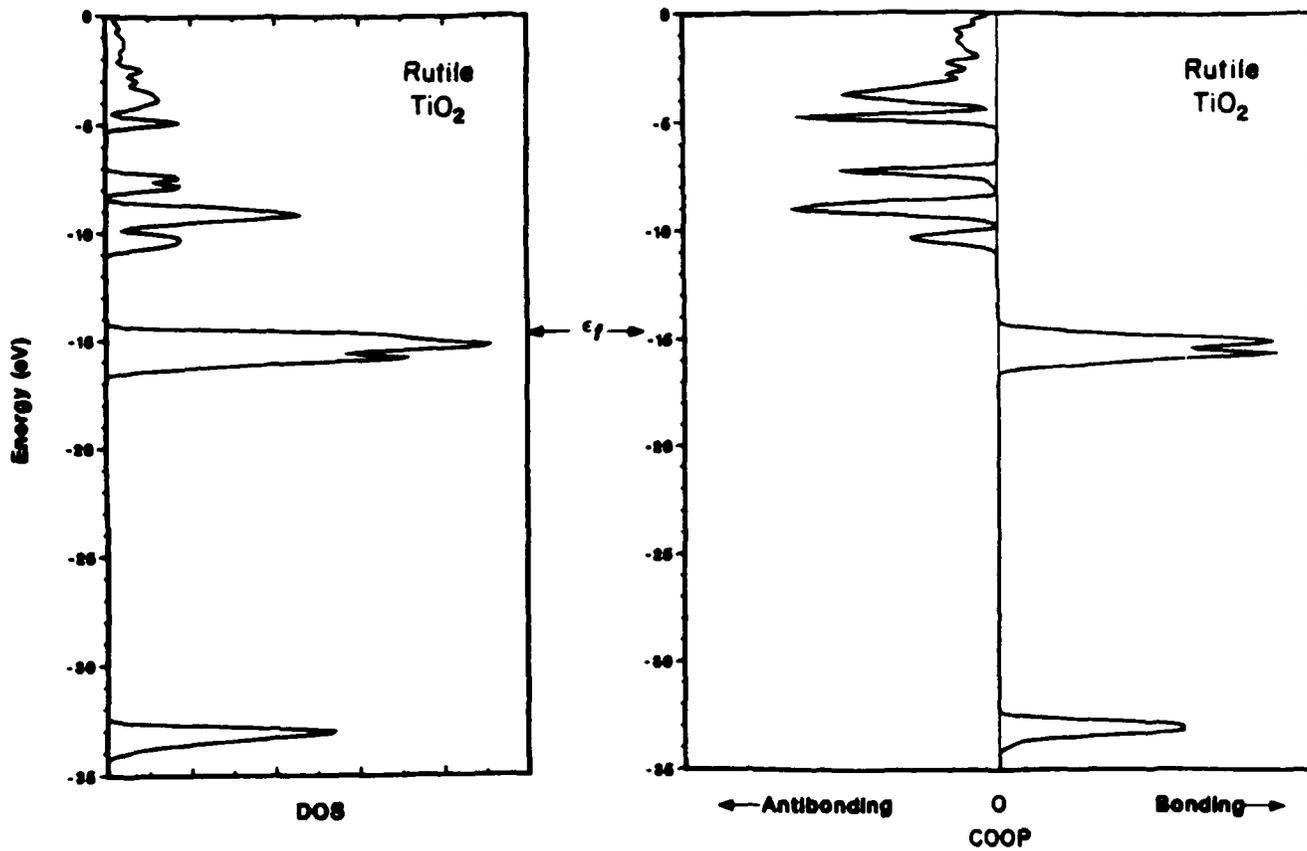


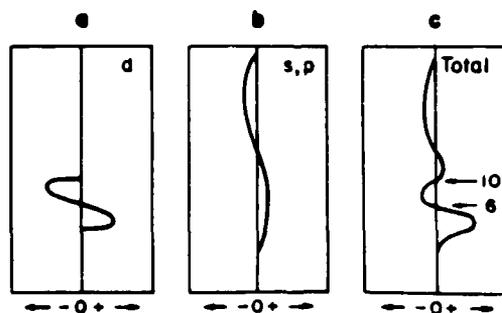
Figure 21. DOS and Ti-O COOP for rutile.

extensively. The d orbitals are contracted, and so will give rise to a relatively narrow band.

The computed DOS for bulk Ni (bypassing the actual band structure) is shown in Fig. 22, along with the Ni s and p contributions to that DOS. What is not s or p is d and s contributions. The general features of 37 are reproduced. At the Fermi level, a substantial part of the s band is occupied, so that the calculated³⁵ Ni configuration is $d^{9.15}s^{0.62}p^{0.23}$.

Figure 22

What would one expect of the COOP curve for bulk Ni? As a first approximation we could generate the COOP curve for each band separately, as in 38a & b. Each band in 37 has a lower Ni-Ni bonding part, an upper Ni-Ni antibonding part. The composite



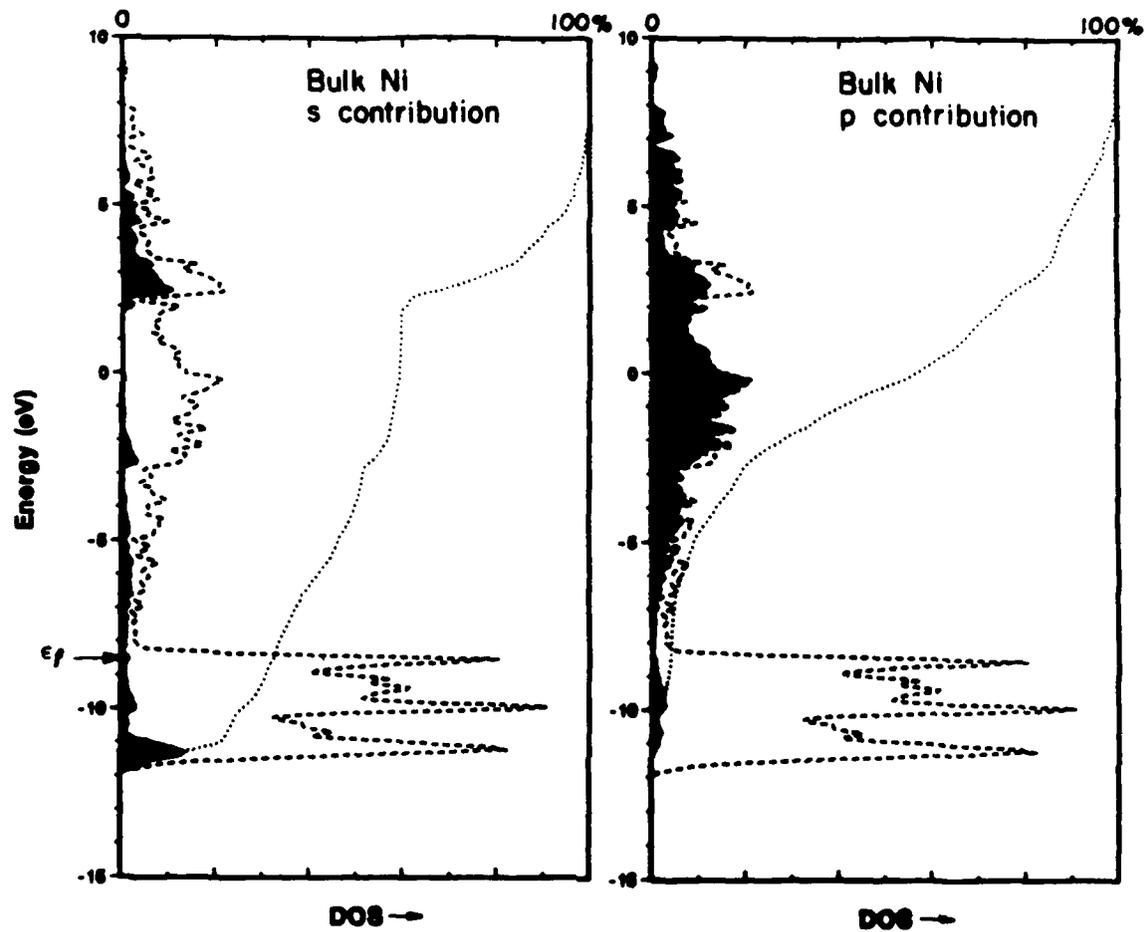


Figure 22. Total DOS (dashed line) and 4s and 4p contributions to it in bulk Ni. The dotted line is an integration of the occupation of a specified orbital, on a scale of 0 to 100% given at top.

is 38c. The computed COOP curve is in Fig. 23. The expectations of 38c are met reasonably well.

Figure 23

A metal-metal COOP curve like that of 38c or Fig. 23 is expected for any transition metal. The energy levels might be shifted up, they might be shifted down, but their bonding characteristics are likely to be the same. If we assume that a similar band structure and COOP curve hold for all metals (in the solid state trade this would be called the rigid band model), then Fig. 23 gains tremendous power. It summarizes, simply, the cohesive energies of all metals. As one moves across the transition series, the M-M overlap population (which is clearly related to the binding or cohesive energy) will increase, peaking at about 6 electrons/metal -- Cr, Mo, W. Then it will decrease toward the end of the transition series and rise again for small s, p electron counts. For more than 14 electrons, a metal is unlikely; the net overlap population for such high coordination becomes negative. Molecular allotropes with lower coordination are favored. There is much more to cohesive energies and the metal-nonmetal transition than this. Still, a lot of physics and chemistry flows from the simple construction of 38.

COOP curves are a useful tool in the tracing down of surface-adsorbate interactions. Let's see, for instance, how this indicator may be used to support the picture of CO chemisorption that was described above. The relevant curve is in

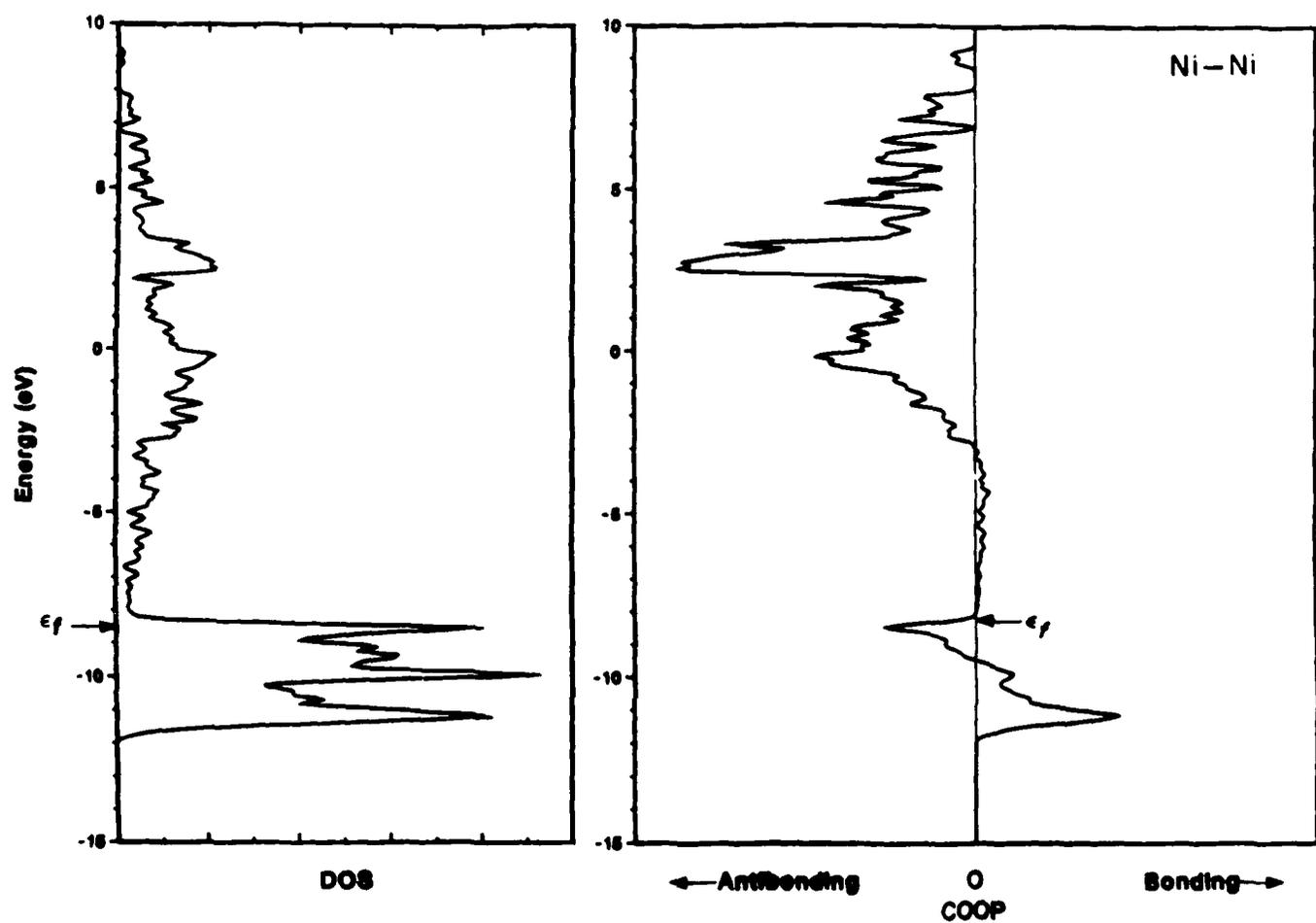


Figure 23. The total DOS and nearest neighbor Ni-Ni COOP in bulk Ni.

Fig. 24. The solid line describes Ni-C bonding, the dotted line C-O bonding. The C-O bonding is largely concentrated in orbitals

Figure 24

which are out of the range (below) this figure. Note the major contribution to Ni-C bonding in both the 5σ peak and the bottom of the d band. The 5σ contribution is due to σ -bonding, 31a. But the bottom of the d band contributes through π -bonding, 31b. This is evident from the "mirroring" C-O antibonding in the same region. The antibonding component of that $d_{\pi}-2\pi^*$ interaction is responsible for the Ni-C and C-O antibonding above the Fermi level.²⁷

It may be useful to emphasize that these curves are not only descriptive, but also form a part of the story of tracing down interaction. For instance, supposing we were not so sure that it is the $d_{\pi}-2\pi^*$ interaction which is responsible for a good part of the bonding. Instead, we could have imagined π bonding between 1π and some unfilled d_{π} orbitals. The interaction is indicated schematically in 39. If this mixing were important, the d block orbitals, interacting in an antibonding way with 1π below them, should become in part Ni-C antibonding and C-O bonding. Nothing of this sort is seen in Fig. 24. The C-O antibonding in the d block region is, instead, diagnostic of $2\pi^*$ mixing being important.

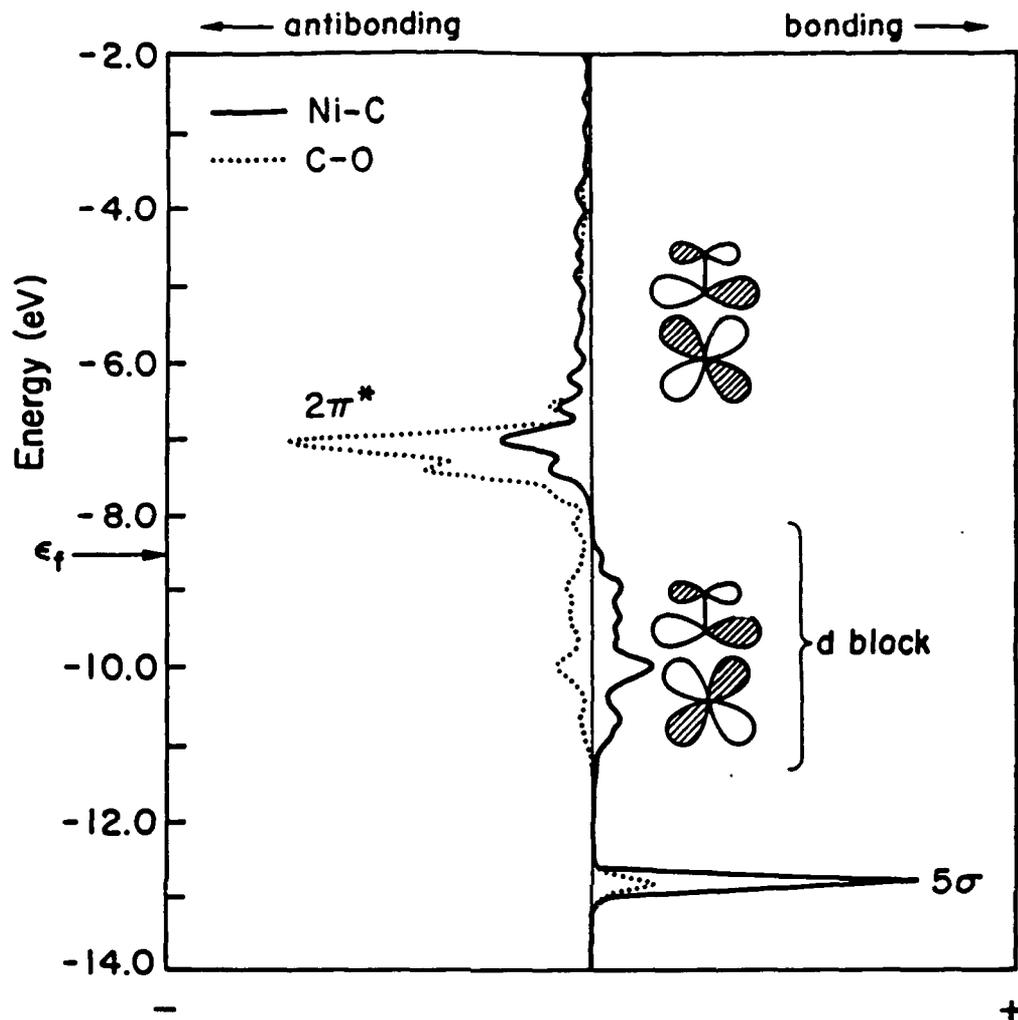
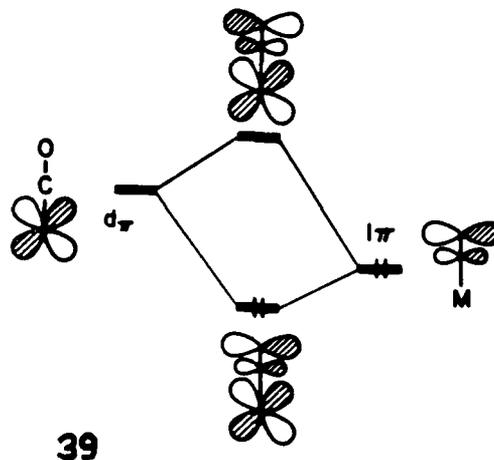


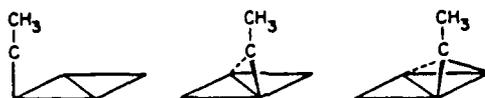
Figure 24. Crystal orbital overlap population for CO, on-top, in a $c(2 \times 2)CO-Ni(100)$ model. Representative orbital combinations are drawn out.



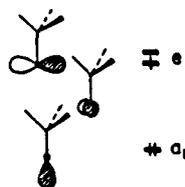
Incidentally, the integrated overlap populations up to the Fermi level are Ni-C 0.84, C-O 1.04. In free CO the corresponding overlap population is 1.21. The bond weakening is largely due to population of $2\pi^*$ on chemisorption.

Another illustration of the utility of COOP curves is provided next by a question of chemisorption site preference. On many surfaces, including Pt(111), a particularly stable dead end in the surface chemistry of acetylene is ethylidyne, CCH_3 .³⁶ How that extra hydrogen is picked up is a fascinating question. But let's bypass that and think about where the CCH_3 wants to be. 40 shows three alternatives -- 1-fold or "on-top," 2-fold or "bridging," and 3-fold or "capping." Experiment and theory show a great preference for the capping site. Why?

The important frontier orbitals of a carbyne, CR, are shown in 41. The C 2p orbitals, the e set, are a particularly attractive acceptor set, certain to be important in any chemistry



40



41

of this fragment. We could trace its involvement in the three alternative geometries 40 via DOS plots, but instead we choose to show in Fig. 25 the Pt-C COOP curve for 1-fold and 3-fold adsorption.

Figure 25

In both on-top and capping sites the carbyne e set finds metal orbitals to interact with. Bonding and antibonding combinations form. The coupling overlaps are much better in the capping site. The result is that the carbon-metal e-type antibonding combinations do not rise above the Fermi level in the 1-fold case, but do so in the 3-fold case. Figure 25 clearly shows this -- the bonding and antibonding combinations are responsible for recognizable positive and negative COOP peaks.

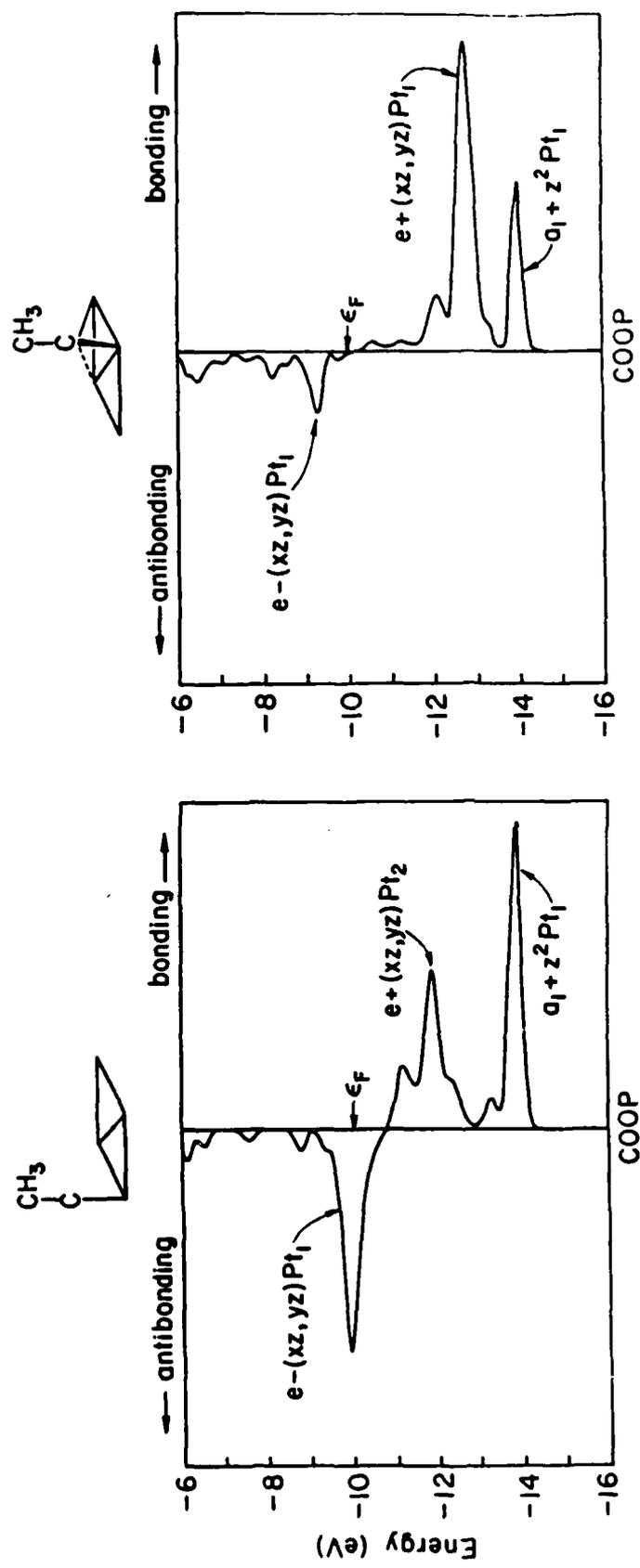


Figure 25. COOP curve for the α -carbon-Pt₁ bond in the 1-fold (left) and 3-fold (right) geometry of ethylidyne, CCH₃, on Pt(111).

The total surface-CCH₃ overlap populations are 0.78 in the 1-fold case, 1.60 in the 3-fold case. The total energy follows these bonding considerations; the capping site is much preferred.²⁹

With a little effort, we have constructed the tools -- density of states, its decompositions, the crystal orbital overlap population -- which allow us to move from a complicated, completely delocalized set of crystal orbitals or Bloch functions to the localized, chemical description. There is no mystery in this motion. In fact, what I hope I have shown here is just how much power there is in the chemists' concepts. The construction of the approximate DOS and bonding characteristics of a PtH₄²⁻ polymer, or rutile, or bulk Ni, is really easy.

Of course, there is much more to solid state physics than band structures. The mechanism of conductivity, the remarkable phenomenon of superconductivity, the multitude of electric and magnetic phenomena that are special to the solid state, for these one needs the tools and ingenuity of physics.⁹ But as for bonding in the solid state, I think (some will disagree) there is nothing new, only a different language.

A Solid State Sample Problem: The ThCr₂Si₂ Structure

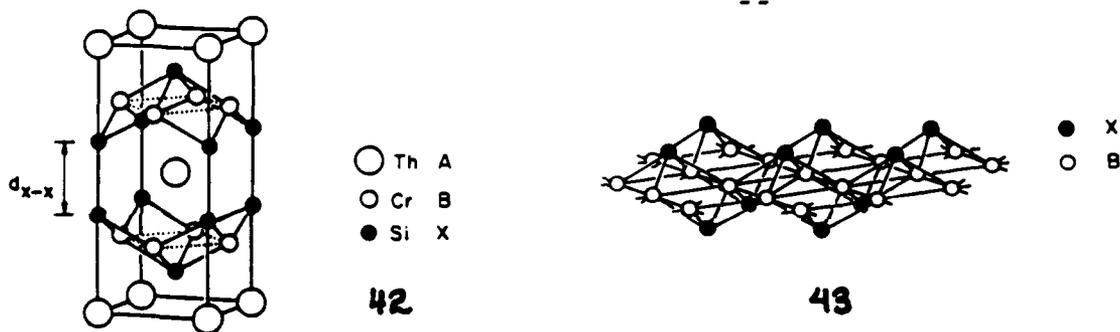
The preceding sections have outlined some of the theoretical tools for analysis of bonding in the solid state. To see how these ideas can be integrated, let's discuss a specific problem.

More than 200 compounds of AB₂X₂ stoichiometry adopt the ThCr₂Si₂ type structure³⁷. But you are not likely to find any mention of these in any modern textbook of general inorganic chemistry. Which just tells us something about the ascendancy of molecular inorganic chemistry, especially transition metal organometallic chemistry, in the last three decades. However, these compounds are there, we know their structures and they have interesting properties. A is typically a rare earth, alkaline earth, or alkali element, B is a transition metal or main group element, and X comes from group 15, 14, and occasionally 13. Since the synthesis of AB₂X₂ with A = a rare earth element, by Parthé, Rossi, and their coworkers, the unusual physical properties exhibited by these solids have attracted much attention. Physicists speak with enthusiasm of valence fluctuation, p-wave or heavy fermion superconductivity and of many peculiar magnetic properties of these materials. The very structure of these materials carries much that is of interest to the chemist.

The ThCr₂Si₂ structure type for AB₂X₂ stoichiometry compounds is shown in 42. It consists of B₂X₂²⁻ layers interspersed with A²⁺ layers. The bonding between A and B₂X₂

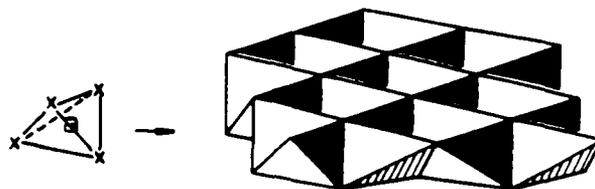
layers appears largely ionic, which is why we write the charge partitioning as A^{2+} and $B_2X_2^{2-}$. But in the $B_2X_2^{2-}$ layer there is indication not only of covalent B-X bonding, but also some metal-metal B-B bonding. Typical metal-metal distances are in the range of 2.7 - 2.9 Å.

A way to describe the B_2X_2 layers in these compounds is to imagine a perfect square-planar two-dimensional lattice of metal atoms, above and below the four-fold hollows of which lie the main group X atoms. This is shown in 43, below. The



coordination environment of the metal (B) is approximately tetrahedral in the main group elements (X), with four additional square planar near neighbor metals. The coordination of the X atoms is much more unusual -- they reside at the apex of a square pyramid.

It may be noted here that there are alternative ways to describe the layer structure. For instance, the B_2X_2 layer may be thought of as being built up by sharing four of the six edges of a BX_4 tetrahedron by infinite extension in 2 dimensions, as in 44. Such packing diagrams, or alternative ways of looking at the



44

same structure are inherently useful -- a new view often leads to new insight. I would just introduce a very personal prejudice, voiced above, for views of structure that make as many connections as possible to other subfields of chemistry. On that basis, I would give a slight preference to 43 over 44 -- the latter pulls one a little away from bonds.

There is a long $X \cdots X$ contact within the layer, but what becomes the main focus of this section is a remarkable tunable $X \cdots X$ contact between all layers, along the edges (and across top and bottom faces) of the tetragonal unit cell 42. This contact (d_{X-X}) is the primary geometrical variable in these structures.

Sometimes d_{X-X} is long, sometimes it is short. In Table 1 are shown two series of compounds studied by Mewis.³⁸ In these the cation is kept constant, and so is the main group element, P. Only the metal varies.

Table 1 here

Table 1. The X-X Distance in Some Phosphide Compounds of the AB_2X_2 Type.

AB_2X_2	$d_{X-X}(\text{Å})$	AB_2X_2	$d_{X-X}(\text{Å})$
$CaCu_{1.75}P_2$	2.25	$SrCu_{1.75}P_2$	2.30
$CaNi_2P_2$	2.30	$SrCo_2P_2$	3.42
$CaCo_2P_2$	2.45	$SrFe_2P_2$	3.43
$CaFe_2P_2$	2.71		

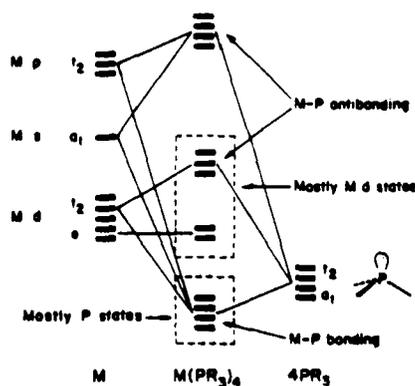
For reference the P-P distance in P_4 is 2.21 Å and 2.192 Å in Me_2P-PMe_2 . The P-P single bond distance in many compounds is remarkably constant at 2.19-2.26 Å. The P=P double bond and P≡P triple bond lengths are around 2.03 Å and 1.87 Å respectively. It is clear that the short distances in the $ThCr_2Si_2$ -type phosphides are characteristic of a full P-P single bond. The long contacts, such as 3.43 Å, imply essentially no bonding at all. All the compounds known with a nonbonding $X \cdots X$ separation contain metals from the left-hand side of the Periodic Table. In fact, examination of all the structures reveals a trend. As one moves left to right in the transition series, the P-P contact shortens. Clearly there is an electronic effect of work here -- a $P \cdots P$ bond is made or broken in the solid state. We would like to understand how and why this happens.

Incidentally, let's see what happens if one takes a Zintl viewpoint of these structures. The long $P \cdots P$ contact would be associated with a filled octet P^{3-} , the full P-P single bond with a $p-p^4-$. For a divalent A^{2+} we would be left with a metal in oxidation state II for the case of no $P \cdots P$ bond, oxidation state I for a single P-P bond. One could make some sense of the trend in terms of the energetics of the various metal oxidation states, but one way or another the Zintl picture has a difficult time with intermediate distances. How does one describe a $P \cdots P$ bond length of 2.72 Å? A delocalized approach has no problems with describing such partial bonding.

Chong Zheng and I³⁹ approached the AB_2X_2 structure, represented by a typical $BaMn_2P_2$ compound, in stages. First we looked at a single two-dimensional $Mn_2P_2^{2-}$ layer. Then we formed a three-dimensional $Mn_2P_2^{2-}$ sublattice by bringing many such layers together in the third dimension.

Consider a single Mn_2P_2 layer, 43. The Mn-P distance is 2.855 Å. The latter is definitely in the metal-metal bonding range, so a wide band, delocalized picture is inevitable. But in some hierarchy or ranking of interactions, it is clear the Mn-P bonding is stronger than Mn-Mn. So let's construct this solid conceptually or think of it in terms of first turning on Mn-P bonding, and then Mn-Mn interaction.

The local coordination environment at each Mn is approximately tetrahedral. If we had a discrete tetrahedral Mn complex, e.g. $Mn(PR_3)_4$, we might expect a qualitative bonding picture such as 45. Four phosphine lone pairs, a_1+t_2 in



symmetry, interact with their symmetry match, mainly Mn 4s and 4p, but also with the t_2 component of the Mn 3d set. Four orbitals, mainly on P, P-Mn σ bonding, go down. Four orbitals, mainly on Mn, P-Mn σ antibonding, go up. The Mn d block splits in the expected two below three way.

Something like this must happen in the solid. In addition, there are Mn-Mn bonding contacts in the layer, and these will lead to dispersion in those bands which are built up from orbitals containing substantial metal character. The combined construction is shown in Figure 26.

Figure 26

Can we see this local, very chemical bonding construction in a delocalized band structure? Most certainly. The calculated (extended Hückel) band structure and total density of states of a single $\text{Mn}_2\text{P}_2^{2-}$ layer is illustrated in Fig. 27.

Figure 27

The unit cell is a rhomboid of two Mn and two P atoms. P is clearly more electronegative than Mn, so we expect two mainly P 3s bands below six P 3p bands below 10 Mn 3d bands. The number of bands in Fig. 27 checks. A decomposition of the DOS (Fig. 28) confirms the assignment.

Figure 28

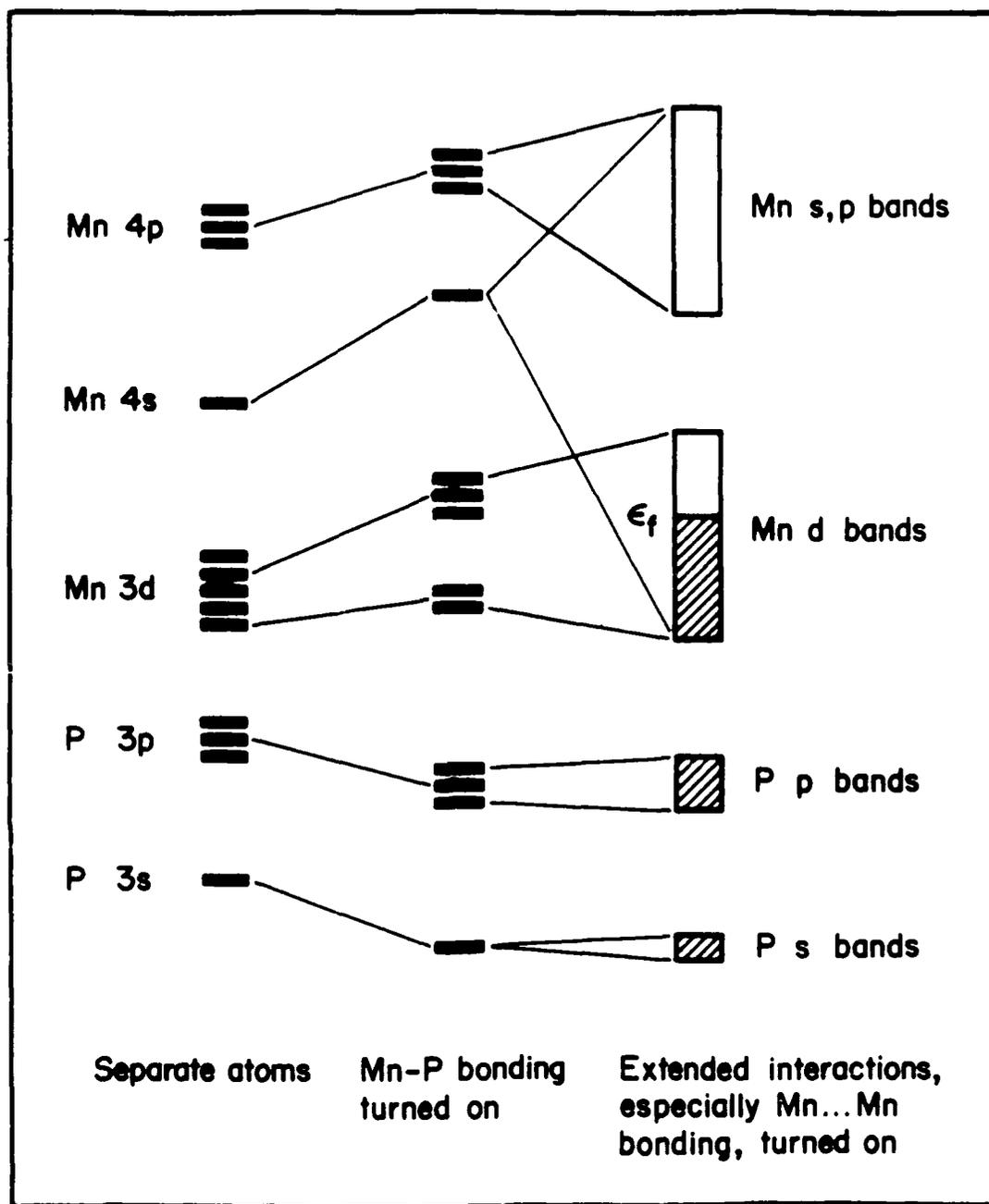


Figure 26. A schematic picture of the $\text{Mn}_2\text{P}_2^{2-}$ layer band structure as derived by first turning on local Mn-P interactions and then the two-dimensional periodicity and Mn-Mn interactions.

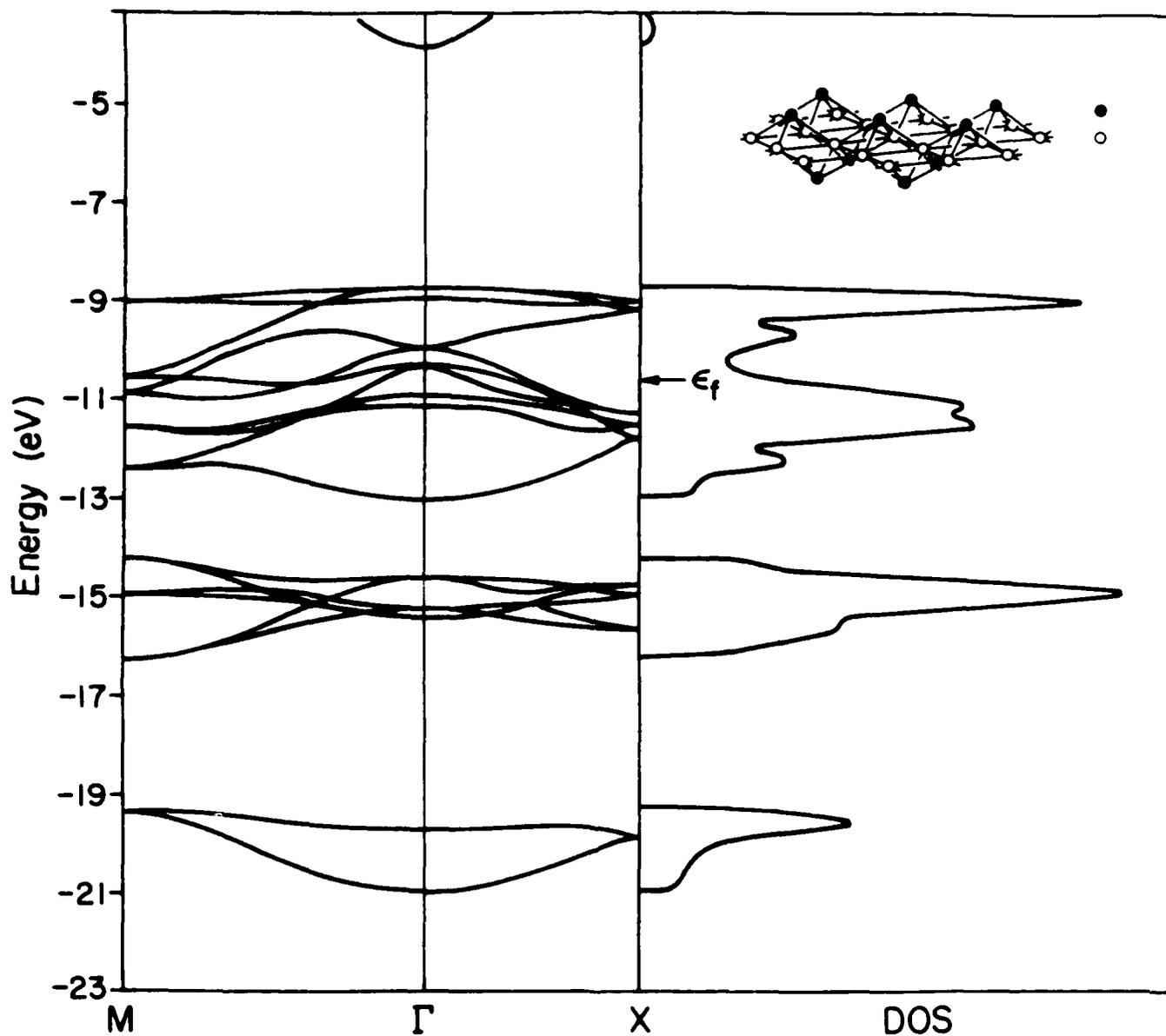


Figure 27. Band structure and DOS of a single $\text{Mn}_2\text{P}_2^{2-}$ layer.

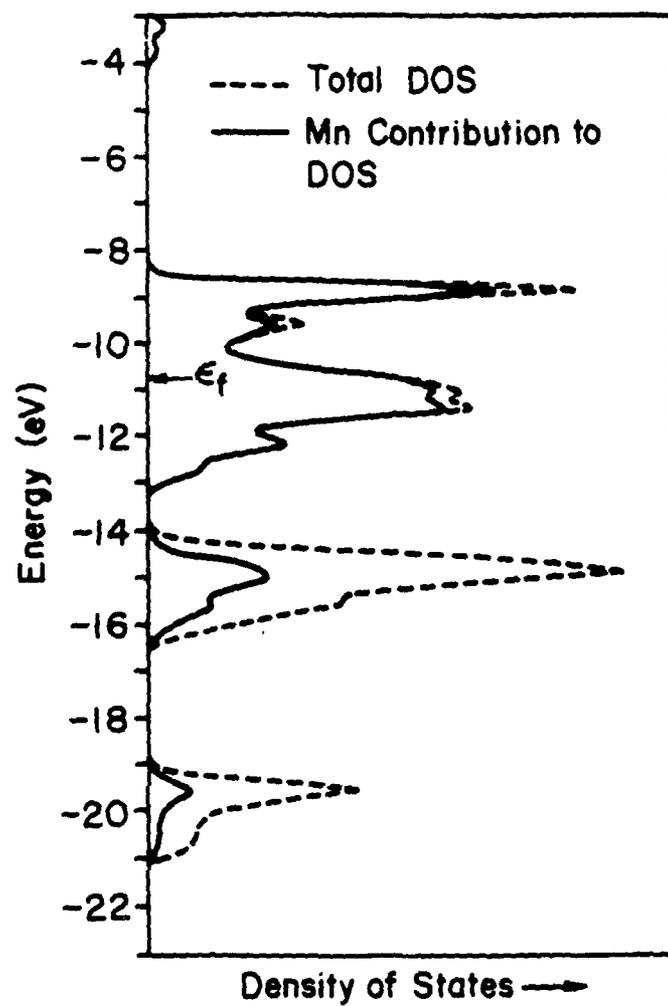


Figure 28. Total DOS of the composite $Mn_2P_2^{2-}$ layer lattice (dashed line) and the contributions of Mn orbitals to that DOS (solid line). What is not on Mn is on P.

What about the bonding characteristics predicted by the qualitative bonding scheme 45. This is where a COOP curve is useful, constructed in Fig. 29. Note that the two lower bands (at -15 and -19eV), which by the previous decomposition were seen to be mainly P, are Mn-P bonding, whereas the mainly metal bands around -12eV are Mn-P nonbonding. The bunch of levels at approximately -9eV is Mn-P antibonding -- it corresponds to the crystal-field destabilized t_2 level in 45. The bottom of the mainly metal band is Mn-Mn bonding, the top Mn-Mn antibonding. Everything is as expected.

Figure 29

An interesting, slightly different approach to the bonding in the layer is obtained if we, so to speak, turn on Mn-Mn bonding first, then Mn-P bonding by "inserting" or "intercalating" a P sublattice. This is done in Fig. 30. At left is the P sublattice. We see P 3s (around -19eV) and P 3p (around -14eV) bands. Both are narrow, because the P atoms are $\sim 4 \text{ \AA}$ apart. The Mn sublattice (middle of Figure 30) shows a nicely dispersed density of states (DOS). The Mn-Mn separation is only 2.855 \AA . Thus we have a two-dimensional metal, with a familiar wide s, p plus narrow d band pattern. The bottom part of the DOS in the middle of Figure 30 is the 3d band, the top is the lower part of the 4s, 4p band. At the right in Figure 30 is the density of states of the composite Mn_2P_2 layer. Note how the

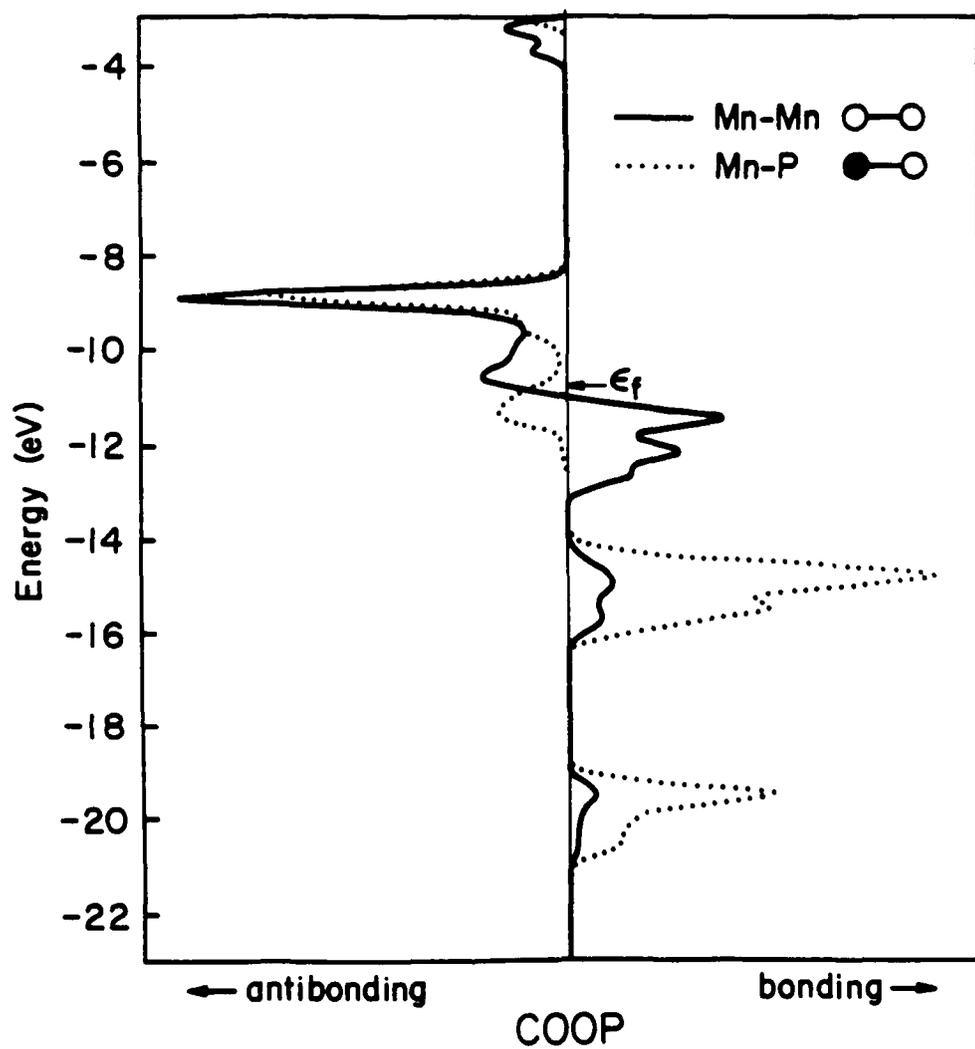


Figure 29. Crystal orbital overlap population curves for the Mn-Mn bonds (solid line) and Mn-P bonds (dotted line) in the $\text{Mn}_2\text{P}_2^{2-}$ single layer.

individual P and Mn bunches of states repel each other on forming the composite lattice. Note also how part of the Mn d band stays where it is, part moves up. Here is the memory, within this delocalized structure, of the local e below t_2 crystal field splitting. There is no more graphic way of showing that what happens in the inorganic solid is similar to what happens in an isolated inorganic molecule.

Figure 30

Still another, more chemical detail. Each phosphorus in the slab is in an unusual coordination environment, at the apex of a square pyramid of Mn atoms. A chemist looks for a lone pair, 46,



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pointing away from the ligands. We can look for it, theoretically, by focussing on its directionality. P $3p_z$ should contribute most to this lone pair, so we interrogate the DOS for its z contribution, Fig. 31. The p_z orbital is indeed well localized, 70% of it in a band at approximately -15eV . Here is the lone pair.

Figure 31

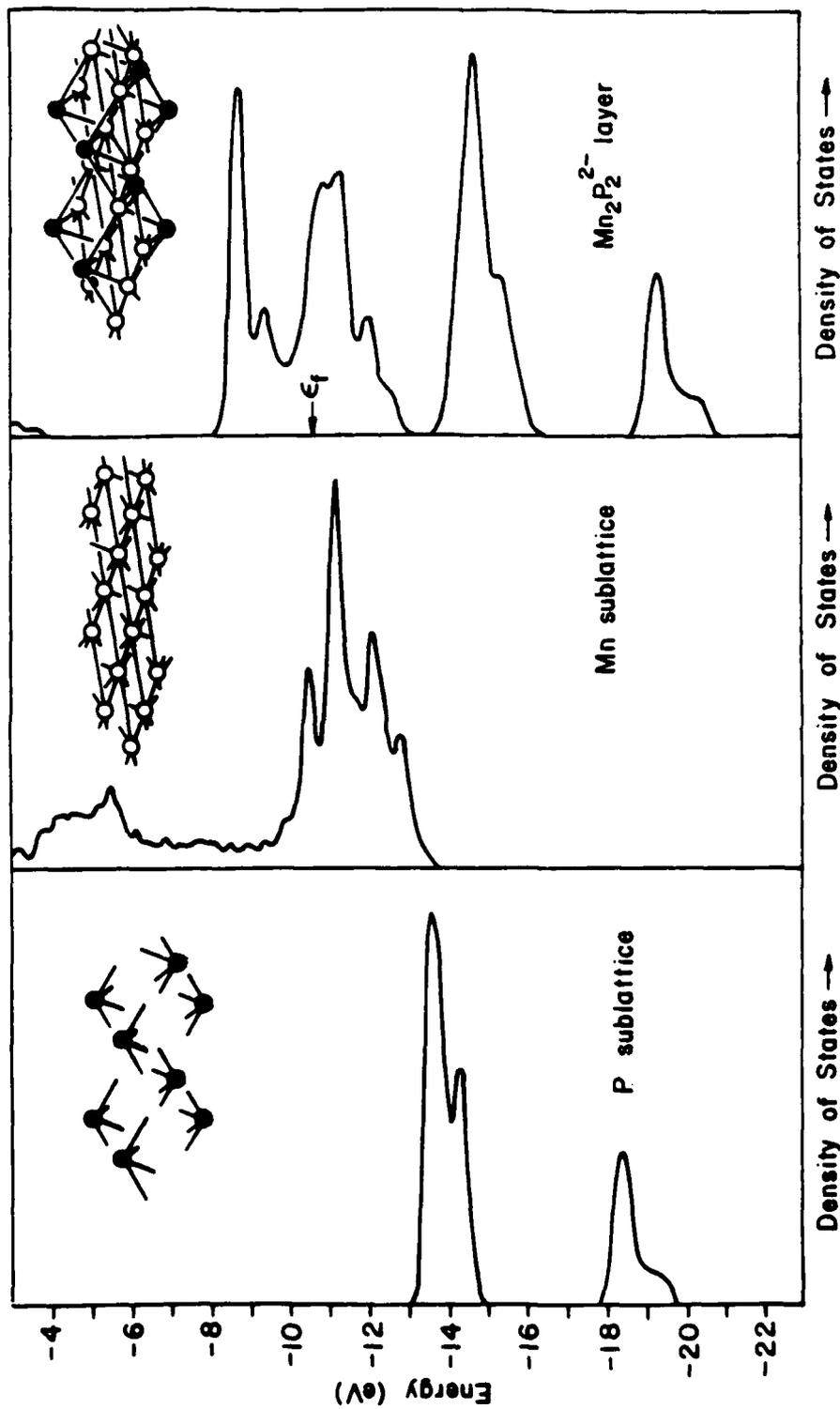


Figure 3C. Total DOS of the P sublattice (left), the Mn sublattice (middle) and the composite $\text{Mn}_2\text{P}_2^{2-}$ layer lattice (right).

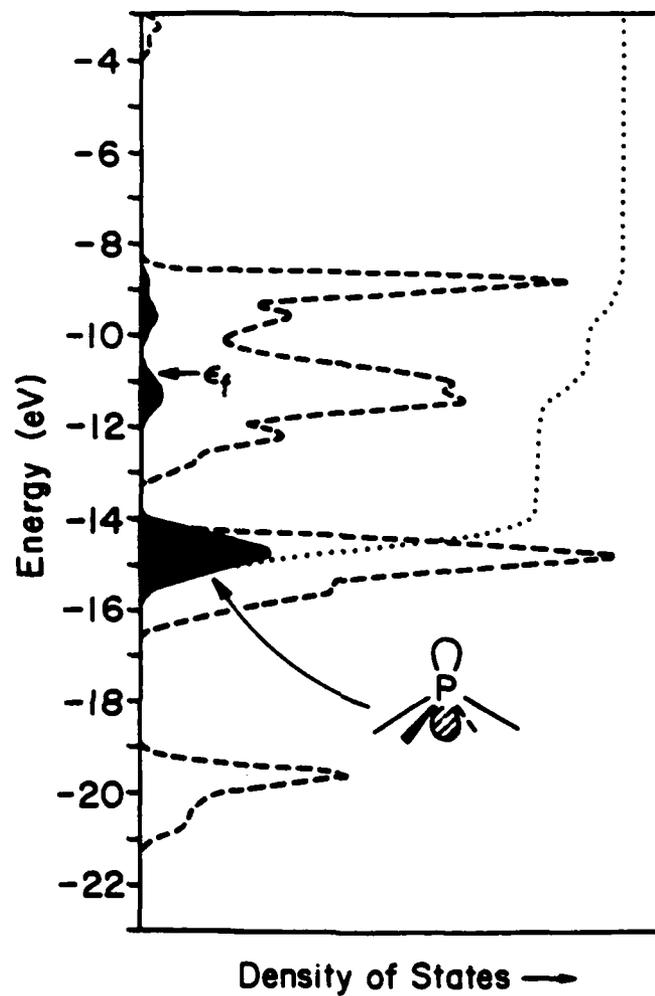


Figure 31. Phosphorus $3p_z$ orbital contribution (dark area) to the total DOS (dashed line) of the $\text{Mn}_2\text{P}_2^{2-}$ single layer. The dotted line is an integration of the dark line, on a scale of 0 to 100%.

A point that can be made here is that localization in energy space (such as we see for the P p_z projection) implies localization in real space. The easiest way to think this through is to go back to the construction of bands at the beginning of this book. The molecular orbitals of a crystal are always completely delocalized Bloch functions. But there is a difference between what we might call symmetry-enforced delocalization (formation of Bloch functions, little overlap) and real, chemical delocalization (overlap between unit cells). The former gives rise to narrow bands, the latter to highly dispersed ones. Turning the argument around, if one sees narrow bands, that's a sign of chemical localization, whereas wide bands imply real delocalization.

On to the three-dimensional solid. When the two-dimensional $\text{Mn}_2\text{P}_2^{2-}$ layers are brought together to form the three-dimensional solid ($\text{Mn}_2\text{P}_2^{2-}$, still without the counterions), the P $3p_z$ orbitals or lone pairs in one layer form bonding and antibonding combinations with the corresponding orbitals in the layers above or below. Figure 32 shows the P $3p_z$ density of states at interlayer P-P = 2.4 Å. The wide band at -8 to -12eV is Mn 3d.

Figure 32

Below and above this metal band are P bands, and in these, quite well localized, are P-P σ and σ^* combinations, 47. These bands are narrow, because the lateral P-P distance is long.

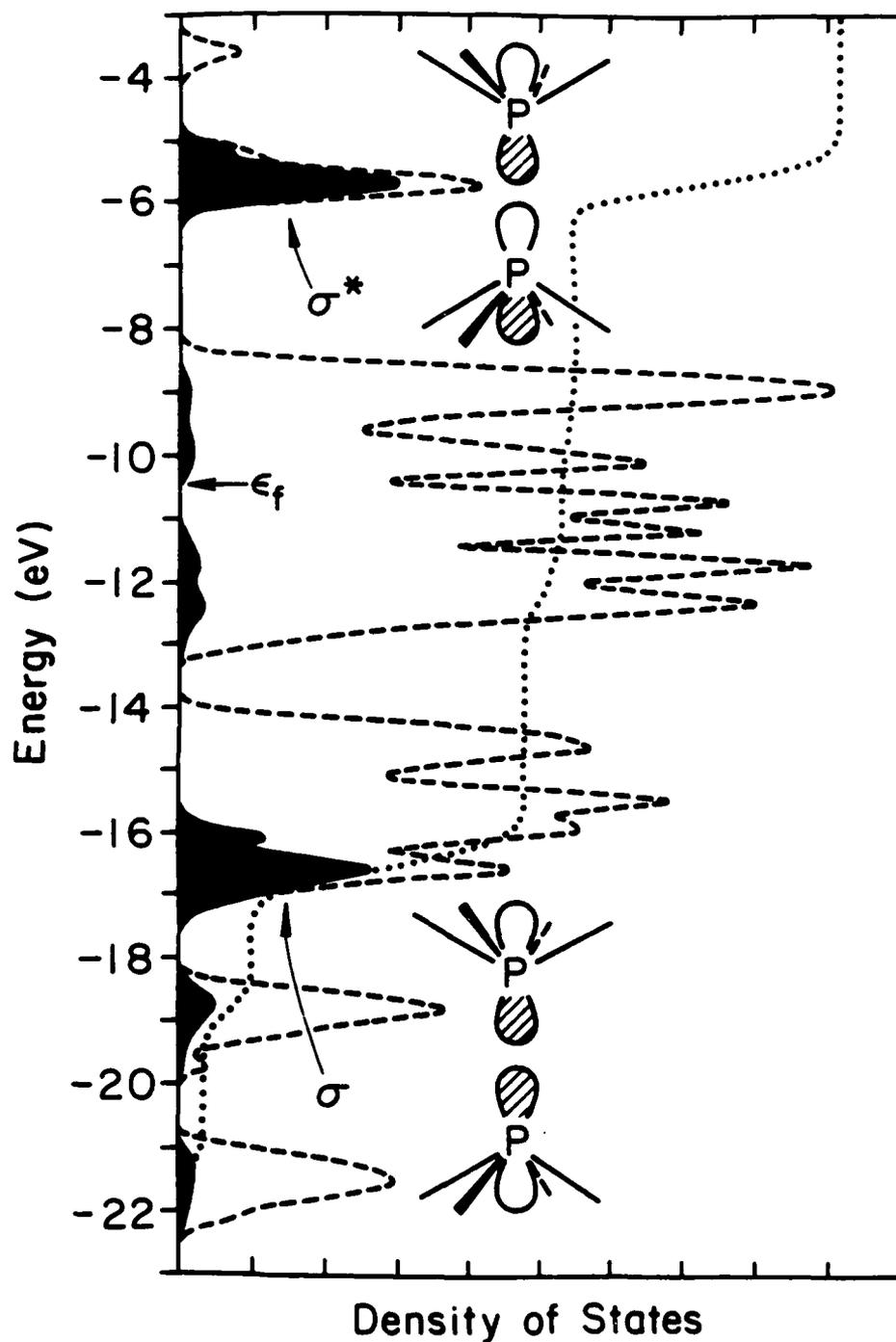


Figure 32. Phosphorus 3p_z orbital contribution (dark area) to the total DOS (dashed line) of the three-dimensional Mn₂P₂²⁻ lattice. The phosphorus-phosphorus bond length here is 2.4 Å. The dotted line is an integration, on a scale of 0 to 100%.



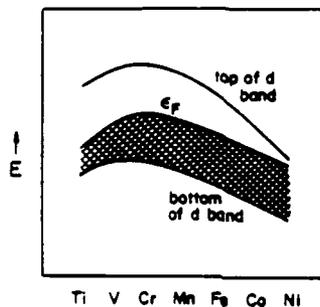
47

Perhaps it's appropriate to stop here and reflect on what has happened. There are Avogadro's number of levels per atomic orbital in the solid. It's all delocalized bonding, but with our theoretical tools we have been able to see, quite localized in energy, orbitals of a diatomic molecule. The localization in energy reflects the validity of a localization in space, i.e. a bond.

If the three-dimensional calculation is repeated at different interslab or P...P distances all that happens is that the localized P-P σ and σ^* bands occur at different energies. Their splitting decreases with increasing P...P separation, as one would expect from their respective bonding and antibonding nature.

We are now in a position to explain simply the effect of the transition metal on the P-P separation. What happens when the transition metal moves to the right-hand side of the Periodic Table? The increased nuclear charge will be more incompletely screened and the d electrons more tightly bound. As a result, the d band comes down in energy and becomes narrower. At the same time, the band filling increases as one moves to the right

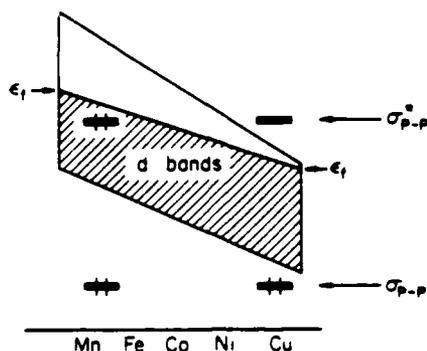
in the transition series. The balance is complicated, and it is important. 48 shows the result. For details the reader is referred to the definitive work of O. K. Andersen.⁴⁰



48

48 is the most important single graph of metal physics. It is analogous in its significance to the plot of the ionization potentials of atoms or diatomic molecules. At the right side of the transition series, the area of concern to us, the Fermi level falls as one moves to the right, the work function of the metal increases.

Now imagine superimposed on this variable energy sea of electrons the P-P σ and σ^* bands for some typical, moderately bonding P-P distance, 49. In the middle of the transition series, the metal Fermi level is above the P-P σ^* . Both σ and σ^* are occupied, there is no resultant P-P bond. As P-P stretches in response, the σ^* only becomes more filled. On the right side of the transition series, the P-P σ^* is above the Fermi level of the metal, and so is unfilled. The filled P-P σ makes a P-P



49

bond. Making the P-P distance shorter only improves this situation.

The steady, gradual variation of the P-P distance would seem to be as inconsistent with the molecular orbital model shown here as it was with the Zintl concept. This is not so. If we turn on the interaction between the P atoms and the metal layer (and we have seen before this interaction is substantial) we will get mixing of P and Mn orbitals. The discontinuity of the above picture (either single bond or no bond) will be replaced by a continuous variation of P σ and σ^* orbitals' occupation between 2 and 0.

The experimentally observed trend has been explained. There is much more to the AB_2X_2 structures than I have been able to present here^{37,39}, of course. More important than the rationalizations and predictions of the experimental facts that one is able to make in this case, is the degree of understanding one can achieve and the facility of motion between chemical and physical perspectives.

The Frontier Orbital Perspective

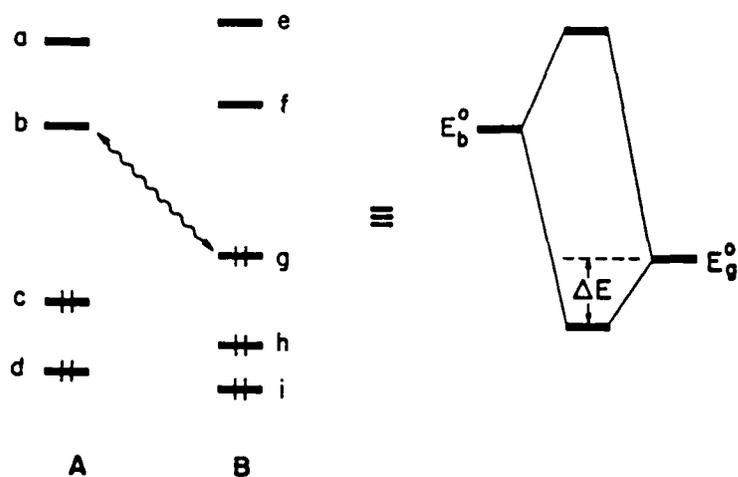
The analytical tools for moving backward from a band calculation to the underlying fundamental interactions are at hand. Now let's discuss the motion in the forward direction, the model of orbitals and their interaction, as analyzed by perturbation theory. In a sense we already used this in 27, 29 and in Fig. 26, the mental construction of what we anticipated in building the Mn_2P_2 layer.

This is the frontier orbital picture.^{11,41} A chemical interaction (between two parts of a molecule) or reaction (between two molecules) can be analyzed from the starting point of the energy levels of the interacting fragments or molecules. The theoretical tool one uses is perturbation theory. To second order, the interactions between two systems are pairwise additive over the MO's and each pair interaction is governed by the expression:

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

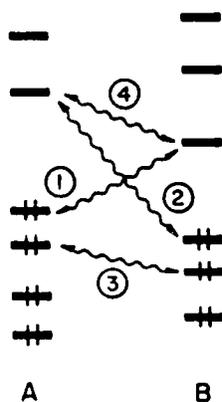
That's what a squiggly line in the interaction diagram 50 indicates.

Individual interactions may be classified according to the total number of electrons in the two orbitals involved; thus ① and ② in 51 are two-electron, ③ is four-electron, ④ is zero-electron. ① and ② are clearly stabilizing (see the right side of



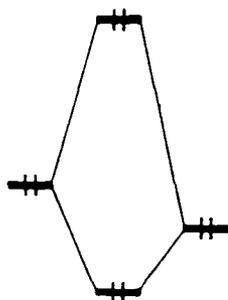
50

50). This is where true bonding is found, with its range between covalent (orbitals balanced in energy and extent in space) or dative (orbitals unequal partners in interaction, charge transfer from donor to acceptor an inevitable correlate of bonding).



51

Interaction ④ has no direct energetic consequences, since the bonding combination is unoccupied. And interaction ③ is repulsive, because what happens when the overlap is included in the calculations (52) is that the antibonding combination goes up



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more than the bonding one goes down. The total energy is greater than that of the separate isolated levels.¹¹

The electronic energy levels of molecules are separated by energies of the order of an electron volt. This makes them quantum systems par excellence, and allows the singling out of certain levels as controlling a geometrical preference or a reactivity. For instance, in 50 acceptor level $|b\rangle$ of fragment A is closer in energy to donor level $|g\rangle$ of fragment B, compared to $|h\rangle$ and $|i\rangle$. If it should happen that the overlaps $\langle b|h\rangle$ and $\langle b|i\rangle$ are also much smaller than $\langle b|g\rangle$ then both the numerator and the denominator of the perturbation expression single out the $b(A)-g(B)$ interaction as an important, perhaps the most important, one. In general, it turns out that the highest

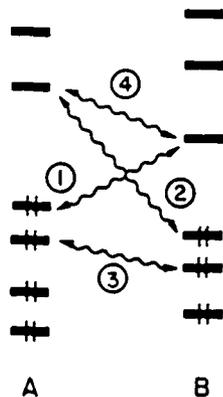
occupied molecular orbital (HOMO) or a small subset of higher lying levels, and the lowest unoccupied molecular orbital (LUMO), or some subset of unoccupied MO's, dominate the interaction between two molecules. These are called the frontier orbitals. They are the valence orbitals of the molecule, the orbitals most easily perturbed in any molecular interaction. In them resides control of the chemistry of the molecule.

It should be realized that this description, while of immense interpretative power, is only a one-electron model. To analyze orbital interactions properly, in a many-electron way, is not easy. The simple picture of 51 seems to be lost; competing interaction or partition schemes have been suggested.⁴² One way to appreciate the problem a true many-electron theory has in analyzing interactions is to realize that the energy levels of A and B are not invariant to electron transfer. They change in energy depending on the charge: on fragments A and B a positive charge makes all the energy levels go down, a negative charge go up. Actually realizing this, one has learned the most important correction to the simple one-electron picture.

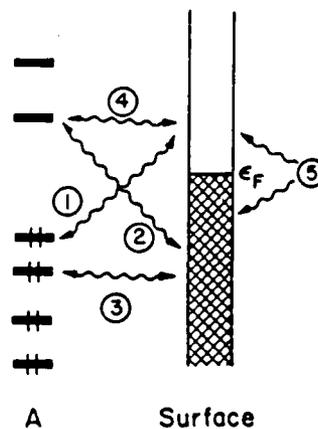
Orbital Interaction on a Surface

It is now clear that what the apparatus of densities of states and crystal orbital overlap populations has done is to restore to us a frontier orbital or interaction diagram way of thinking about the way molecules bond to surfaces, or the way atoms or clusters bond in three-dimensional extended structures. Whether it is $2\pi^*$ CO with d_{π} of Ni(100), or e of CR with some part of the Pt(111) band, or the Mn and P sublattices in $Mn_2P_2^{2-}$, or the Chevrel phases discussed below, in all of these cases we can describe what happens in terms of local action. The only novel feature so far is that the interacting orbitals in the solid often are not single orbitals localized in energy or space, but bands.

A side-by-side comparison of orbital interactions in discrete molecules and of a molecule with a surface is revealing. 53 is a typical molecular interaction diagram, 54 a molecule-surface one. Even though a molecule is, in general, a



53



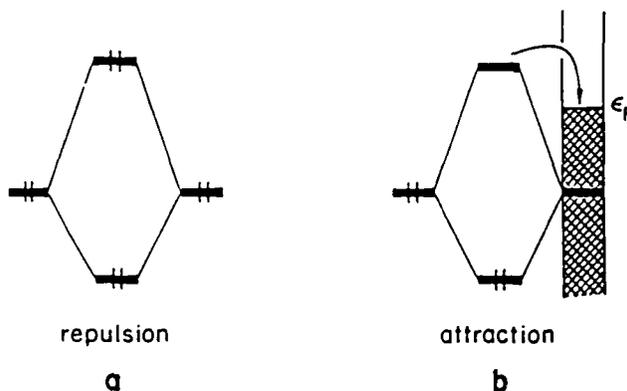
54

many-level system, let's assume, in the spirit of a frontier orbital analysis, that a small set of frontier orbitals dominates. This is why the squiggly lines symbolizing interaction go to the HOMO and LUMO of each component.

Within a one-electron picture the following statements can be made (and they apply to both the molecule and the surface unless specifically said not to do so).

(i) The controlling interactions are likely to be the two-orbital, two-electron stabilizing interactions ① and ②. Depending on the relative energy of the orbitals and the quality of the overlap, each of these interactions will involve charge transfer from one system to the other. In interaction ①, A is the donor or base, B, or the surface, the acceptor or acid. In interaction ②, these roles are reversed.

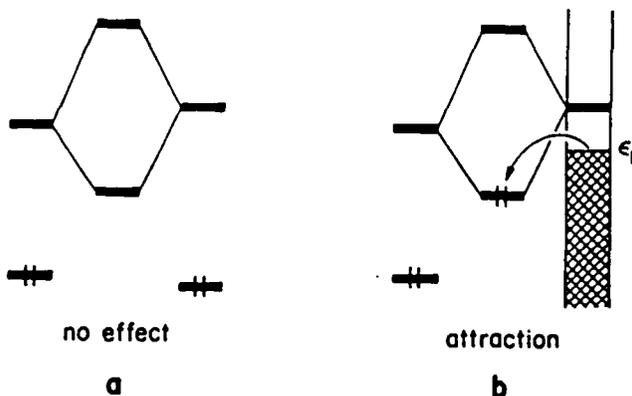
(ii) Interaction ③ is a two-orbital, four-electron one. It is destabilizing, repulsive, as 55a shows. In one-electron theories, this is where steric effects, lone pair repulsions, etc. are to be found.^{11,41} These interactions may be important. They may prevent bonding, interactions ① ②, from being realized. There is a special variant of this interaction which may occur in the solid, but is unlikely in discrete molecules. This is sketched in 55b -- the antibonding component of a four-electron, two-orbital interaction may rise above the Fermi level. It will dump its electrons at the Fermi level, and can no longer destabilize the system. Only the intersystem bonding combination remains filled.



55

The effect on molecule-surface bonding is clear -- it is improved by this situation. What happens in the surface is less clear; let's defer discussion until we get to interaction ⑤

(iii) Interaction ④ involves two empty orbitals. In general, it would be discounted as having no energetic consequences. This is strictly true in molecular cases, 56a. But in the solid, where there is a continuum of levels, the result of such interaction may be that the bonding combination of the two interacting levels may fall below the Fermi level, 56b.



56

Becoming occupied, it will enhance fragment A-surface bonding. Again, there may be an effect on the surface, because it has to supply the electrons for the occupation of that level.

(iv) Interaction ⑤ is something special to the metallic solid, that comes from the states of the metal surface forming a near continuum. The interaction describes the second order energetic and bonding consequences of shifts of electron density around the Fermi level. First order interactions ① ② ③ and ④ all will move metal levels up and down. These metal levels, the ones that move, will belong to the atoms on the surface interacting with the adsorbate. The Fermi level remains constant -- the bulk and surface are a nice reservoir of electrons. So electrons (holes) will flow in the surface and in the bulk underneath it, in order to compensate for the primary interactions. These compensating electrons or holes are, however, not innocent of bonding themselves. Depending on the electron filling, they may be bonding or antibonding in the bulk, between surface atoms not involved with the adsorbate, even in surface atoms so involved, but in orbitals that are not used in bonding to the chemisorbed molecule.

Before I leave this section, I should like to say quite explicitly that there is little novel in the use my coworkers and I have made of interaction diagrams and perturbation theory applied to surfaces. A.B. Anderson⁴³ has consistently couched his explanations in that language, and so have Shustorovich and

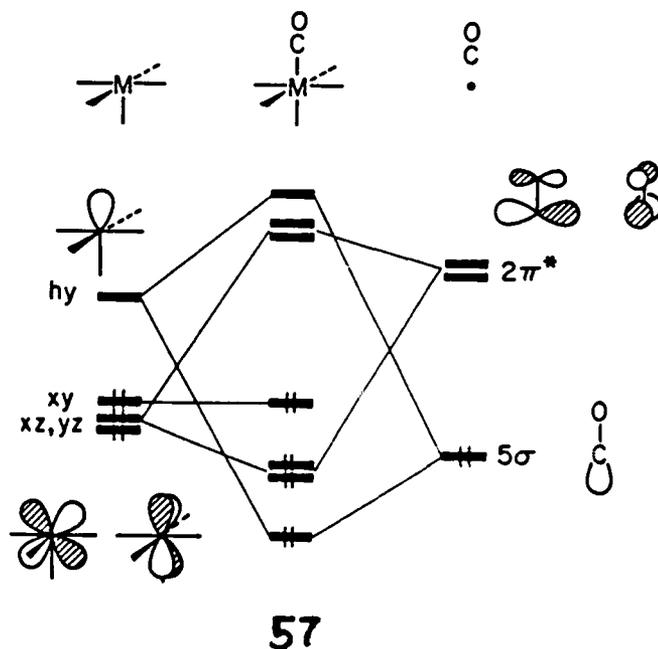
Baetzold^{31,32} -- Shustorovich's account of chemisorption is based on an explicit perturbation-theoretic model. There is a very nice, quite chemical treatment of such a model in the work of Gadzuk⁴⁴, based on earlier considerations by Grimley⁴⁵. van Santen⁴⁶ draws interaction diagrams quite analogous to ours. Salem and his coworkers⁴⁷ have developed a related perturbation theory based on a way of thinking about catalysis that includes a discussion of model finite Hückel crystals, privileged orbitals, generalized interactions diagrams, and the dissolution of adsorbate into catalyst bands. There are also other workers who have discussed interaction diagrams, privileged orbital sets, or orbital symmetry considerations in the solid.⁴⁸

Let's make these interactions and interactions diagrams come to life through some specific applications.

A Case Study: CO on Ni(100)

The Ni(100)-CO system already discussed²⁶ seemed to provide an excellent example of the primary two-electron interactions at work. We found charge transfer from 5σ (its population going from 2.0 in the free CO to 1.62 in the CO-surface complex) and back donation from the surface to $2\pi^*$ (whose population rose from 0 to 0.74). Actually, there is an interesting wrinkle here, in that the 4 and 0 electron interactions mentioned in point (3), above, manifest themselves.

To set a basis for what we will discuss, let's prepare a model molecular system for comparison. We'll build a metal-carbonyl bond between a d^6 ML_5 system and a carbon monoxide. The interaction diagram, 57, will be familiar to a chemist; the acceptor function of the ML_n fragment is provided by a low-lying



dsp hybrid.^{11,49} The two-electron bonding interactions are quite explicit. They result ($M = \text{Ni}$, $L = \text{H}^-$, $M\text{-H}$ 1.7 Å, $M\text{-CO}$ 1.9 Å) in a depopulation of 5σ by 0.41, and a population of $2\pi^*$ by 0.51 electrons. The metal functions involved in these interactions react correspondingly: so xz, yz loses 0.48 electrons, and the hybrid orbital gains 0.48. The net charge drifts are pretty well-described by the sum of what happens in these orbitals: CO as a whole gains 0.01e-, and the ML_n fragment loses the same. The information is summarized in Table 2.

If one just looks at the CO, what happens on the surface seems to be similar, as I noted above. And the d_π orbitals, xz, yz are depopulated in $c(2 \times 2)\text{CO-Ni}(100)$. But the d_σ , the z^2 , the surface analogue of the hybrid, actually loses electron density on chemisorption of CO.

What is happening here is that the CO 5σ is interacting with the entire z^2 band, but perhaps more with its bottom, where the coupling overlap is greater. The z^2 band is nearly filled (1.93 in the metal slab). The net $5\sigma\text{-}d_\sigma$ band interaction would be repulsive, mainly due to four-electron two-orbital interactions, were it not for the pushing of some antibonding combinations above the Fermi level (see 58 for a schematic). The net result is some loss of z^2 density and concomitant bonding.⁵⁰

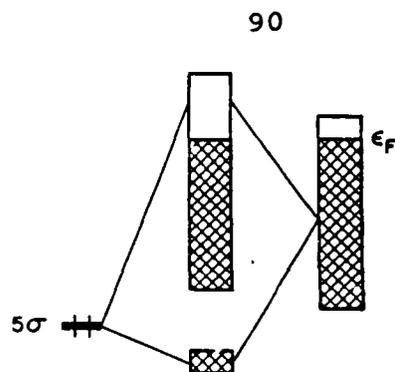
Where do those "lost" electrons go? Table 2 indicates that some, but certainly not all, go to the CO. Many are "dumped" at the Fermi level into orbitals that are mainly d band, but on the

Table 2. Some Electron Densities in a Model H_5NiCO^- and the $c(2 \times 2)\text{CO-Ni}(100)$ System

	NiH_5^-	$\text{NiH}_5(\text{CO})^-$	CO		Ni(100)	$c(2 \times 2)\text{CO-Ni}(100)$	CO
5σ	--	1.59	2.0	5σ	--	1.62	2.0
$2\pi^*$	--	0.51	0.0	$2\pi^*$	--	0.74	0.0
hy	0.0	0.48	--	d_σ^a	1.93	1.43	--
d_π	4.0	3.52	--	d_π^a	3.81	3.31	--
CO	--	10.01	10.0	CO	--	10.25	10.0
H_5Ni	16.0	15.99	--	Ni^a	10.17^b	9.37	--

a) for those surface atoms which have CO on them.

b) this number is not 10.0, because the surface layer of the slab is negative relative to the inner layer.



inner metal atoms, or on surface atoms not under CO. We will return to the bonding consequences of these electrons, interaction ⑤, in a while.

Before leaving this instructive example, I trust that point is not lost that the primary bonding interaction ① and ②, are remarkably alike in the molecule and on the surface. These forward and back donations are, of course, the consequence of the classical Dewar-Chatt-Duncanson model of ethylene (or another fragment) bonding in an organometallic molecule.⁵¹ In the surface case, this is often termed the Blyholder model, the reference being to a perceptive early suggestion of such bonding for CO on surfaces.^{41b} More generally, interactions ① and ② are the fundamental electronic origins of the cluster-surface analogy. This is a remarkably useful construction of a structural, spectroscopic and thermodynamic link between organometallic chemistry and surface science.⁵²

Barriers to Chemisorption

The repulsive two-orbital four-electron interaction that turns into an attractive, bonding force when the electrons, rising in energy, are dumped at the Fermi level is not just a curiosity. I think that it is responsible for observed kinetic barriers to chemisorption and the possible existence of several independent potential energy minima as a molecule approaches a surface.

Consider a model molecule, simplified here to a single occupied level, approaching a surface. Some schematic level diagrams and an associated total energy curve are drawn in Fig. 33. The approach

Figure 33

coordinate translates into electron interaction. Far away there is just repulsion, which grows as the molecule approaches the surface. But when the antibonding combination is pushed up to the Fermi level, the electrons leave it for the reservoir of hole states, empty metal band levels. Further interaction is attractive.

This simple picture was first given, to my knowledge, by E.L. Garfunkel and by C. Minot and their coworkers.⁵³ In reality, the repulsion at large metal adsorbate distances will be mitigated and, in some cases overcome, by attractive two-electron interactions of type ① or ② (see 54). But the presence of the interaction, I think, is quite general. It is responsible, in my opinion, for some of the large kinetic barriers to CO chemisorption and CH₄ decomposition measured in the elegant beam experiments of S.T. Ceyer, R.J. Madix and their coworkers.⁵⁴

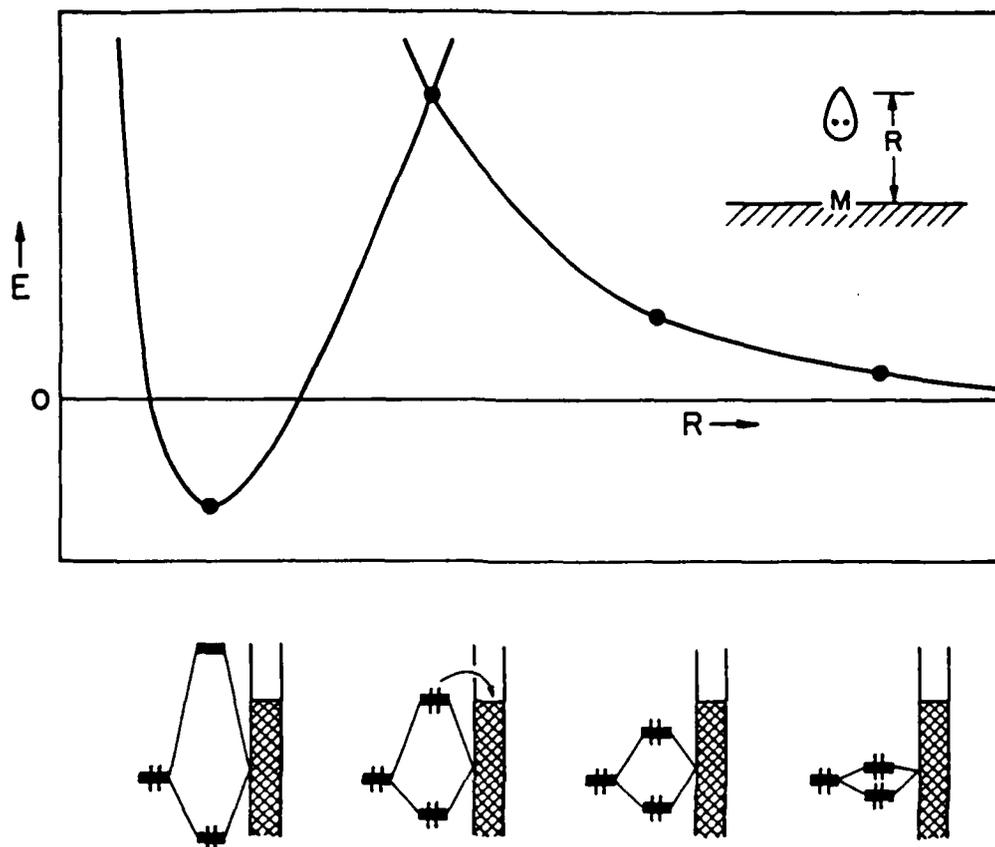


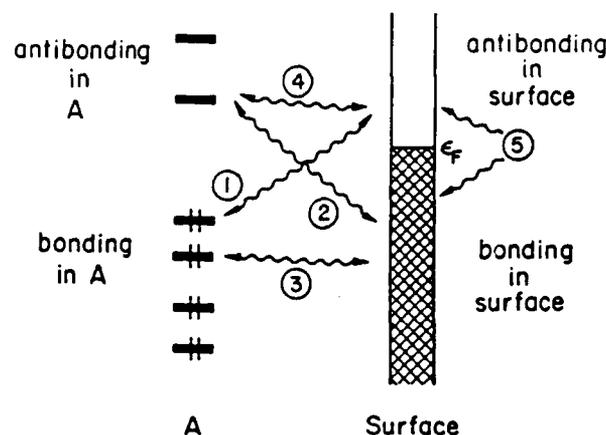
Figure 33. A schematic drawing showing how the interactions of levels (bottom) can lead to a potential energy curve (top) which has a substantial barrier to chemisorption. R measures the approach of a molecule, symbolized by a single interacting electron pair, to a surface. At large R repulsive four-electron interactions dominate. At some R (second point from left), the anti-bonding combination crosses the Fermi level, and dumps its electrons. At shorter R there is bonding.

In reality, what we are describing is a surface crossing. And there may be not one, but several such, for it is not a single level, but groups of levels which are "pushed" above the Fermi level. There may be several metastable minima, precursor states, as a molecule approaches a surface.⁵⁵

In this section I have mentioned, for the second time, the bonding consequences of emptying, at the Fermi level, molecular orbitals delocalized over adsorbate and surface, and antibonding between the two. Salahub⁵⁰ and Anderson⁵⁶ stress the same effect. There is a close relationship between this phenomenon and a clever suggestion made some time ago by Mango and Schachtschneider⁵⁷ on the way in which metal atoms (with associated ligands) lower the activation barriers for forbidden concerted reactions. They pointed out that such electrons, instead of proceeding on to high antibonding levels, can be transferred to the metal. We, and others, have worked out the details of this kind of catalysis for some specific organometallic reactions, such as reductive elimination.⁵⁸ It's quite a general phenomenon, and we will return to it again in a subsequent section.

Chemisorption is a Compromise

Consider again the basic molecule-surface interaction diagram 59, now drawn specifying the bonding within each component. The occupied orbitals of the molecule A are generally bonding or nonbonding within

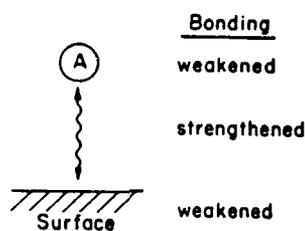


59

that molecule, the unfilled orbitals of A are usually antibonding. The situation on the metal depends on where in a band the Fermi level lies: the bottom of the d band is metal-metal bonding, the top is metal-metal antibonding. This is why the cohesive energy of the transition metals reaches a maximum around the middle of the transition series. Most of the metals of catalytic interest are in the middle or right part of the transition series. It follows that at the Fermi level the orbitals are generally metal-metal antibonding.

What is the effect of the various interactions on bonding within and between the adsorbate and the surface? Interaction ① and ② are

easiest to analyze -- they bind the molecule to the surface, and in the process they transfer electron density from generally bonding orbitals in one component to antibonding orbitals in the other. The net result: a bond is formed between the adsorbed molecule A and the surface. But bonding within the surface and within A is weakened, 60.



60

Schematically this is indicated in 60. What about interactions (3) and (4)? For moderate interaction, (3) is repulsive and (4) has no effect. Neither does anything to bonding within A or the surface. When interaction grows, and antibonding ((3)) or bonding ((4)) states are swept past the Fermi level, these interactions provide molecule-surface bonding. At the same time, they weaken bonding in A, transferring electron density into antibonding levels and out of bonding ones. What the effect of such strong interaction of type (3) or 4 or, more generally, of second order electron shifts, type (5), is on bonding within the surface -- that depends on the position of the Fermi level and the net electron drift.

The sum total of these interactions is still the picture of 60: metal-adsorbate bonding is accomplished at the expense of bonding within the metal and the adsorbed molecule. This is the compromise alluded to in the heading of this section.

A specific case will illustrate this point, and show the way to an important consequence of this very simple notion.

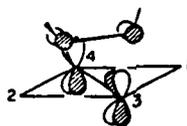
Earlier we drew four possible geometries for a layer of acetylene, coverage = $\frac{1}{4}$, on top of Pt(111), 3. Table 2 shows some of the indices of the interaction in the four alternative geometries, in particular the occupations of the four acetylene fragment orbitals ($\pi, \pi_\sigma, \pi_\sigma^*, \pi^*$), the various overlap populations, and calculated binding energies.

Table 3

The three-fold bridging geometry (3c) is favored, in agreement with experiment and other theoretical results.²⁹ One should say right away that this may be an accident -- the extended Hückel method is not especially good at predicting binding energies. The two-fold (3b) and four-fold (3d) sites are slightly less bound, but more stable than the one-fold site, 3a. But this order of stability is not a reflection of the extent of interaction. Let's see how and why this is so.

The magnitude of interaction could be gauged by looking at the acetylene fragment orbital populations, or the overlap population. In the detailed discussion of the two-fold site in an earlier section, we saw π and π^* more or less unaffected, π_σ depopulated, π_σ^* occupied. As a consequence, Pt-C bonds are formed, the C-C bond weakened, and

(interaction ⑤) some Pt-Pt bonds on the surface weakened. A glance at the fragment MO populations and overlap populations in Table 3²⁹ shows that all this happens much more in the four-fold site 3d -- note that even π and π^* get strongly involved. The most effective interaction here is that shown in 61. Note that it is primarily of type ④.



61

By any measure, interaction is least in the on-top or one-fold geometry, most in the four-fold one. See, for instance, the trend in C-C overlap populations, or the Pt-Pt bond weakening. In the four-fold geometry one Pt-Pt overlap population is even negative -- bonding between metal atoms in the surface is being destroyed. It is clear that the favorable condition for chemisorption, or the preference of a hydrocarbon fragment for a specific surface site, are determined by a balance between increased surface-adsorbate bonding and loss of bonding within the surface or in the adsorbed molecules.

Adsorbate induced surface reconstruction and dissociative chemisorption are merely natural extremes of this delicate balance. In each case, strong surface-adsorbate interactions direct the course of the transformation, either breaking up bonding in the surface so that it reconstructs, or disrupting the adsorbed molecule.⁵⁹ An incisive

Table 3. Bonding Characteristics of Several Acetylene Adsorption Sites on Pt(111).

	C ₂ H ₂	Bare Surface				
Binding energy ^a (eV)			3.56	4.68	4.74	4.46
Overlap Population						
C-C	1.70		1.41	1.32	1.21	1.08
Pt ₁ -Pt ₂		0.14	0.12	0.08	0.09	-0.02
Pt ₂ -Pt ₃		0.14	0.14	0.13	0.07	0.06
Pt ₁ -Pt ₄		0.14	0.13	0.13	0.15	0.06
Pt ₁ -C ^b			0.30	0.54	0.52	0.33
Pt ₃ -C			0.00	0.01	0.19	0.27
Occupations						
π*	0.0		0.08	0.17	0.33	0.53
π _σ *	0.0		0.81	1.06	1.03	0.89
π _σ	2.0		1.73	1.59	1.59	1.57
π	2.0		1.96	1.96	1.73	1.53

^a Taken as the difference: $E(\text{slab}) + E(\text{C}_2\text{H}_2) - E(\text{geometry})$ in eV.

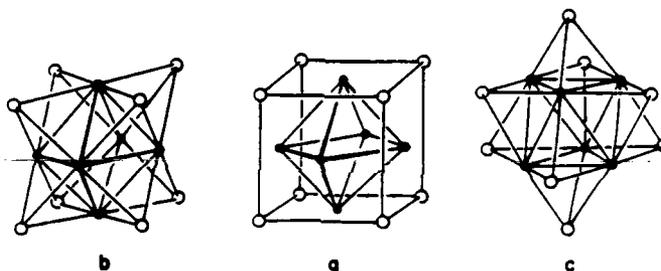
^b The carbon atom here is the closest to the particular Pt atom under consideration.

discussion of the latter situation, for the case of acetylene on iron and vanadium surfaces has been provided by A.B. Anderson.⁶⁰

Frontier Orbitals in Three-Dimensional Extended Structures

The frontier orbital way of thinking, especially with respect to donor-acceptor interactions, is of substantial utility in the solid state. Let me give one example here.

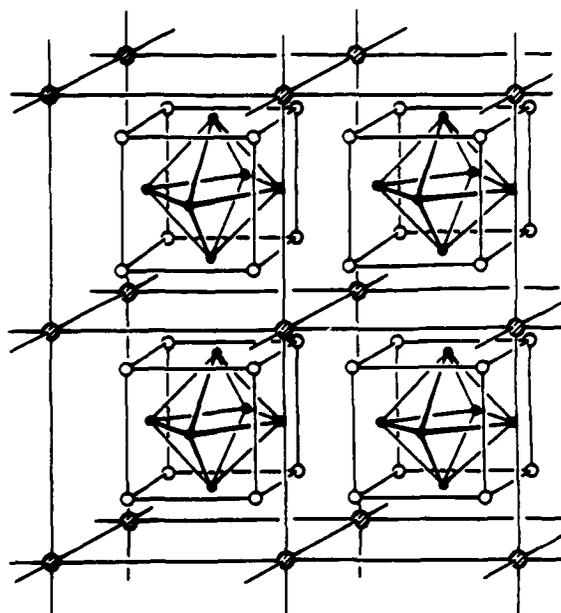
The Chevrel phases are a fascinating set of ternary molybdenum chalcogenide materials of varying dimensionality and interesting physical properties.⁶¹ In the parent phase, epitomized by PbMo_6S_8 , one has recognizable Mo_6S_8 clusters. In these clusters, shown in three views in 62, sulfurs cap the eight



62

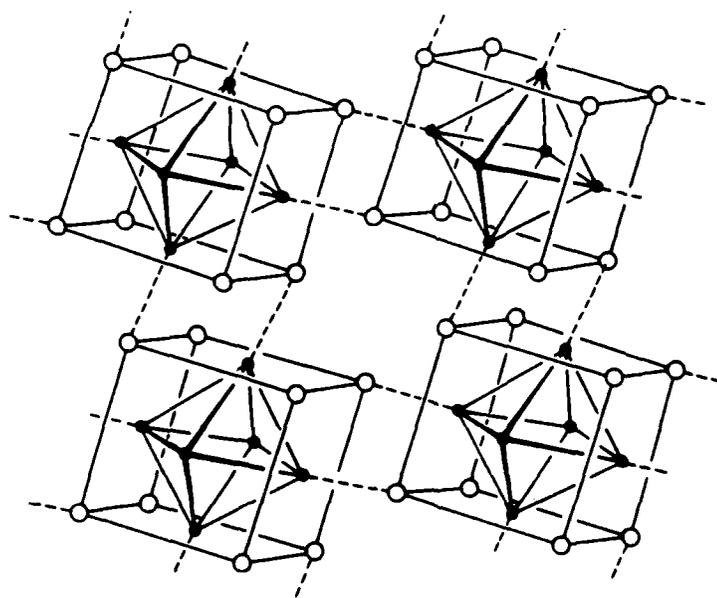
faces of an octahedron of molybdenums. The Mo_6S_8 clusters are then embedded in a substructure of lead cubes (this is a thought construction of the structure!), as in 63. But the structure doesn't remain here. In every cubical cell, the Mo_6S_8 rotates by $\sim 26^\circ$ around a cube diagonal, to reach structure 64 (Pb's are missing in this drawing, for clarity).

Why? The answer is implicit in 64. A rotation of roughly this magnitude is required to give each Mo within one unit a fifth bonding interaction with a sulfur of a cluster in the



63

⊗ Pb
 ○ S
 ● Mo



64

○ : X = S, Se, Te
 ● : Mo (Re, Ru)

neighboring cube. If one does a molecular orbital calculation on the isolated cluster, Fig. 34, one finds that the five lowest

Figure 34

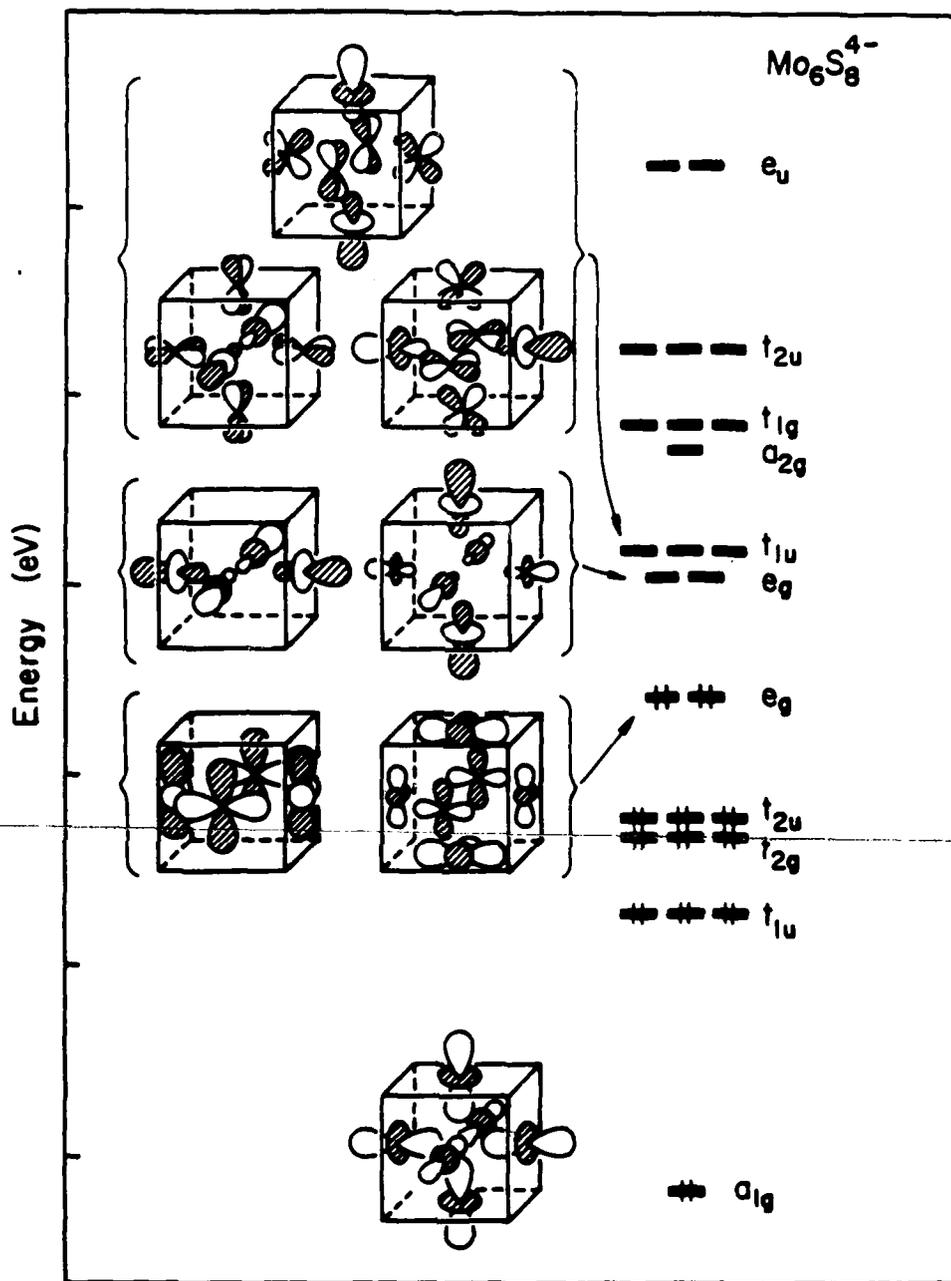
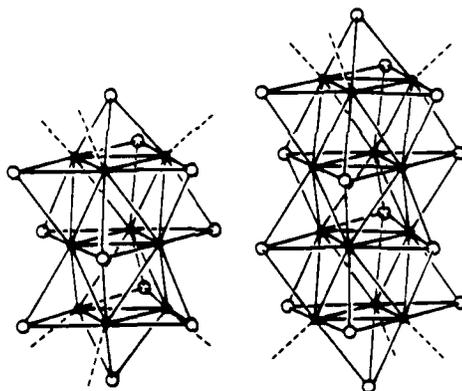


Figure 34. The frontier orbitals of an $\text{Mo}_6\text{S}_8^{4-}$ cluster, with some selected orbitals sketched. The lowest a_{1g} and the higher e_g and t_{1u} orbitals have substantial local z^2 character, i.e. point "out".

empty orbitals of the cluster point out, away from the molybdenums, hungry for the electron density of a neighboring sulfur.^{62,63}

The structure of this material is driven by donor-acceptor interactions. So it is for $\text{In}_3\text{Mo}_{15}\text{Se}_{19}$ and $\text{K}_2\text{Mo}_9\text{S}_{11}$, which contain $\text{Mo}_{12}\text{X}_{14}$ and Mo_9X_{11} clusters drawn in 65.⁶¹ A molecular orbital calculation on each of these clusters shows prominent low-lying orbitals directed away from the terminal Mo's, just where the dashed lines are. That's how these clusters link and aggregate in their respective solid state structures.



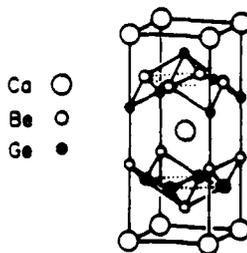
65

This donor-acceptor analysis of the crystal structure indicates that if one wants to "solubilize" these clusters as discrete molecular entities, one must provide an alternative, better base than the molecule itself. Only then will one get discrete $\text{Mo}_6\text{X}_8 \cdot \text{L}_6^q$ complexes.

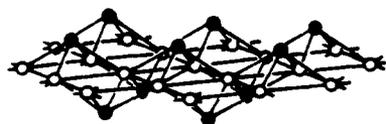
One more conclusion easily drawn from Fig. 34, one applying what we know: when the clusters assemble into the lattice 64,

the five LUMO's of Fig. 34 will be pushed up by interactions with neighboring cube sulfurs. All the cluster levels will spread out into bands. Will the HOMO band be broad or narrow? That band is crucial, because if you do the electron counting in PbMo_6S_8 you come to 22 electrons per Mo_6S_8 , the top level in Fig. 34 half-filled. A glance at Fig. 34 shows that the level in question, of e_g symmetry, is made up of Mo d functions which are of δ type with respect to the Mo-S external axis. Bringing in the neighboring cells will provide little dispersion for this band. The result is a high DOS at the Fermi level, one requirement (of several) for superconductivity.⁶⁴

An interesting variation on the donor-acceptor theme in the solid is that the donor or acceptor need not be a discrete molecule, as one Mo_6S_8 cluster is toward another in the Chevrel phases. Instead, we can have electron transfer from one sublattice, one component of a structure, to another. We've already seen this in the explanation of the tuning of the $X \cdots X$ pairs. A further example is provided by the remarkable CaBe_2Ge_2 structure, 66.⁶⁵ In this structure one B_2X_2 layer, 68, has B and

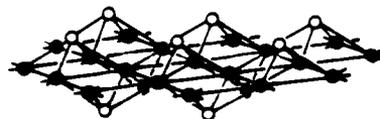


X components interchanging places relative to another layer, 67. These layers are not identical, but isomeric. They will have different Fermi levels. One layer in the crystal will be a donor relative to the other. Can you reason out which will be the donor, which the acceptor layer? We will return to these molecules below.



● X
○ B

67

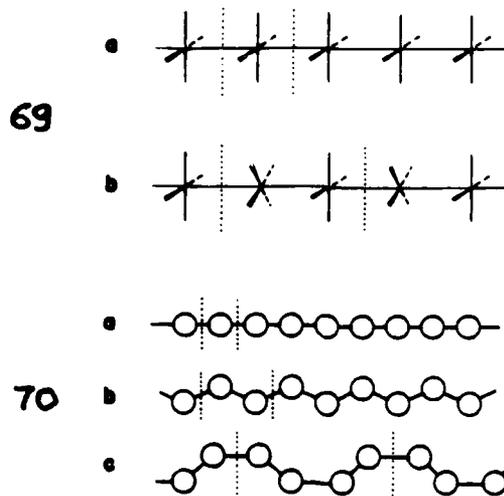


● X
○ B

68

More Than One Electronic Unit in the Unit Cell. Folding Bands

Do you remember the beautiful platinocyanide stack? It has not yet exhausted its potential as a pedagogic tool. The oxidized platinocyanides are not eclipsed, 69a, but staggered, 69b. A polyene is not a simple linear chain, 70a, but, of course, at least s-trans, zig-zag 70b. Or it could be s-cis, 70c. Obviously there will be still other feasible arrangements - indeed nature always seems to find one we haven't thought of.

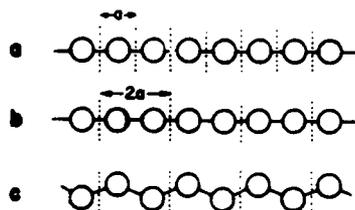


In 69a and 70a, the unit cell contains one basic electronic unit, PtH_4^{2-} , a CH group. In 69b and 70b, the unit is doubled, approximately so in unit cell dimension, exactly so in chemical composition. In 70c, we have 4CH units per unit cell. A purely physical approach might say each is a case unto itself. A chemist is likely to say that probably not much has changed on doubling or quadrupling or multiplying by 17 the contents of a unit cell. If the geometrical distortions of the basic

electronic unit that is being repeated are not large, it is likely that any electronic characteristics of that unit are preserved.

The number of bands in a band structure is equal to the number of molecular orbitals in the unit cell. So if the unit cell contains 17 times as many atoms as the basic unit, it will contain 17 times as many bands. The band structure may look messy. The chemist's feeling that the 17-mer is a small perturbation on the basic electronic unit can be used to simplify a complex calculation. Let's see how this goes, first for the polyene chain, then for the PtH_4^{2-} polymer.

70a, b, c differ from each other not just in the number of CH entities in the unit cell, but also in their geometry. Let's take these one at a time. First prepare for the distortion from 70a to 70b by doubling the unit cell. Then, subsequently, distort. This sequence of actions is indicated in 71.

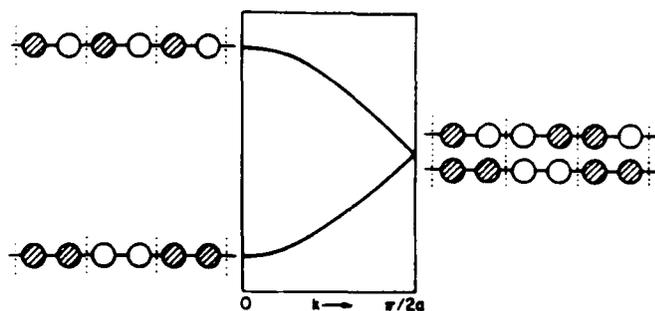


Suppose we construct the orbitals of 71b, the doubled unit cell polymer, by the standard prescription: (1) get MO's in unit cell, (2) form Bloch functions from them. Within the unit cell the MO's of the dimer are π and π^* , 72. Each of these spreads



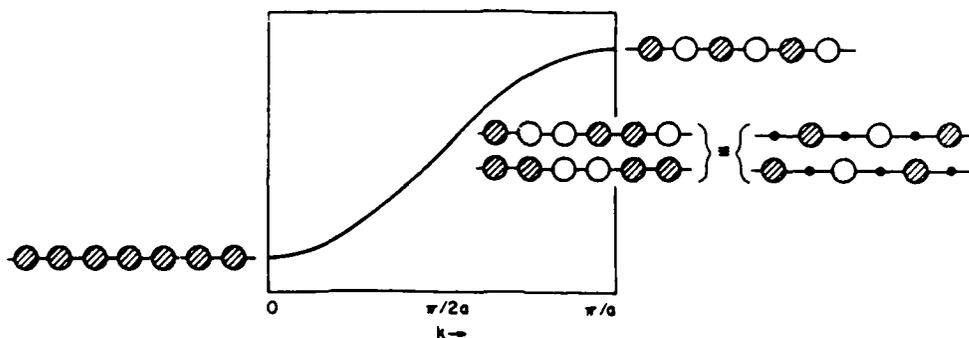
72

out into a band, that of the π "running up", that of π^* running down, 73. The orbitals are written out explicitly at the zone boundaries. This allows one to see that the top of the π band and the bottom of the π^* band, both at $k = \pi/2a$, are precisely degenerate. There is no bond alternation in this polyene (yet), and the two orbitals may have been constructed in a different way, but they obviously have the same nodal structure -- one node every two centers.



73

If we now detach ourselves from this viewpoint and go back and construct the orbitals of the one CH per unit cell linear chain 71a, we get 74. The Brillouin zone in 71b is half as long as it is here, because the unit cell is twice as long.

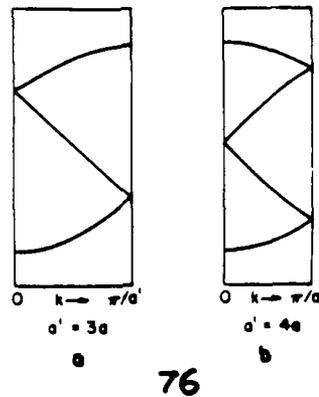
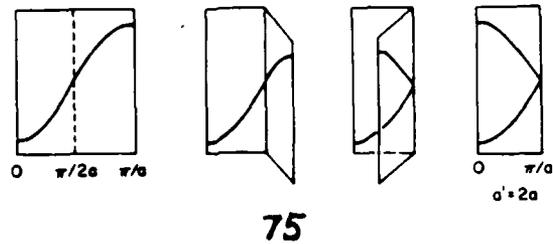


74

At this point, the realization hits us that, of course, the orbitals of these polymers are the same. The polymers are identical, it is only some peculiar quirk that made us choose one CH unit as the unit cell in one case, 2 CH units in the other. I have presented the two constructions independently to make explicit the identity of the orbitals.

What we have is two ways of presenting the same orbitals. Band structure 73, with two bands, is identical to 74, with one band. All that has happened is that the band of the minimal polymer, one CH per unit cell, has been "folded back" in 74. The process is shown in 75.⁶⁶

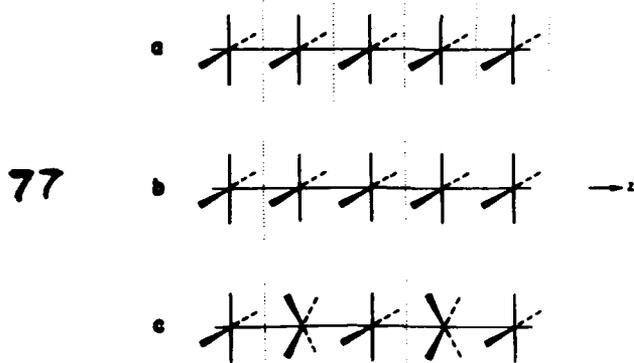
The process can be continued. If the unit cell is tripled, the band will fold as in 76a. If it is quadrupled, we get 76b,



and so on. However, the point of all this is not just redundancy, seeing the same thing in different ways. There are two important consequences or utilizations of this folding. First, if a unit cell contains more than one electronic unit (and this happens often) then a realization of that fact, and the attendant multiplication of bands (remember 74 \rightarrow 73 \rightarrow 76a \rightarrow 76b), allows a chemist to simplify in his or her mind the analysis. The multiplicity of bands is a consequence of an enlargement of the unit cell. By reversing, in our minds in a model

calculation, the folding process, by unfolding, we can go back to the most fundamental electronic act -- the true monomer.

To illustrate this point, let me show the band structure of the staggered PtH_4^{2-} chain, 69b. This is done in Fig. 35, left. There are twice as many bands in this region as there are in the case of the eclipsed monomer (the xy band is doubly degenerate). This is no surprise, the unit cell of the staggered polymer is $[\text{PtH}_4^{2-}]_2$. But it's possible to understand Fig. 35 as a small perturbation on the eclipsed polymer. Imagine the thought process 77a \rightarrow b \rightarrow c, i.e. doubling the unit cell in an eclipsed polymer and then rotating every other unit by 45° around the z axis.



To go from 77a to b is trivial, a simple folding back. The result is shown at the right of Fig. 35. The two sides of the figure are nearly identical. There is a small difference in the xy band, which is doubled, nondegenerate, in the folded-back eclipsed polymer (right-hand side of Fig. 13), but degenerate in the staggered polymer. What happened here could be stated in two

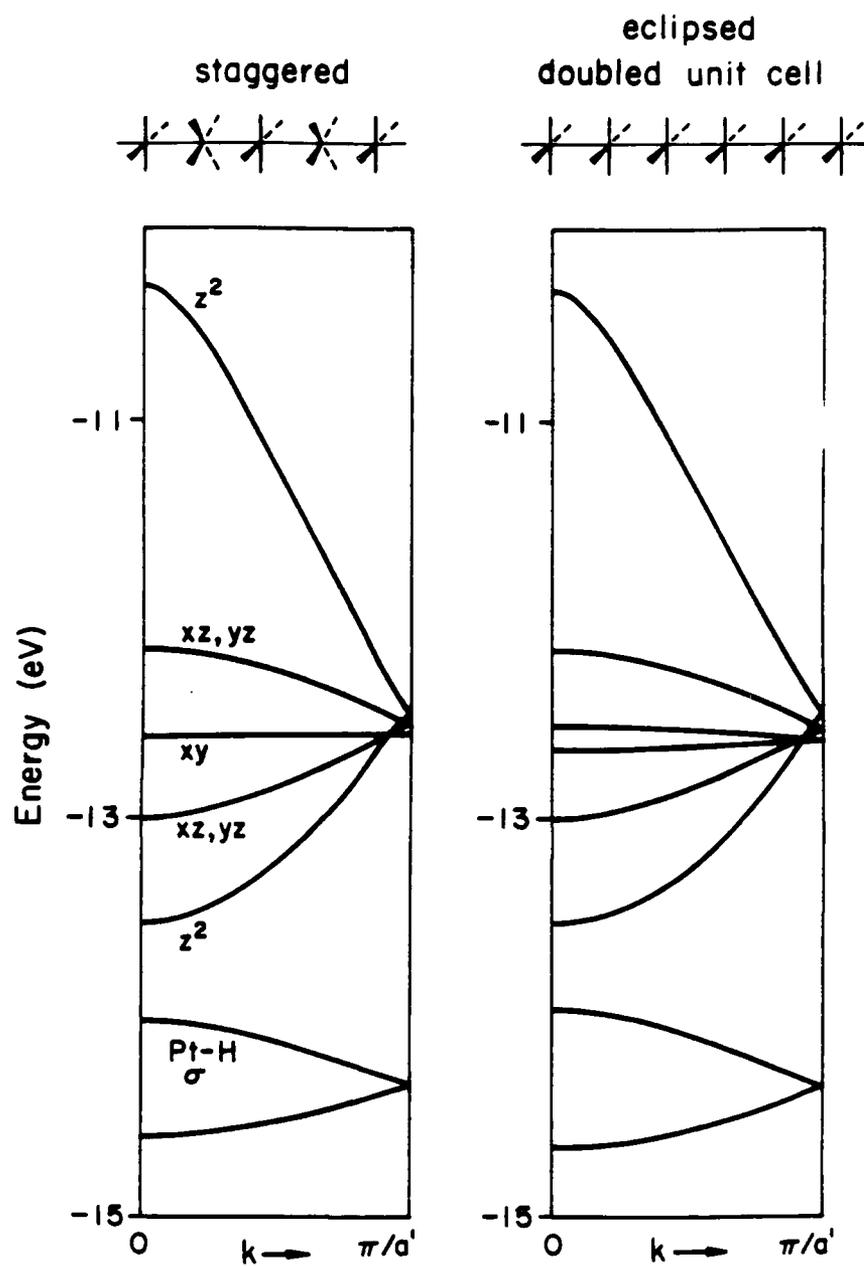


Figure 35. The band structure of a staggered PtH_4^{2-} stack (left), compared with the folded back band structure of an eclipsed stack, 2PtH_4^{2-} in a unit cell (right).

ways, both the consequence of the fact that a real rotation intervenes between 77b and c. From a group theoretical point of view, the staggered polymer has a new, higher symmetry element, an eight-fold rotation-reflection axis. Higher symmetry means more degeneracies. It is easy to see that the two combinations, 78, are degenerate.



78

Except for this minor wrinkle, the band structures of the folded-back eclipsed polymer and the staggered one are very, very similar. That allows us to reverse the argument, to understand the staggered one in terms of the eclipsed one plus the here minor perturbation of rotation of every second unit.

The chemist's intuition is that the eclipsed and staggered polymers can't be very different. At least until the ligands start bumping into each other, and for such steric effects there is, in turn, much further intuition. The band structures may look different, for one polymer has one, the other two basic electronic units in the cell. Chemically, however, they should be similar, and we can see this by returning from reciprocal space to real space. Fig. 36, comparing the DOS of the staggered and eclipsed polymers, shows just how alike they are in their distribution of levels in energy.

Figure 36

There is another reason for feeling at home with the folding process. The folding-back construction may be a prerequisite to understanding a chemically significant distortion of the polymer. To illustrate this point, we return to the polyene 71. To go from 71a (the linear chain, one CH per unit cell) to 71b (linear chain, two CH's per unit cell) involves no distortion. However, 71b is a way point, a preparation for a real distortion to the more realistic "kinked" chain, 71c. It behooves us to analyze the process stepwise, 71a → 71b → 71c, if we are to understand the levels of 71c.

Of course, nothing much happens to the π system of the polymer on going from 71a, b to c. If the nearest neighbor distances are kept constant, then the first real change is in the 1,3 interactions. These are unlikely to be large in a polyene, since the π overlap falls off very quickly past the bonding region. We can estimate what will happen by writing down some explicit points in the band, and deciding whether the 1,3 interaction that is turned on is stabilizing or destabilizing. This is done in 79. Of course, in a real CH polymer this kinking distortion is significant, but that has nothing to do with the π -system, it's a result of strain.

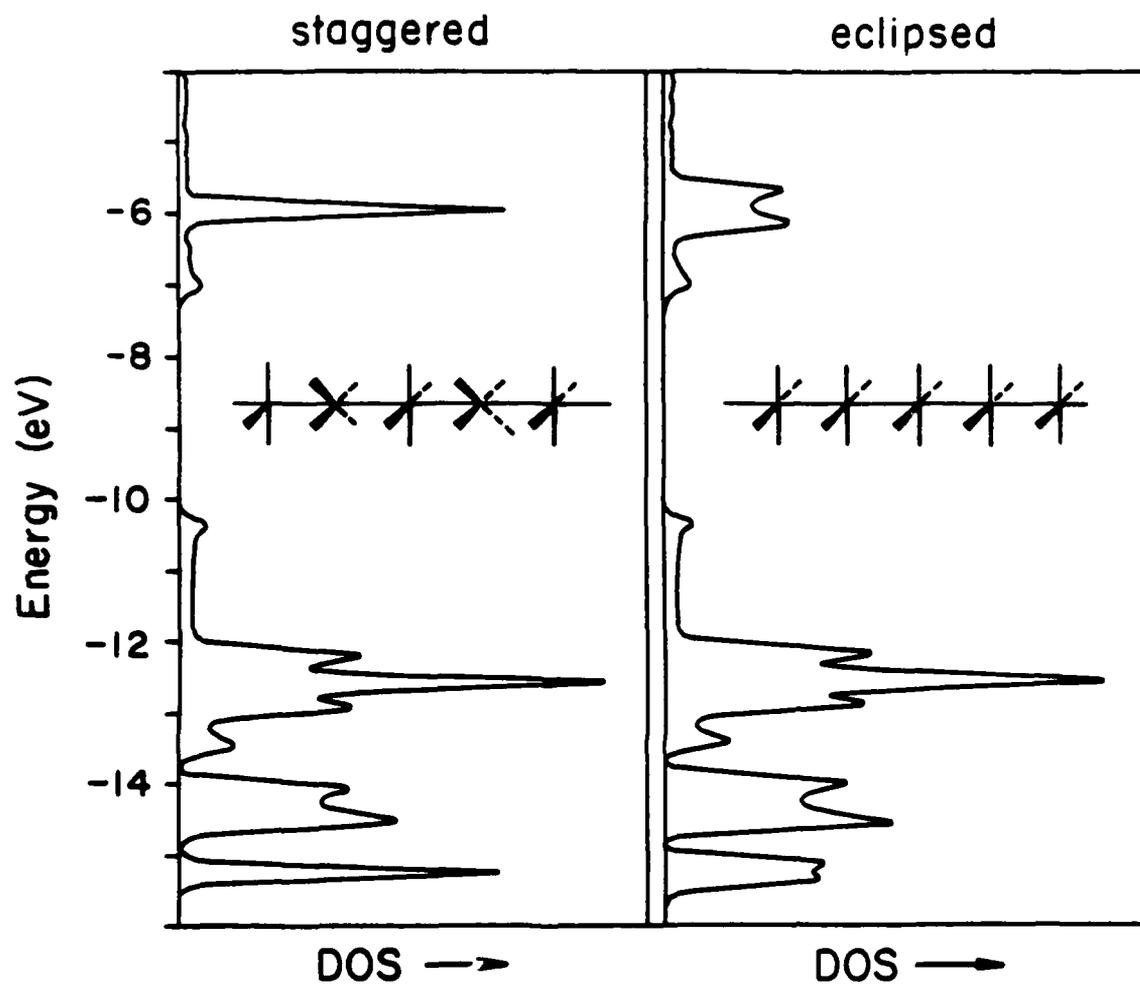
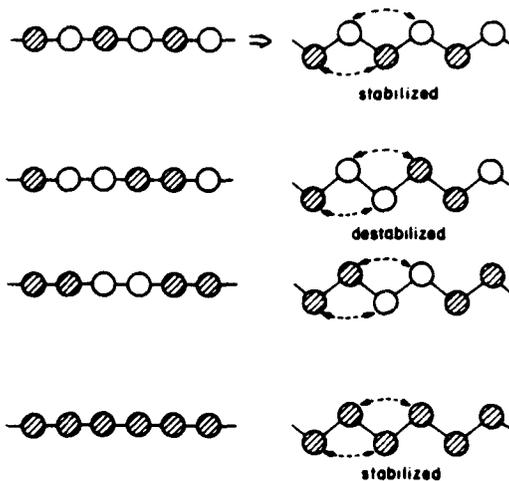


Figure 36. A comparison of the DOS of staggered (left) and eclipsed (right) PtH_4^{2-} stacks.

79

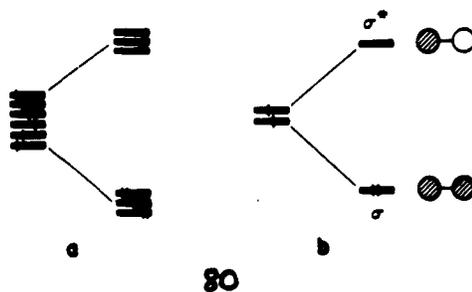


However, there is another distortion which the polyene can and does undergo. This is double bond localization, an example of the very important Peierls distortion, the solid state analogue of the Jahn-Teller effect.

Making Bonds in a Crystal

When a chemist sees a molecular structure which contains several free radicals, orbitals with unpaired electrons, his or her inclination is to predict that such a structure will undergo a geometry change in which electrons will pair up, forming bonds. It is this reasoning, so obvious as to seem almost subconscious, which is behind the chemist's intuition that a chain of hydrogen atoms will collapse into a chain of hydrogen molecules.

If we translate that intuition into a molecular orbital picture, we have 80a, a bunch (here 6) of radicals forming bonds. That process of bond formation follows the H_2 paradigm, 80b, i.e. in the process of making each bond a level goes down, a level goes up, and two electrons are stabilized by occupying the lower, bonding orbital.



In solid state physics, bond formation has not stood at center stage, as it has in chemistry. The reasons for this are obvious: the most interesting developments in solid state

physics have been around metals and alloys, and in these often close-packed or nearly close-packed substances by and large localized, chemical viewpoints have seemed irrelevant. For another large group of materials, ionic solids, it also seemed useless to think of bonds. My contention is that there is a range of bonding, including what are usually called metallic, covalent and ionic solids, and that there is, in fact, substantial overlap between seemingly divergent frameworks of describing the bonding in these three types of crystals. I will take the view that the covalent approach is central and look for bonds when others wouldn't think they're there. One reason for tolerating such foolhardiness might be that the other approaches (metallic, ionic) have had their day -- why not give this one a chance? A second reason, one I've mentioned earlier, is that, in thinking and talking about bonds in the crystal, one makes a psychologically valuable connection to molecular chemistry.

To return to our discussion of molecular and solid state bond formation, let's pursue the trivial chemical perspective of the beginning of this section. The guiding principle, implicit in 80, is: Maximize bonding. There may be impediments to bonding: one might be electron repulsions, another steric effects, i.e. the impossibility of two radicals to reach within bonding distance of each other. Obviously, the stable state is a compromise -- some bonding may have to be weakened to strengthen some other bonding. But, in general, a system will distort so as

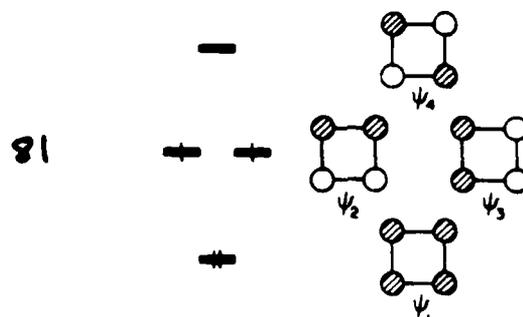
to make bonds out of radical sites. Or to translate this into the language of densities of states: maximizing bonding in the solid state is connected to lowering the DOS at the Fermi level, moving bonding states to lower energy, antibonding ones to high energy.

The Peierls Distortion

In considerations of the solid state, a natural starting point is high symmetry -- a linear chain, a cubic or close-packed three-dimensional lattice. The orbitals of the highly symmetrical, idealized structures are easy to obtain, but they do not correspond to situations of maximum bonding. These are less symmetrical deformations of the simplest, archetype structure.

The chemist's experience is usually the reverse, beginning from localized structures. However, there is one piece of experience we have that matches the way of thinking of the solid state physicist. This is the Jahn-Teller effect⁶⁷, and it's worthwhile to show its working by a simple example.

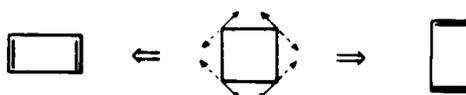
The Hückel π MO's of a square planar cyclobutadiene are well known. They are the one below two below one set shown in 81. We



have a typical Jahn-Teller situation -- two electrons in a degenerate orbital. (Of course, we need worry about the various

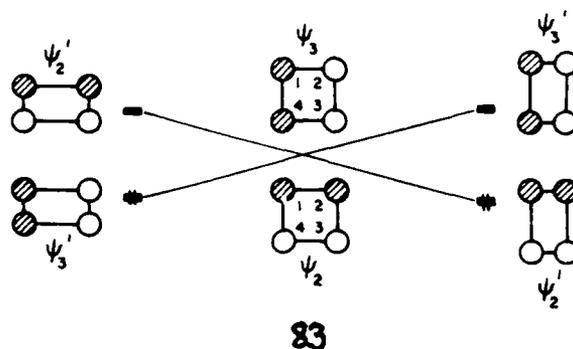
states that arise from this occupation, and the Jahn-Teller theorem really applies to only one.⁶⁷⁾ The Jahn-Teller theorem says that such a situation necessitates a large interaction of vibrational and electronic motion. It states that there must be at least one normal mode of vibration which will break the degeneracy and lower the energy of the system (and, of course, lower its symmetry). It even specifies which vibrations would accomplish this.

In the case at hand the most effective normal mode is illustrated in 82. It lowers the symmetry from D_{4h} to D_{2h} , and, to use chemical language, localizes double bonds.



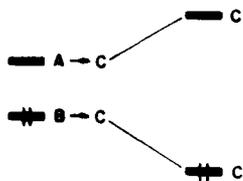
82

The orbital workings of this Jahn-Teller distortion are easy to see. 83, ψ_2 is stabilized: the 1-2, 3-4 interactions which were bonding in the square are increased; the 1-4, 2-3 interactions which were antibonding are decreased by the deformation. The reverse is true for ψ_3 -- it is destabilized by the distortion at right. If we follow the opposite phase of the vibration, to the left in 82 or 83, ψ_3 is stabilized, ψ_2 destabilized.



The essence of the Jahn-Teller theorem is revealed here: a symmetry-lowering deformation breaks an orbital degeneracy, stabilizing one orbital, destabilizing another. Note the phenomenological correspondence to 80 at the beginning of this section.

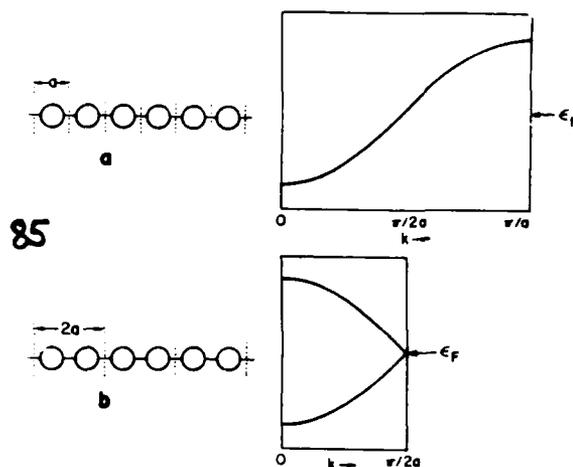
One doesn't need a real degeneracy to benefit from this effect. Consider a non-degenerate two-level system, 84, with the two levels of different symmetry (here labeled A, B) in one geometry. If a vibration lowers the symmetry so that these two levels transform as the same irreducible representation, call it C, then they will interact, mix, repel each other. For two electrons, the system will be stabilized. The technical name of this effect is a second-order Jahn-Teller deformation.⁶⁷



The essence of the Jahn-Teller effect, first or second order, is: a high symmetry geometry generates a degeneracy, which can be broken, with stabilization, by a symmetry-lowering deformation. Note a further point: the level degeneracy is not enough by itself -- one needs the right electron count. The cyclobutadiene (or any square) situation of 83 will be stabilized by a D_{2h} deformation for 3, 4 or 5 electrons, but not for 2 or 6 (S_4^+).

This framework we can take over to the solid. There is degeneracy and near degeneracy for any partially filled band. The degeneracy is that already mentioned, for $E(k) = E(-k)$ for any k in the zone. The near degeneracy is, of course, for k 's just above or just below the specified Fermi level. For any such partially-filled band there is, in principle, available a deformation which will lower the energy of the system. In the jargon of the trade one says that the partial filling leads to an electron-phonon coupling which opens up a gap just at the Fermi level. This is the Peierls distortion⁶⁸, the solid state counterpart of the Jahn-Teller effect.

Let's see how this works on a chain of hydrogen atoms (or a polyene). The original chain has one orbital per unit cell, 85a, and an associated simple band. We prepare it for deformation by doubling the unit cell, 85b. The band is typically folded. The Fermi level is halfway up the band -- the band has room for two electrons per orbital, but for H or CH we have one electron per orbital.

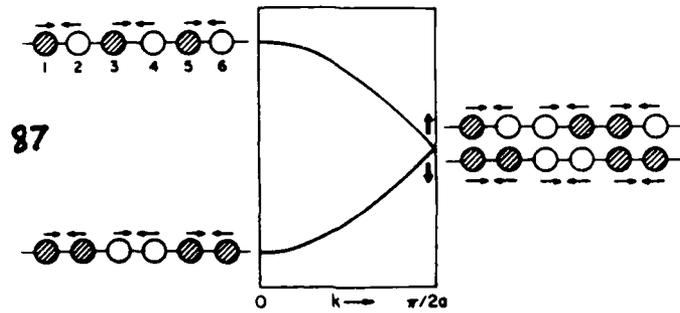


The phonon or lattice vibration mode that couples most effectively with the electronic motions is the symmetric pairing vibration, 86. Let's examine what it does to typical orbitals at

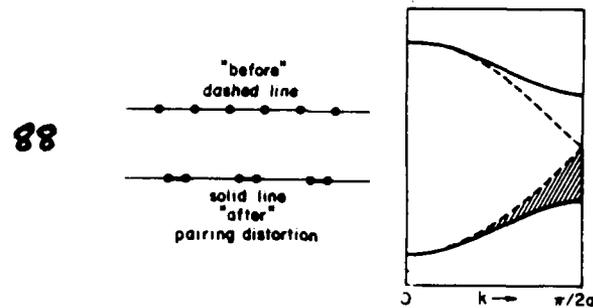


86

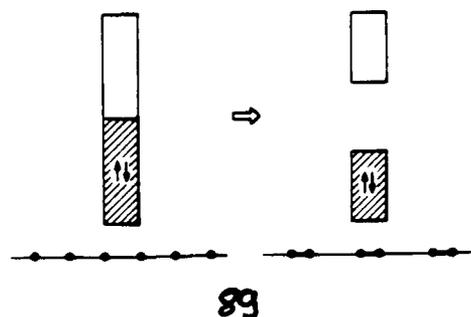
the bottom, middle (Fermi level), and top of the band, 87. At the bottom and top of the band nothing happens. What is gained (lost) in increased 1-2, 3-4, 5-6, etc. bonding (antibonding) is lost (gained) in decreased 2-3, 4-5, 6-7 bonding (antibonding). But in the middle of the band, at the Fermi level, the effects are dramatic. One of the degenerate levels there is stabilized by the distortion, the other destabilized. Note the phenomenological similarity to what happened for cyclobutadiene.



The action does not take place just at the Fermi level, but in a second order way the stabilization "penetrates" into the zone. It does fall off with k , a consequence of the way perturbation theory works. A schematic representation of what happens is shown in 88. A net stabilization of the system occurs



for any Fermi level, but obviously it is maximal for the half-filled band, and it is at that ϵ_F that the band gap is opened up. If we were to summarize what happens in block form, we'd get 89. Note the resemblance to 80.



The polyene case (today it would be called polyacetylene) is especially interesting, for some years ago it occasioned a great deal of discussion. Would an infinite polyene localize, 90? Eventually, Salem and Longuet-Higgins demonstrated that it

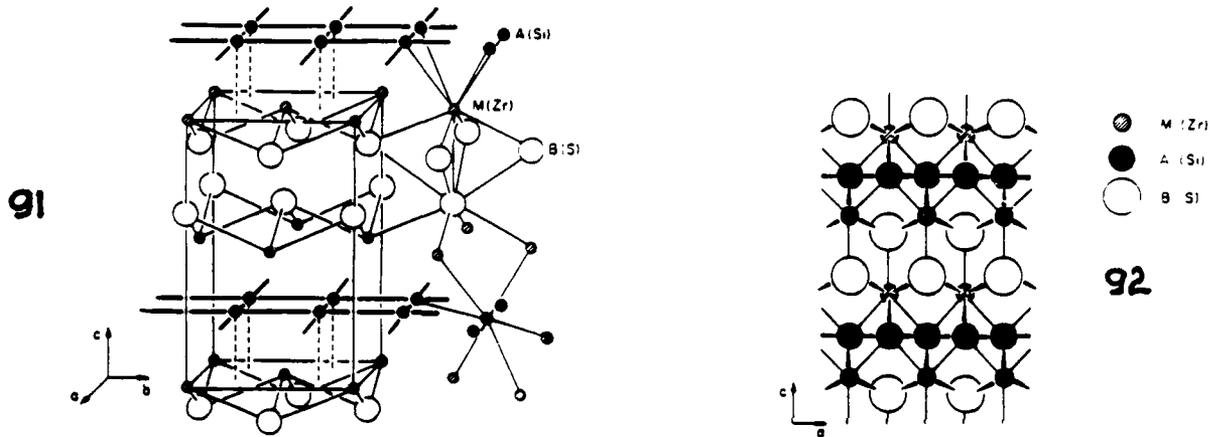


would.⁶⁹ Polyacetylenes are an exciting field of modern research.⁷⁰ Pure polyacetylene is not a conductor. When it is doped, either partially filling the upper band in 89 or emptying the lower, it becomes a superb conductor.

There are many beautiful intricacies of the first- and second-order and low- or high-spin Peierls distortion, and for these the reader is referred to the very accessible review by Whangbo.⁸

The Peierls distortion plays a crucial role in determining the structure of solids in general. The one-dimensional pairing distortion is only one simple example of its workings. Let's move up in dimensionality.

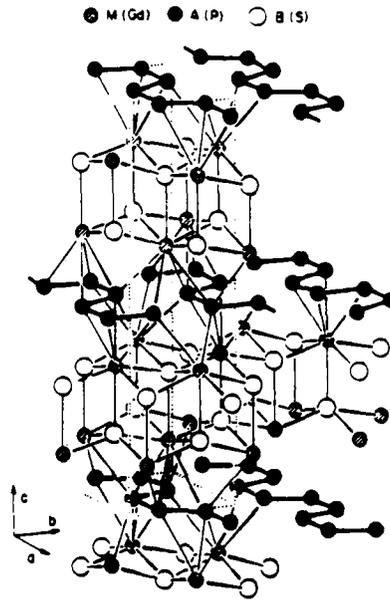
One ubiquitous ternary structure is that of PbFCl (ZrSiS , BiOCl , Co_2Sb , Fe_2As).^{16,71} We'll call it MAB here, because in the phases of interest to us the first element is often a transition metal, the other components, A, B, often main group elements. 91 shows one view of this structure, 92 another.



In this structure we see two associated square nets of M and B atoms, separated by a square net layer of A's. The A layer is twice as dense as the others, hence the MAB stoichiometry. Most interesting, from a Zintl viewpoint, is a consequence of that A layer density, a short $\text{A}\cdots\text{A}$ contact, typically 2.5 Å for Si. This is definitely in the range of some bonding. There are no short $\text{B}\cdots\text{B}$ contacts.

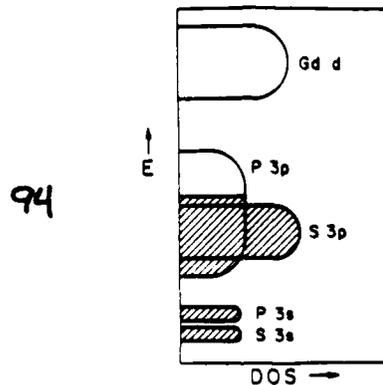
Some compounds in this series in fact retain this structure. Others distort. It is easy to see why. Take GdPS . If we assign normal oxidation states of Gd^{3+} and S^{2-} we come to a formal charge of P^- on the dense-packed P^- net. From a Zintl viewpoint P^- is like S and so should form two bonds per P. This is exactly

what it does. The GdPS structure⁷² is shown in 93, which is drawn after the beautiful representation of Hulliger, et al.⁷² Note the P-P cis chains in this elegant structure.



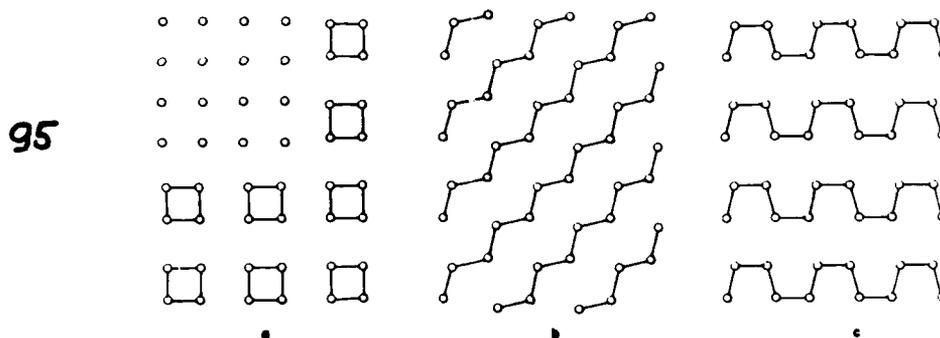
93

From the point of view of a band structure calculation one might also expect bond formation, a distortion of the square net. 94 shows a qualitative DOS diagram for GdPS. What goes into the construction of this diagram is a judgment as to the



electronegativities of $Gd < P < S$. And the structural information that there are short $P \cdots P$ interactions in the undistorted square net, but no short $S \cdots S$ contacts. With the normal oxidation states of Gd^{3+} , S^{2-} one comes to P^- , as stated above. This means the P 3p band is 2/3 filled. The Fermi level is expected to fall in a region of a large DOS, as 94 shows. A distortion should follow.

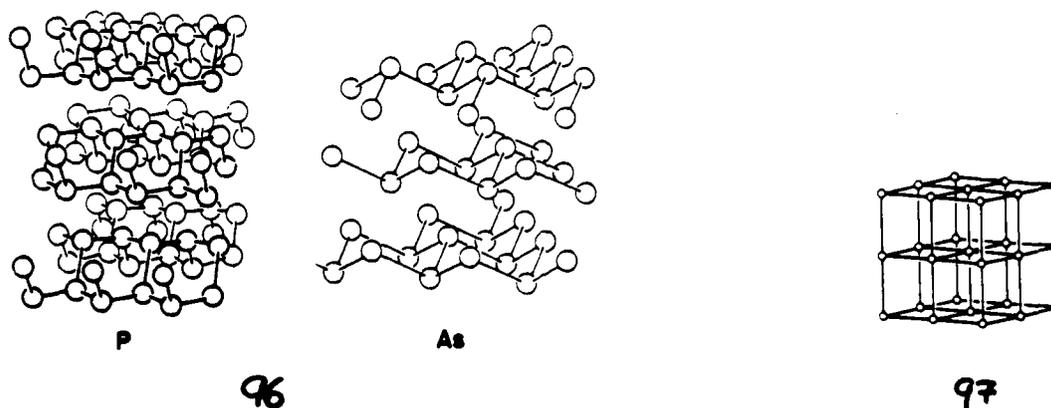
The details of what actually happens are presented elsewhere.¹⁶ The situation is intricate; the observed structure is only one of several likely ways for the parent structure to stabilize -- there are others. 95 shows some possibilities



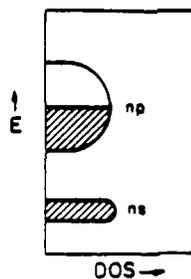
suggested by Hulliger et al.⁷² CeAsS chooses 95c.⁷³ Nor is the range of geometrical possibilities of the MAB phases exhausted by these. Other deformations are possible; many of them can be rationalized in terms of second-order Peierls distortions in the solid.¹⁶

An interesting three-dimensional instance of a Peierls distortion at work (from one point of view) is the derivation of the observed structures of elemental arsenic and black phosphorus

from a cubic lattice. This treatment is due to Burdett and coworkers.^{6,74} The two structures are shown in their usual representation in 96, below. It turns out that they can be easily related to a simple cubic structure, 97.

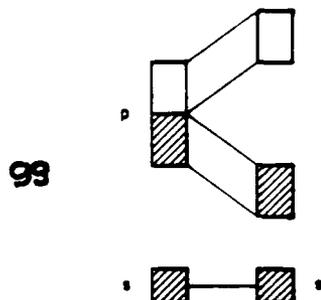


The DOS associated with the band structure of 97, with one main group element of group 15 per lattice site, must have the block form 98. There are 5 electrons per atom, so if the s band is completely filled, we have a half-filled p band. The detailed DOS is given elsewhere.⁷⁴ What is significant here is what we

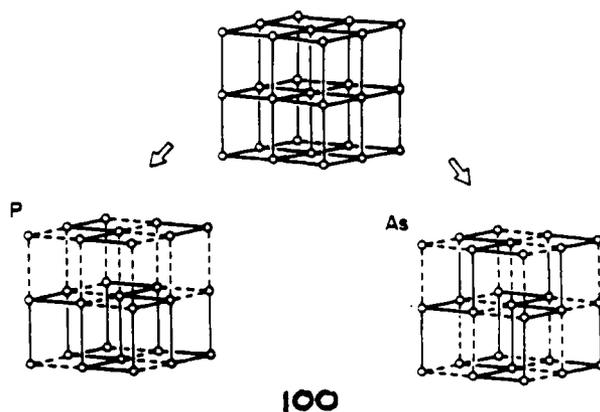


98

see without calculations, namely a half-filled band. This system is a good candidate for a Peierls distortion. One pairing up all the atoms along x , y , and z directions will provide the maximum stabilization indicated schematically in 99.



Burdett, McLarnan and Haaland ^{74,a,c} have shown that there are no less than 36 different ways to so distort. Two of these correspond to black phosphorus and arsenic, 100. There are other possibilities.



There is one aspect of the outcome of a Peierls distortion, the creation of a gap at the Fermi level, that might be taken from the last case as being typical, but which is not necessarily so. In one dimension one can always find a Peierls distortion to

create a gap. In three dimensions, atoms are much more tightly linked together. In some cases a stabilizing deformation leads to the formation of a real band gap, to an insulator or semiconductor. In other cases, a deformation is effective in producing bonds, 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.

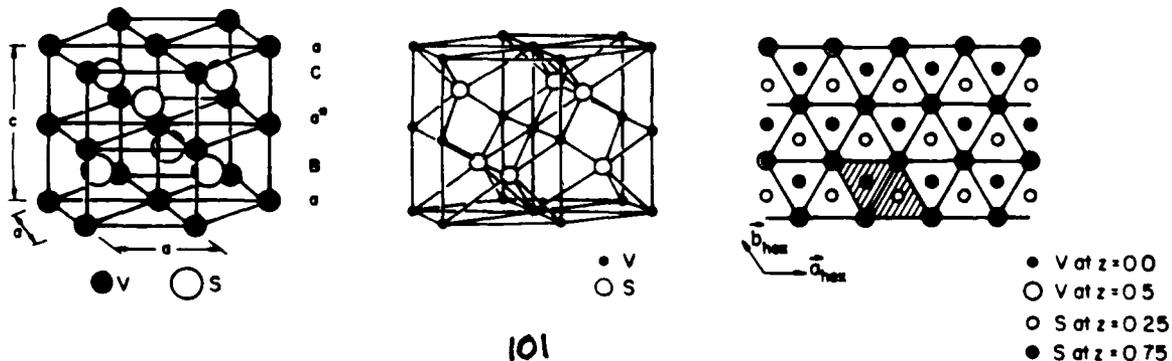
One final comment, on the ThCr_2Si_2 structure. The reader will note that we did not use a Peierls distortion argument in the resolution of the P-P pairing problem in that common structural type, when we discussed it above. We could have done so, somewhat artificially, by choosing a structure in which 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 geometrical 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 introduce little 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 First, the chemical motivation. 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 way in 101, consists of hexagonal close-packed layers

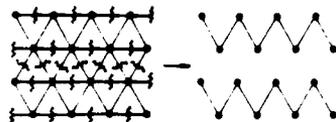


which alternate metal and non-metal atoms. To be specific, let's discuss the VS representative. The structure contains a hexagonal layer of vanadium atoms at $z = 0$, then a layer of sulfur atoms at $z = 1/4$, then a second layer of metal atoms at $z = 1/2$, superimposable on the one at $z = 0$, and, 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

The MnP structure is a small but significant perturbation on the NiAs 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

**102**

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 discernible 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 ten valence electrons favor the NiAs structure (for phosphides), 11 to 14 the MnP, and a greater number of electrons prefers the NiP alternative. For the arsenides this trend is less clear.

The details of these fascinating transformations are given elsewhere.⁷⁵ 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.

Figure 37

A veritable spaghetti diagram this, seemingly beyond the powers of comprehension of any human being. Why not abdicate

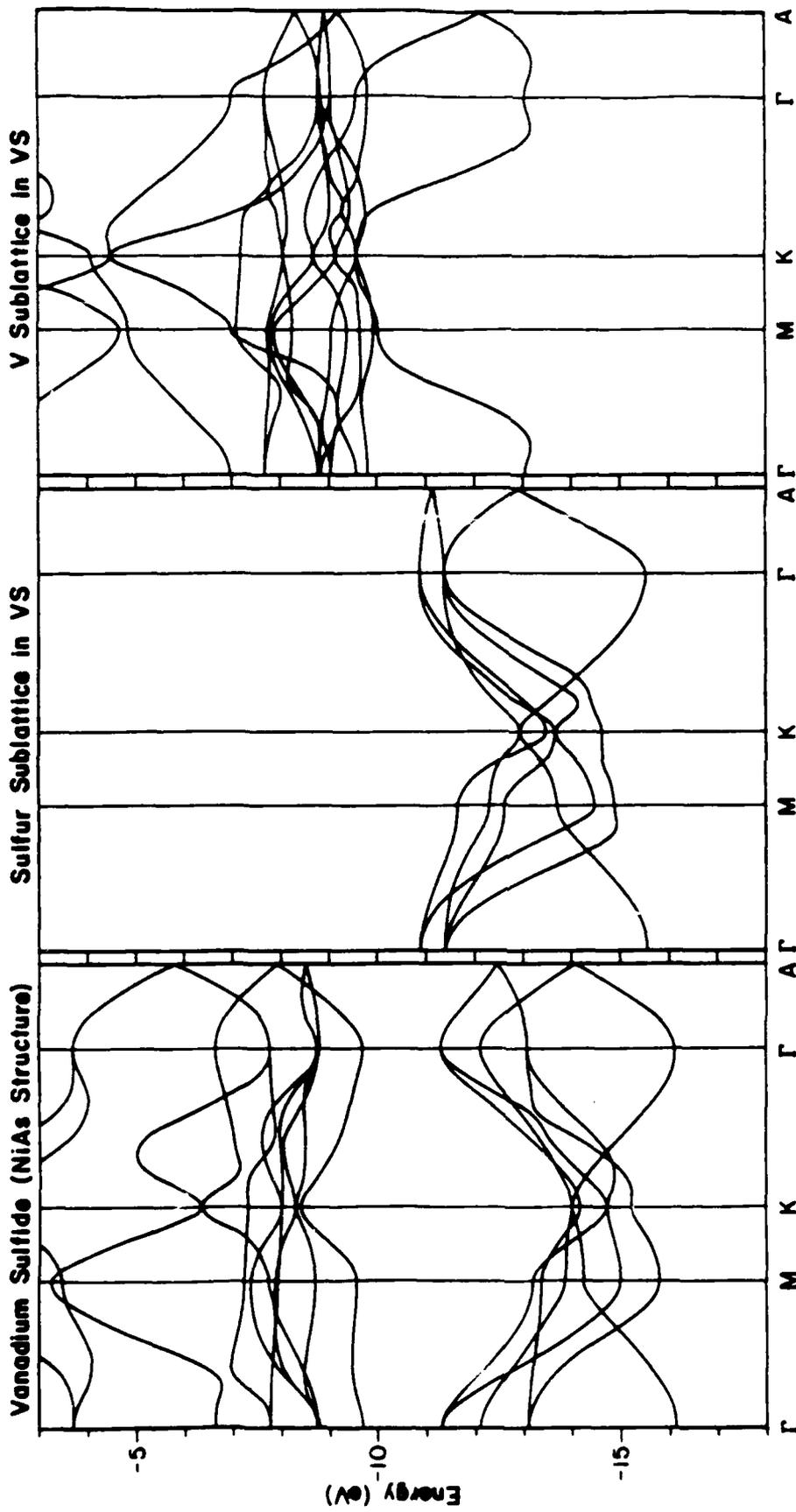
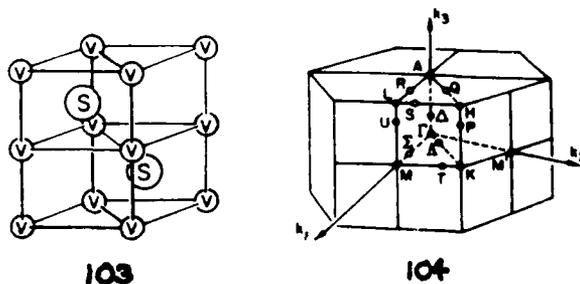


Figure 37. The band structure for VS in the NiAs structure (left), together with the band structures of its S (middle) and V (right) sublattices.

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, below. It contains two formula units V_2S_2 . That tells us immediately that we should expect $4 \times 2 = 8$ sulfur bands, two 3s separated from six 3p. And $9 \times 2 = 18$ vanadium bands, of which 10, the 3d block, should be lowest.

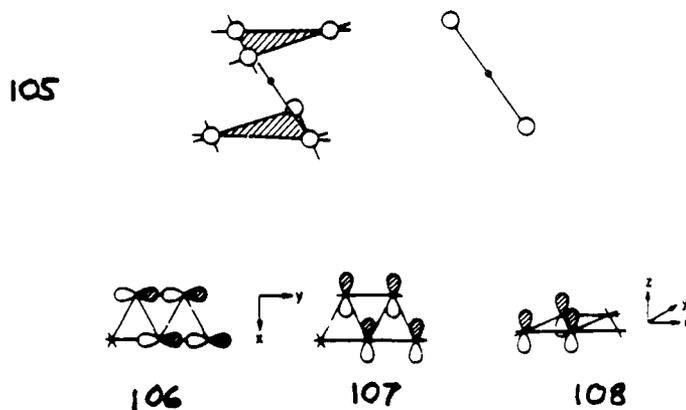


The Brillouin zone, 104, has some special points labeled in it. There are conventions for this labeling.^{9,15} The zone is, of course, three-dimensional. The band structure (Fig. 37) shows the evolution of the levels along several directions in the zone. Count the levels, to confirm the presence of six low-lying bands (which a decomposition of the DOS shows to be mainly S 3p) and ten 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 do. Note the relatively narrow V d bands around -8 to -9eV. There is metal-metal bonding in the V sublattice, the widths of the V s,p bands show this. 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. 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. 37b and 37a.



109

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?

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 "this level does (or does not) interact with another one", we may have to say "this level interacts more (or less) effectively with such

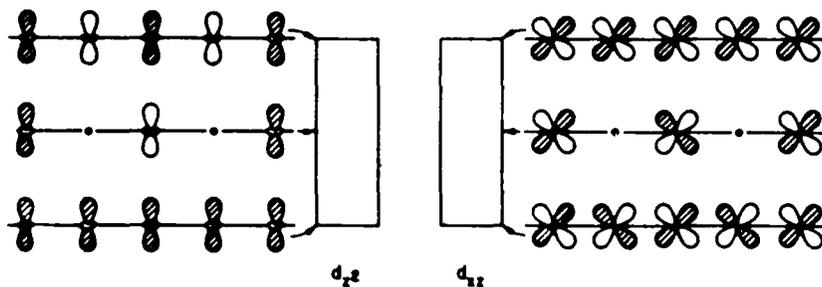
and such part of a band". Let me illustrate this with some examples.

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 radical orbital n , for 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?

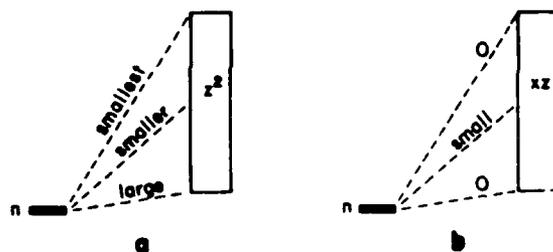
It's useful to take things apart and consider the metal levels one by one. 111, below, illustrates schematically some



111

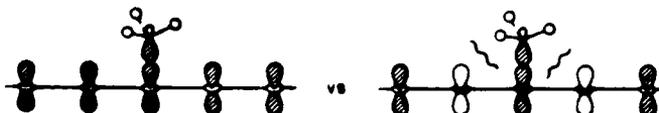
representative orbitals in the z^2 and xz bands. The orbitals at the bottom of a band are metal-metal bonding, those in the middle non-bonding, at the top of the band antibonding. While things are assuredly more complicated in three dimensions, these one-dimensional pictures are indicative of what transpires.

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.



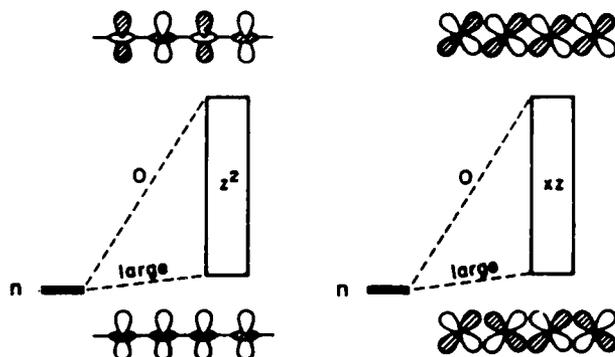
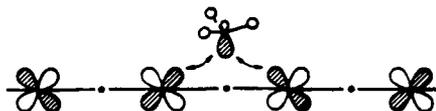
112

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



113

114

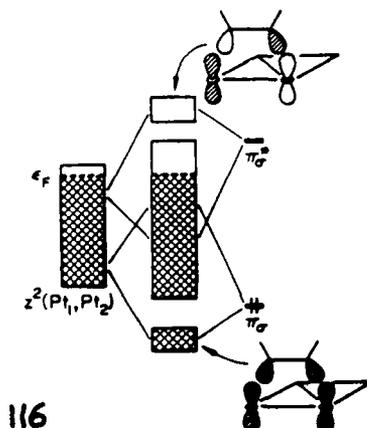


115

theoretic apparatus and specifically the role of k in delimiting interactions on surfaces goes back to the work of Grimley⁴⁵ and Gadzuk⁴⁴, and has been consistently stressed by Salem.⁴⁷

For a second example, let's return to acetylene on Pt(111), specifically in the two-fold and four-fold geometries.²⁹ In the two-fold 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. 116 shows this -- in the two-fold 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.

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 four-fold 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.

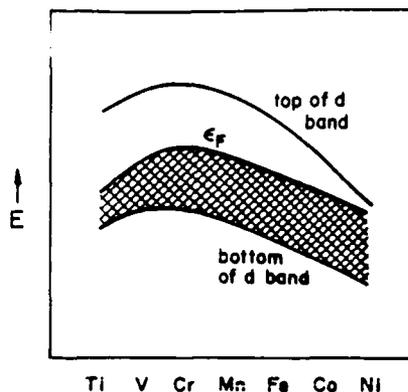
The Fermi Level Matters

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, on the coverage of the surface. Theory is quite far behind in understanding these determining factors of surface reactivity, but some pieces of understanding emerge. One such 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 not a bad approximation to the configuration or effective valence state of any metal is $d^{x-1}s^1$. 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? Over the greater part of the transition series it falls, or its magnitude is greater.

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 definite 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 ionization

117

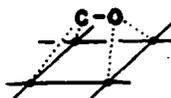


potential of a single d electron increases to the right. The orbitals also become more contracted, therefore the less dispersed band at the right. At the same time, the band filling increases. The position of the band center of gravity and the filling compete; the former wins out. Thus the Fermi level falls at the right side of the transition series. What happens in the middle is a little more complicated.⁴⁰

Let's see the consequences of this trend for two chemical reactions. One is well-studied, the dissociative chemisorption of CO. The other is less well-known, but certainly matters, for it must occur in Fischer-Tropsch catalysis. This is the coupling of two alkyl groups on a surface to give an alkane.

In general, early and middle transition metals break up carbon monoxide, late ones just bind it molecularly.⁷⁹ How the CO is broken up, in detail, is not known experimentally. Obviously, at some point the oxygen end of the molecule must come in contact with the metal atoms, even though the common coordination mode on surfaces, as in molecular complexes, is

through the carbon. In the context of pathways of dissociation, the recent discovery of CO lying down on some surfaces, 118, is intriguing.⁸⁰ Perhaps such geometries intervene on the way to splitting the diatomic to chemisorbed atoms. There is a good theoretical model for CO bonding and dissociation.⁸¹



118

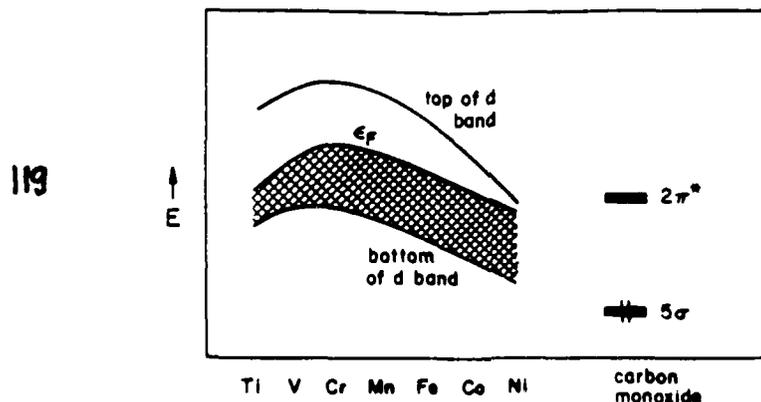
Parenthetically, the discovery of 118, and of some other surface species bound in ways no molecular complex shows, should make inorganic and organometallic chemists read the surface literature not only to find references with which to decorate grant applications. The surface-cluster analogy, of course, is a two-way street. So far, it has been used largely to provide information (or comfort for speculations) for surface studies, drawing on known molecular inorganic examples of binding of small molecules. But now surface structural studies are better, and cases are emerging of entirely novel surface binding modes. Can one design molecular complexes inspired by structures such as 118?

Returning to the problem of the metal surface influence on the dissociation of CO, we can look at molecular chemisorption, C end bonded, and see if there are any clues. Table 4 shows one symptom of the bonding on several different surfaces, the population of CO 5σ and $2\pi^*$.²⁷

 Table 4

The population of 5σ is almost constant, rising slowly as one moves from the right to the middle. The population of $2\pi^*$, however, rises sharply. Not much is left of the CO bond by the time one gets to Ti. If one were to couple, dynamically, further geometry changes -- allowing the CO to stretch, tilt toward the surface, etc. -- one would surely get dissociation on the left side of the series.

The reason for these bonding trends is obvious. 119 superimposes the position of CO 5σ and $2\pi^*$ levels with the metal d band. 5σ will interact more weakly as one moves to the left, but the dramatic effect is on $2\pi^*$. At the right it interacts,

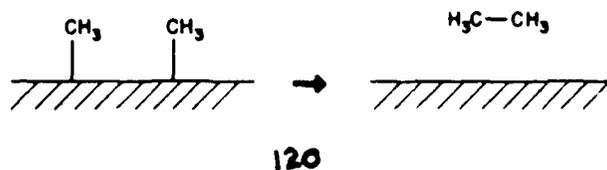


that is required for chemisorption. But $2\pi^*$ lies above the d band. In the middle and left of the transition series, the Fermi level rises above $2\pi^*$. $2\pi^*$ interacts more, is occupied to a greater extent. This is the initial indicator of CO disruption.²⁷

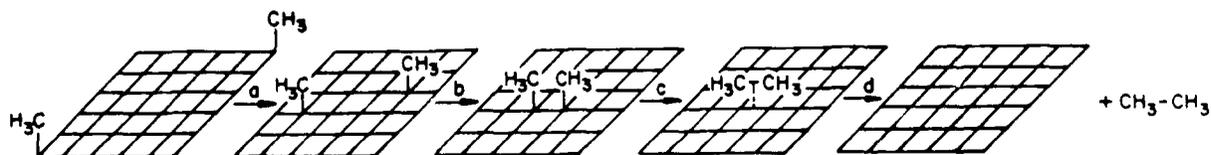
Table 4. Some Orbital Populations in CO Chemisorbed on First Transition Series Surfaces (From Ref. 27)

	Electron Densities in Fragment Orbitals					
	Ti(0001)	Cr(110)	Fe(110)	Co(0001)	Ni(100)	Ni(111)
5 σ	1.73	1.67	1.62	1.60	1.60	1.59
2 π^*	1.61	0.74	0.54	0.43	0.39	0.40

The second case we studied is one specific reaction likely to be important in the reductive oligomerization of carbon monoxide over a heterogeneous catalyst, the Fischer-Tropsch synthesis. The reaction is complicated and many mechanisms have been suggested. In the one I think likely, the "carbide/methylene" mechanism⁸², one follows a sequence of breaking up CO and H₂, hydrogenating the carbon to produce methyl, methylene, methyne on the surface, followed by various chain-forming associations of these and terminating reductive eliminations. It is one of those terminal steps I want to discuss here, a prototype associative coupling of two adsorbed methyls to give ethane, 120.⁷⁸

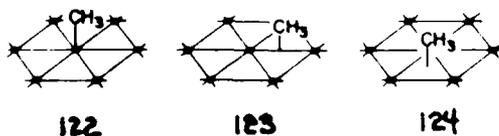


It's simple to write down 120, but it hides a wonderful variety of processes. These are schematically dissected in 121. First, given a surface and a coverage, there is a preferred site which methyls occupy, perhaps an equilibrium between several sites. Second, these methyls must migrate over the surface so as to come near each other. A barrier, call it the "migration

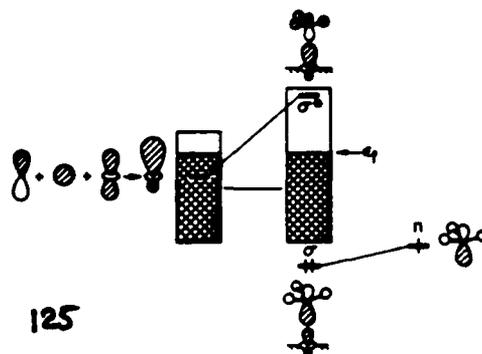


energy", may intervene. Third, one methyl coming into the neighborhood of another may not be enough. It may have to come really close, for instance, on-top of a neighboring metal atom. That may cost energy, for one is creating locally a high-coverage situation, one so high that it might normally be inaccessible. One could call this a steric effect, but let's call it a "proximity energy". Fourth, there is the activation energy to the actual C-C bond formation, once the components are in place. Let's call this the "coupling barrier". Fifth, there might be an energy binding the product molecule to the surface. It is unlikely to be important for ethane, but might be substantial for other molecules. It is artificial to dissect the reaction in this way, nature does it all at once. But in our poor approach to reality (and here we are thinking in terms of static energy surfaces; we haven't even begun to do dynamics, to allow molecules to move on these surfaces), we can think of the components of the barrier impeding coupling: migration + proximity + coupling + desorption energies.

To be specific, let's choose three dense surfaces: Ti(0001), Cr(110) and Co(0001). The calculations we carried out were for a 3-layer slab, and initially a coverage = 1/3. Three binding sites that were considered were on-top or one-fold, 122, bridging or two-fold, 123, capping or three-fold, 124. The preferred site for each metal is the on-top site, 122.⁷⁸



The total binding energy is greater for Ti than Cr than Co. 125 is an interaction diagram for CH_3 chemisorption. The CH_3 frontier orbital, a carbon-based directed radical lobe, interacts

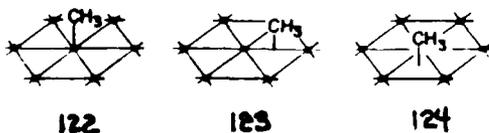


with metal s and z^2 , much like the $\text{CO } 5\sigma$. Some z^2 states are pushed up above the Fermi level, and this is one component of the bonding. The other is an electron transfer factor. We started with a neutral surface and a neutral methyl. But the methyl lobe has room for 2 electrons. Metal electrons readily occupy it. This provides an additional binding energy. And because the Fermi levels increase to the left in the transition series, this "ionic" component contributes more for Ti than for Co.⁷⁸

In a sense, these binding energies of a single ligand are not relevant to the estimation of relative coupling rates of two ligands on different surfaces. But even they show the effect of the Fermi level. A first step in coupling methyls is to consider the migration barriers of isolated groups. This is done in 126.

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The relative energy zero in each case is the most stable on-top geometry.

The implication of 126 is that for Co the preferred migration itineraries are via bridged transition states, 127a, for Ti via capping or hollow sites, 127b, whereas for Cr both are



Relative E (eV):

Co	: 0.0	1.1	1.4
Cr	: 0.0	0.9	0.9
Ti	: 0.0	0.5	0.1

126



a

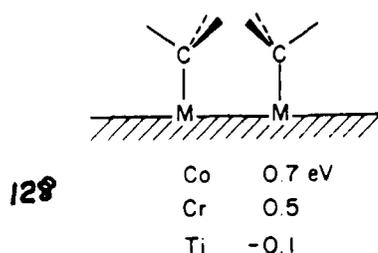
127



b

competitive. For the reasons behind the magnitudes of the computed barriers, the reader is referred to our full paper.⁷⁸ Could one design an experiment to probe these migration alternatives? CH_3 has finally been observed on surfaces, but remains a relatively uncommon surface species.⁵⁴

If we bring two methyl groups to on-top sites on adjacent metals, we see a splitting in the occupied CH_3 states. This is a typical two-orbital four-electron interaction, the way steric effects manifest themselves in one-electron calculations. If we compare the binding energy per methyl group in these proximate structures to the same energy for low coverage isolated methyls, we get the calculated proximity energies of 128. The



destabilization increases with d electron count because some of the d levels occupied carry CH_3 lone pair contributions.

What happens when two CH_3 groups actually couple? The reaction begins with both CH_3 lone pairs nearly filled, i.e. a representation near CH_3^- . A new C-C σ bond forms, and as usual, we must consider σ and σ^* combinations, $n_1 \pm n_2$. Both are filled initially, but as the C-C bond forms, the σ^* combination will be pushed up. Eventually, it will dump its electrons into the metal d-band.

The actual evolution of the DOS and COOP curves allows one to follow this process in detail. For instance, Fig. 38 shows

Figure 38

the contribution of the methyl n orbital, the radical lobe, to the total DOS along a hypothetical coupling reaction coordinate. Note the gradual formation of a two-peaked structure. COOP curves show the lower peak is C-C bonding, the upper one C-C antibonding. These are the σ and σ^* bonds of the ethane that is

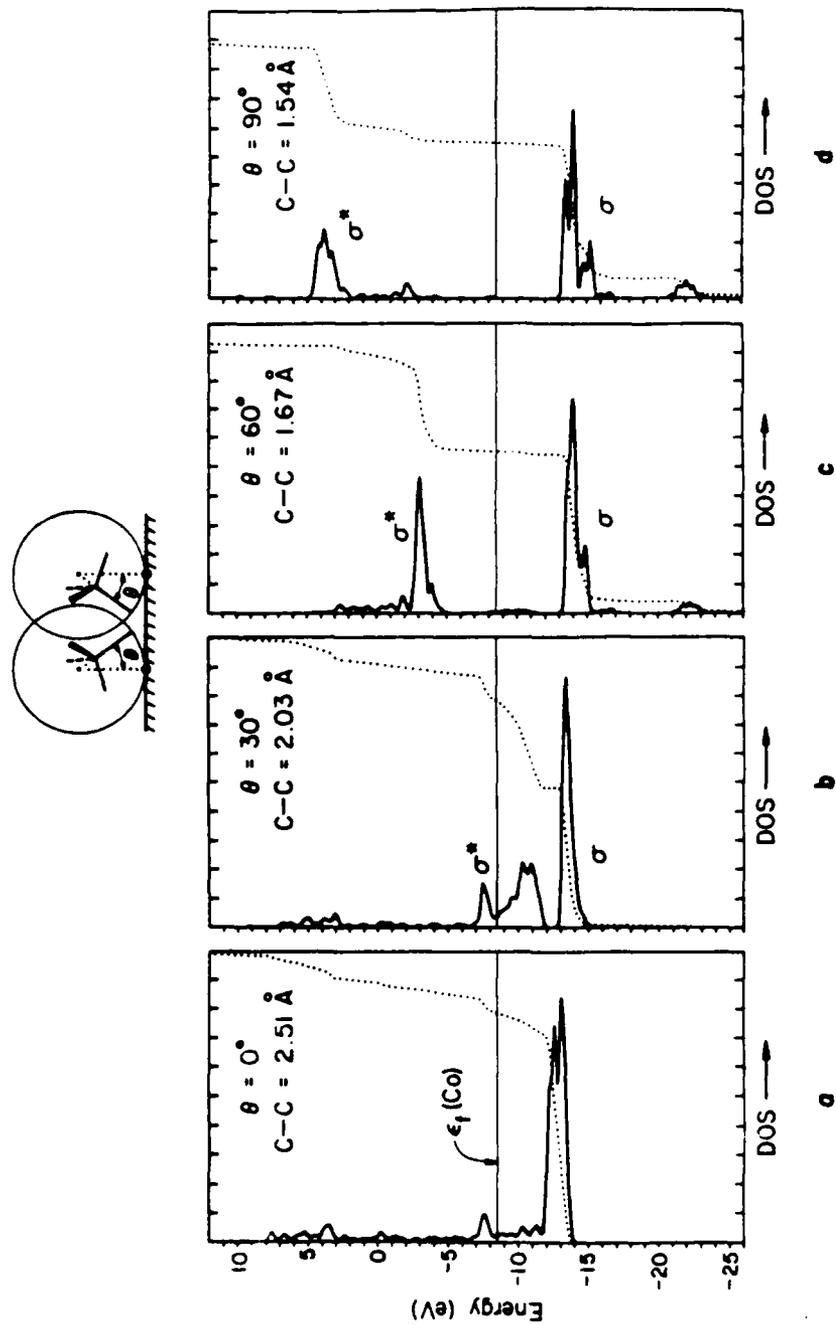


Figure 38. The evolution of the contribution of methyl lone pairs to the DOS of a chemisorption system (CH₃ on Co(0001)) as the two methyls couple to give ethane. θ is defined at top. Note the development of two peaks corresponding to σ and σ^* of the CC bond in ethane.

being formed.

The total energy of the system increases along the reaction path, as n_1-n_2 becomes more antibonding. At the Fermi level, there is a turning point in the total energy. $\sigma^* = n_1-n_2$ is vacated. The energy decreases, following $\sigma = n_1+n_2$. The position of the Fermi level determines the turning point. So the coupling activation energy is expected to be greater for Ti than for Cr than for Co, because, as noted above, the Fermi level is higher for the early transition metals, despite the lower d electron count. The reader familiar with reductive eliminations in organometallic chemistry will note essential similarities.^{58,83b} We also mention here again the relationship of our argument to the qualitative notions of Mango and Schachtschneider on how coordinated metal atoms affect organic reactions.⁵⁷

The position of the Fermi level clearly is an important factor in determining binding and reactivity on metal surfaces.

Another Methodology and Some Credits

There have been an extraordinary number of theoretical contributions to solid state and surface science.⁸⁴ These have come from physicists and chemists, they have ranged from semiempirical molecular orbital (MO) calculations to state-of-the-art Hartree-Fock self-consistent-field + configuration interaction (CI) and advanced density-functional procedures. Some people have used atom and cluster models, some extended slab or film models for surfaces. I will not discuss, I cannot discuss all these contributions, even those relevant to the systems I've mentioned, for the following reasons: (1) This is not an exhaustive review of theoretical methods; (2) I'm lazy; (3) The field is full of conflicting claims of validity for the theoretical methods used. Such claims are of course typical of the reality (rather than the ideology) of all science. But theory especially is prone to them -- because theorists are rarely dealing in the material, but mostly in the spiritual world. That's inherent in the nature of answering the question, the necessary and deep question, of "why?" and "how?". Basically I'm not sure I can answer the question as to whether one or another method is "better" than another, nor do I have the courage to try.

Most of the theoretical methods at hand are just better ways of solving the wave equation for the complex system at hand, not necessarily leading to more chemical and physical understanding.

There is one exception, the complex of ideas on chemisorption introduced and developed by Lundqvist, Nørskov, Lang and their coworkers.⁸⁵ This is a methodology rich in physical understanding, and because of that and the fact that it provides a different way of looking at barriers for chemisorption, I want to mention the method explicitly here.

The methodology focuses, as many density-functional schemes do, on the key role of the electron density. The Schrödinger equation is then solved self-consistently in the Kohn-Sham scheme.⁸⁶ Initial approaches dealt with a jellium-atom system, which would at first sight seem rather unchemical, lacking microscopic detail. But there is much physics in such an effective medium theory, and with time the atomic details at the surface have come to be modeled with greater accuracy.

An example of the information the method yields is shown in Fig. 39, the total energy and density of states profile for H₂ dissociation on Mg(0001).⁸⁷ There are physisorption (P),

Figure 39

molecular chemisorption (M), and dissociative chemisorption wells, with barriers in between. The primary controlling factor in molecular chemisorption is increasing occupation of H₂ σ_u^* , whose main density of states drops to the Fermi level and below as the H₂ nears the surface.

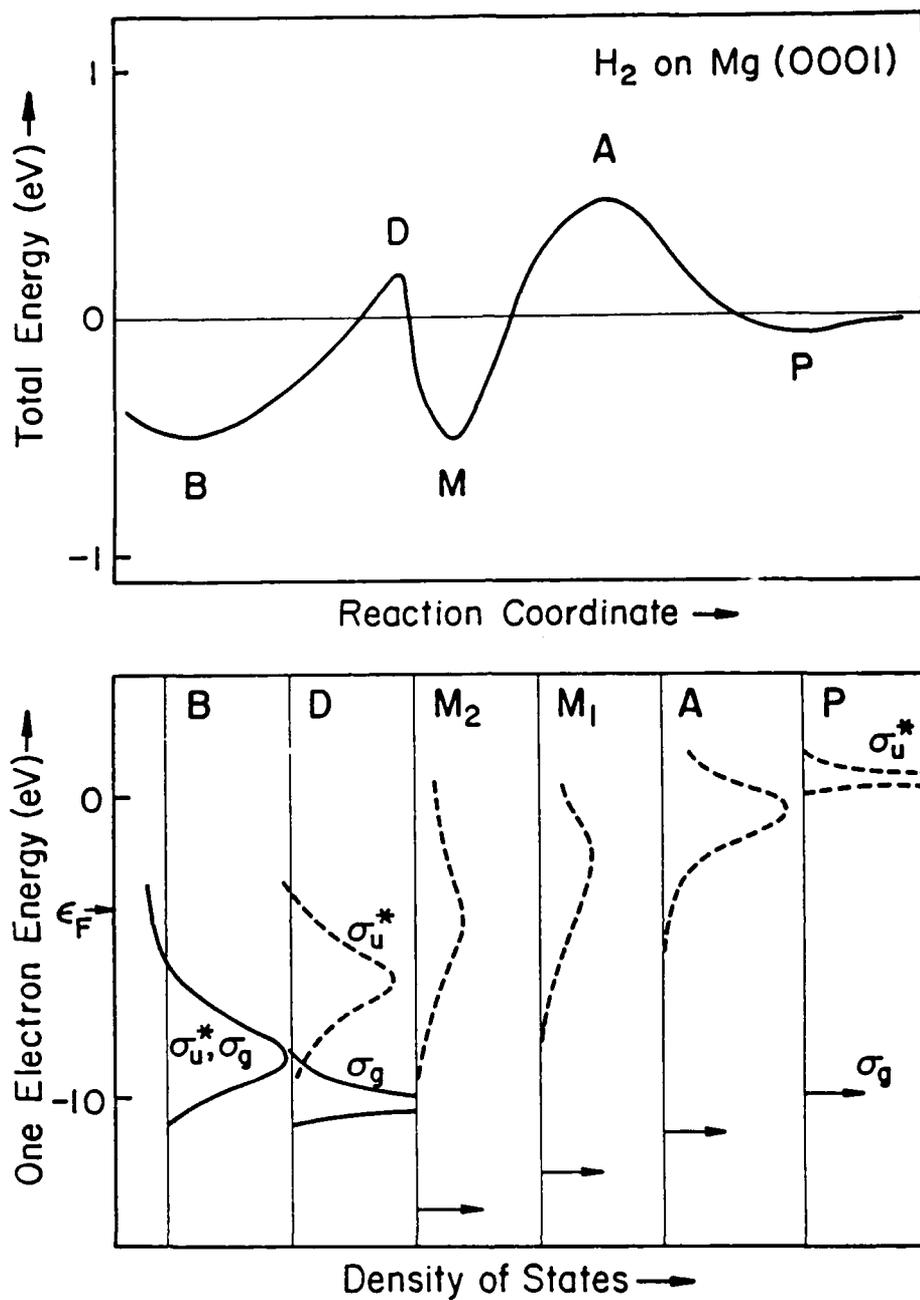


Figure 39. Some calculated characteristics of H₂ on Mg(0001), after Reference 32. Top: schematic potential energy curve. P = physisorption minimum; M = chemisorbed molecule; B = chemisorbed atoms; A and D are transition states for chemisorption and dissociation. Bottom: development of the one electron density of states at certain characteristic points. M₁ and M₂ correspond to two molecular chemisorption points, different distances from the surface. The dashed line is the σ_u^* density, moving to lower energy as the dissociation proceeds.

In this and other studies by this method one sees molecular levels, sometimes spread into bands, moving about in energy space. But the motions seem to be different from those calculated by the extended Hückel procedure. Fig. 18 showed for H_2 on Ni^{88} some σ_u^* density coming below the Fermi level. But the main peak of σ_u^* was pushed up, as a simple interaction diagram might suggest, but in apparent disagreement with the result of Fig. 39. Perhaps (I'm not sure) one way to reconcile the two pictures is by recognizing that mine is not self-consistent, does not account for proper screening of H_2 as it approaches the surface. It is possible that if self-consistency or screening by electrons in the metal were included in the one-electron formalism that the pictures could be reconciled. Also there is less discrepancy between the two approaches than one might imagine. In the reaction coordinate of Fig. 39 the H-H bond is stretched along the progression $P \rightarrow A \rightarrow M_1 \rightarrow M_2 \rightarrow D \rightarrow B$. σ_u^* drops precipitously, in our calculations as well, as the H-H bond is stretched.

The barriers to chemisorption in the work of Nørskov et al⁸⁷ come from the initial dominance of "kinetic-energy repulsion". This is the Pauli effect at work, and I would like to draw a correspondence between our four-electron repulsion and this kinetic energy effect. The problem (as usual) is that different models build in different parts of physical reality. It becomes very difficult to compare them. The reason the effort is worth

making is that the Lundqvist, Nørskov, Lang model has proven itself remarkably useful in revealing trends in chemisorption. It is physically and chemically appealing.

There are some contributors to theoretical solid state chemistry and surface science that I should like to mention because of their special chemical orientation. One is Alfred B Anderson, who has analyzed most important catalytic reactions, anticipating many of the results on surfaces presented in this paper.⁸⁹ Evgeny Shustorovich and Roger C. Baetzold, working separately and together, have both carried out detailed calculations of surface reactions and come up with an important perturbation-theory-based model for chemisorption phenomena.⁹⁰ Christian Minot has worked out some interesting chemisorption problems.⁹¹ Myung-Hwan Whangbo's analyses of the bonding in low-dimensional materials such as the niobium selenides, TTF-type organic conductors and molybdenum bronzes, as well as his recent studies of the high T_C superconductors, have contributed much to our knowledge of the balance of delocalization and electron repulsion in conducting solids.^{7,8} Jeremy Burdett is responsible for the first new ideas on what determines solid state structures since the pioneering contributions of Pauling.^{5,6} His work is consistently ingenious and innovative.⁹³

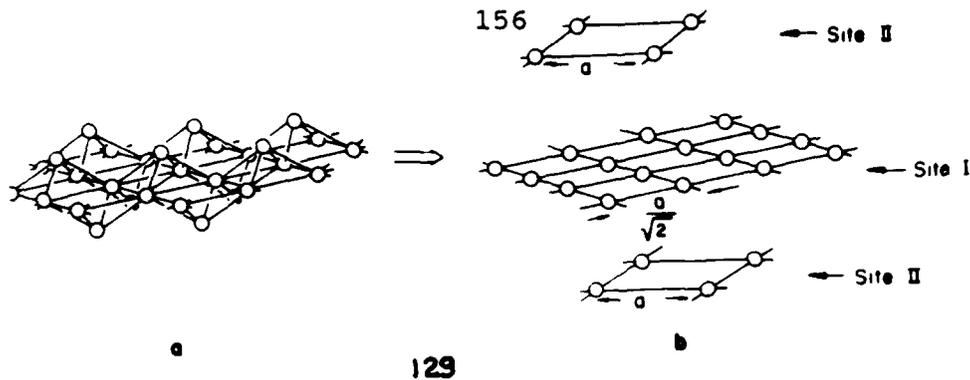
Not the least reason I mention these people is pride: all of them have at some time (prior to doing their important independent work) visited my research group.

What's New in the Solid?

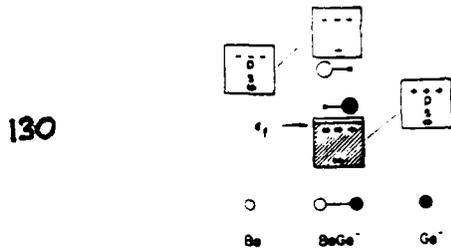
If all the bands in a crystal are narrow (as they are in molecular and most extremely ionic solids), i.e. if there is little overlap between repeating molecular units, then there is no new bonding to speak of. But if at least some of the bands are wide, then there is delocalization, new bonding, a molecular orbital picture is necessary. This is not to say that we cannot recover, even in such a large dispersion, delocalized situation, local bonding. The preceding sections have shown that we can see bonds. But there may be qualitatively new bonding schemes that result from substantial delocalization. Recall in organic chemistry the consequences of aromaticity, and in inorganic cluster chemistry of skeletal electron pair counting algorithms.²¹

The language of orbital interactions, of perturbation theory, provides a tool that is applicable for the analysis of these highly delocalized systems, just as it works for small, discrete, molecules. For instance, take the question posed at the end of a previous section. We have two isomeric two-dimensional lattices 67, 68. Which will be a donor relative to the other? And which will be most stable?

These lattices are built up from two elements B and X in equal numbers, occupying two sublattices, I and II in 129. The elements are of unequal electronegativity, in the general case. In ThCr_2Si_2 one is a transition metal, the other a main-group



element, in CaBe_2Ge_2 each a main-group element. Let's take, for purposes of discussion, the latter case as a model and write an interaction diagram for what happens locally, 130.

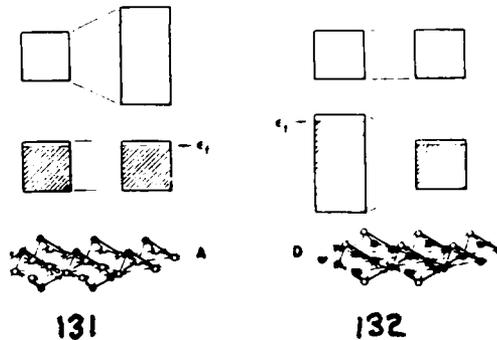


The diagram has been drawn in such a way that the more electronegative element is X. No implication as to band width is yet made -- the orbital blocks are just that, blocks, indicating the rough position of the levels. The lower block of levels is obviously derived from or localized in the orbitals of the more electronegative (here X) element. The band filling is actually appropriate to the CaBe_2Ge_2 structure, i.e. $\text{Be}_2\text{Ge}_2^{2-}$, or BeGe^- , or 7 electrons per two main-group atoms.

The orbitals develop into bands. The width of the bands depends on the inter-unit-cell overlap. The site II atoms are much farther apart from each other than the site I atoms (recall here the short metal-metal contacts in the ThCr_2Si_2 structure).

We can say that sublattice I is more dispersive than sublattice II. The orbitals of atoms placed in sublattice I will form wider bands than those in sublattice II.

Now we have two choices: the more electronegative atoms can enter the less dispersive sites (lattice II) or the more dispersive sites (lattice I). The consequences are shown in 131 and 132.



Which layer will be most stable and which will have the higher Fermi level depends on the electron filling. For a case such as CaBe_2Ge_2 , or in general where the lower band is more than half-filled, the more electronegative atom will prefer the less dispersive site 131 and that layer will have a higher I.P., be a poorer donor.

The stability conclusion bears a little elaboration. It is based on the same "overlap repulsion" argument that was behind the asymmetric splitting of hydrogen chain bands, Fig. 1. When orbitals interact, the antibonding combinations are more antibonding than the bonding ones are bonding. Filling antibonding combinations, filling the tops of widely dispersed

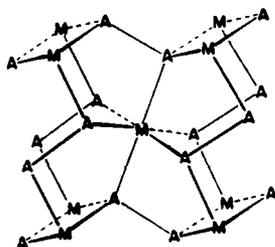
bands, is costly in energy. Conclusions on stability, as is the case in molecular chemistry, depend strongly on the electron count. In this particular case if the lower band were less than half-filled, the conclusion would be reversed, the more electronegative element should prefer the more dispersive site.

For ThCr_2Si_2 AB_2X_2 structures the conclusion we reach, that the more electronegative element should enter the less dispersive site, implies that for most cases the main-group X component will prefer the less dispersive, square pyramidal, sublattice II positions. In CaBe_2Ge_2 , Ge is more electronegative than Be. That means the layer in which the Ge enter the more dispersive sites (the bottom layer in 66) should be a donor relative to the upper layer.

A reasonable question to ask is the following. If one layer (the acceptor layer) in CaBe_2Ge_2 is more stable than the other, the donor layer, why does the CaBe_2Ge_2 structure form at all? Why doesn't it go into a ThCr_2Si_2 structure based on the acceptor layer alone? The answer lies in the balance of covalent and dative interactions; for some elements the binding energy gained in donor-acceptor interlayer interactions overcomes the inherent stability of one layer isolated.^{39c}

At times the perturbation introduced by delocalization may be strong enough to upset the local, more "chemical" bonding schemes. Let me sketch two examples here.

Marcasites and arsenopyrites are a common structural choice for MA_2 compounds, where M is a late transition metal, A a group 15 or 16 element. The structure, 133, is related to the rutile one, in that one can easily perceive in the structure the octahedral coordination of the metal, and one-dimensional chains of edge-sharing octahedra. The ligands are now interacting, however; not $2(O^{2-})$ as in rutile, but S_2^{2-} or P_2^{4-} diatomic units in the marcasites.⁹²



133

Low dimensionality characterizes another set of MS_2 sublattices, now in ternary structures of the type of $KFeS_2$ or $Na_3Fe_2S_4$.^{93,94} In these molecules one finds one-dimensional MS_2 chains, consisting of edge-sharing tetrahedra, 134.



134

In both of these structural types, characterized by their simplicity, the metal-metal separations are in the range (2.6-3.1 Å) where reasonable men or women might disagree whether there is much metal-metal bonding. Cases with bridging ligands are ones in which real metal-metal bonding is particularly difficult to sort out from bonding through the bridge. Certainly the metal-metal bonding doesn't look to be very strong, if it's there at all. So a chemist would start out from the local metal site environment, which is strikingly simple.

One would then predict a three below two orbital splitting at each metal in the octahedral marcasites and a two below three splitting in the tetrahedral MS_2 chains. The magic electron counts for a closed-shell low-spin structure should be then d^6 for the octahedral 133, d^4 for the tetrahedral 134. Forming the one-dimensional chains and then the three-dimensional structure will introduce some dispersion into these bands, one might reason. But not much -- appropriate electron counts for semiconducting or non-magnetic behavior should remain d^6 for 133 and d^4 for 134.

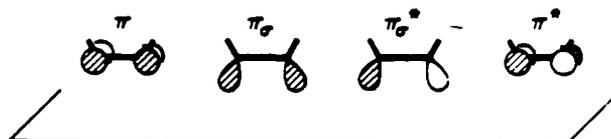
The experimental facts are as follows: the d^6 marcasites and arsenopyrites are semiconducting, but, surprisingly, so are the d^4 ones. Most of the AMS_2 structures synthesized to date feature the metal atom in configurations between d^5 and $d^{6.5}$. The measured magnetic moments are anomalously low.

When calculations on these chains are carried out one finds, to one's initial surprise, that the octahedral marcasite structure has a band gap at d^4 as well as d^6 , and that the tetrahedral chain has a band gap at $d^{5.5}$ and not d^4 . It seems that local crystal field considerations don't work. What in fact happens (and here the reader is referred to the detailed explanation in our papers^{92,94}) is that the local field is a good starting point, but that further delocalizing interactions (and these are ligand-ligand and metal-ligand, and not so much metal-metal in the distance range considered) must be taken into account. The extended interactions modify the magic or gap electron counts that might be expected from just looking at the metal site symmetry.

In a preceding section, I outlined the orbital interactions that are operative in the solid state. These were the same ones as those that govern molecular geometries and reactivity. But there were some interesting differences, a consequence of one of the interacting components, the surface, having a continuum of levels available at the Fermi level. This provided a way to turn strong four and zero electron two-orbital interactions into bonding ones. As a corollary, there are shifts around the Fermi level which have bonding consequences. Let's look at this new aspect in detail on an example we had mentioned before, acetylene chemisorbed in low coverage in a parallel, two-fold bridging mode on Pt(11), 135.²⁹



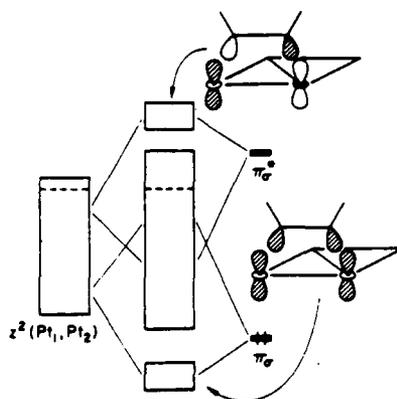
135



136

The most important two-electron bonding interactions that take place are between two of the acetylene π orbitals, π_σ and π_σ^* (see 136) and the d band. π_σ and π_σ^* "point" toward the surface, have greater overlap with metal overlaps, and they interact preferentially with different parts of the band, picking out those metal surface orbitals which have similar nodal patterns as the adsorbate. 137 shows this -- in the "parallel bridging" 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.

137



Both of these interactions are primarily of type ① and ③ (see 54 or 59), four-electron repulsive or two-electron attractive interactions. Actually, the energetic and bonding consequences are a little complicated: the z^2 - π_σ interaction would be destabilizing if the antibonding component of this

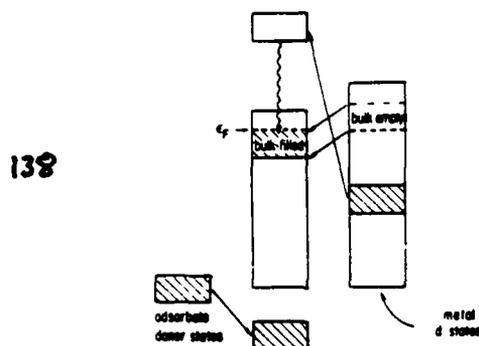
interaction remained filled, below the Fermi level. In fact, many $z^2-\pi_\sigma$ antibonding states are pushed above the Fermi level, vacated. This converts a destabilizing, four-electron interaction into a stabilizing two-electron one.

A counterpart to this interaction is (5). Normally we would not worry about zero-electron interactions, because there is not "power" in them if there are no electrons. However, in the case of a metal with a continuous band of states, some of these levels -- these are bonding combinations of π_σ^* with the top of the z^2 band, as indicated in 137 -- come below the Fermi level and are occupied. Therefore they also contribute to bonding the adsorbate to the surface.

It should be noted that a consequence of all of these interactions is not only strengthening of metal-acetylene bonding, but also a weakening of bonding within the acetylene and within the metal. Interaction means delocalization which in turn implies charge transfer. Interactions (1) and (2), operate to depopulate π_σ , populate π_σ^* , both actions weakening the acetylene π bond. Removing electrons from the bottom of the z^2 band, filling better the top of that bond, both result in a weakening of the Pt-Pt bond.

Interaction (5), peculiar to the solid, is a reorganization of the states around the Fermi level as a consequence of primary interactions (1), (2), (3), (4). Consider, for instance, the levels that are pushed up above the Fermi level as a result of

interaction ③, the four-electron repulsion. One way to think about this is the following: the electrons do not, in fact, go up past the Fermi level (which remains approximately constant), but are dumped at the Fermi level into levels somewhere in the solid. This is shown schematically in 138.



But where is "somewhere"? The electrons that come in come largely from regions that are not directly involved in the bonding with the adsorbate. In the case at hand they may come from Pt bulk levels, from Pt surface atoms not involved with the acetylene, even from the Pt atoms binding the acetylene, but from orbitals of these atoms not used in that binding. While the metal surface is a nice reservoir of such electrons, these electrons are not innocent of bonding. They are near the top of their respective band, and as such are metal-metal antibonding. Thus interaction ⑤ weakens bonding in the surface. Together with the aforementioned electron transfer effects of interactions ①, ②, ③, and ④ it is responsible for adsorbate-induced surface reconstruction.

In general, as I already outlined in a previous section, non-dissociative chemisorption is a delicate balance of the very same interactions, which weaken bonds in the adsorbed molecule and in the surface. Dissociative chemisorption and surface reconstruction are just two extremes of one and the same phenomenon.

So what's new in the solid? My straw-man physicist friend, thinking of superconductivity, charge and spin density waves, heavy fermions, solitons, nonlinear optical phenomena, ferromagnetism in its various guises -- all the fascinating things of interest to him and that I've neglected - he might say "Everything". An exaggeration of what I've said in this paper is "Not much". There are interesting, novel, consequences of delocalization and wide-band formation, but even these can be analyzed in the language of orbital interactions.

It would not surprise anyone if the truth were somewhere in between. It is certainly true that I've omitted, by and large, the origins of most of the physical properties of the solid, especially those such as superconductivity and ferromagnetism, which are peculiar to that state of matter. Chemists will have to learn much more solid state physics than I've tried to teach here if they are to understand these observables, and they must understand them if they are to make rational syntheses.

What I have tried to do in this book and the published papers behind it is to move simultaneously in two directions --

to form a link between chemistry and physics by introducing simple band structure perspectives into chemical thinking about surfaces. And I have tried to interpret these delocalized band structures from a very chemical point of view -- via frontier orbital considerations based on interaction diagrams.

Ultimately, the treatment of electronic structure in extended systems is no more complicated (nor is it less so) than in discrete molecules. The bridge to local chemical action advocated here is through decompositions of the DOS and the Crystal Orbital Overlap Population (COOP) curves. These deal with the fundamental questions: Where are the electrons? Where can I find the bonds?

With these tools in hand, one can construct interaction diagrams for surface reactions, as one does for discrete molecules. One can also build the electronic structure of complicated three-dimensional solids from their sublattices. Many similarities between molecules and extended structures emerge. And some novel effects, the result of extensive delocalization.

I have concentrated on the most chemical notion of all -- the solid is a molecule, a big one, to be sure, but just a molecule. Let's try to extract from the perforce delocalized picture of Bloch functions the chemical essence, the bonds that determine the structure and reactivity of this large molecule. The bonds must be there.

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