

An important factor in the early stages of this work was my renewed collaboration with R. B. Woodward, prompted by our joint interest in organic conductors. Our collaboration was unfortunately cut short by his death in 1979. Thor Rhodin was 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 was played by the Materials Science Center (MSC) at Cornell University, supported by the Materials Research Division of the National Science Foundation. MSC furnished an interdisciplinary setting, which facilitated an interaction among 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 in that regard. Our drawings, a critical part of the way our research is presented, have been beautifully prepared over the years by Jane Jorgensen and Elisabeth Fields. I'd like to thank Eleanor Stagg, Linda Kapitany, and Lorraine Seager for their 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, 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 on which they worked; Mike also taught me something about the relationship between research and teaching. This book is for them—both Earl Muetterties and Mike Sienko—who were so important and dear to me.

INTRODUCTION

Macromolecules extended in one, two, and three dimensions, of biological/natural or synthetic origin, fill the world around us. Metals, alloys, and composites, be they copper or bronze or ceramic, have played a pivotal and a 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—exhibiting unusual electric and magnetic properties, promise to shape the technology of the future. Solid state chemistry is important, alive, and growing.¹

So is surface science. A surface—be it of metal, an ionic or covalent solid, a semiconductor—is a form of matter with its own chemistry. In its structure and reactivity, it will bear resemblance to other forms of matter: bulk, discrete molecules in the gas phase and various aggregated states in solution. And it will have differences. Just as it is important to find the similarities, it is also important to note the differences. The similarities connect the chemistry of surfaces to the rest of chemistry, but the differences 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, e.g., 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 the chemistry took place at the surface. 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 in order to 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. This leads to the problem that learning the language necessary for addressing these problems, the language of solid state physics and band theory, is generally not part of the chemist's education. It should be, and the primary goal of this book is to teach chemists that language. I will show that it is not only easy, but that 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 empirical experience and some simple theory, chemists have gained much intuitive knowledge of the what, how, and why of molecules holding 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" can involve.

Chemists need not enter into 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 very much in control.) This is not to say that it will not take some effort to overcome the skepticism of physicists regarding 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.

I have one further comment 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 has been the idea that there are ions (electrostatic forces, Madelung energies) and that these ions have a certain size (ionic radii, packing considerations). This simple notion has been applied by solid state chemists even in cases of substantial covalency. What can be wrong with an idea that

works, and 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. 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 select 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, to state it provocatively, 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, 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 because it forges a link between solid state chemistry and organic, or main group, chemistry.

In this book I will 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 parts. Where detailed computational results are displayed, they will be of the extended Hückel type⁴ 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 similar to what we know happens for molecules. And there will be some differences.

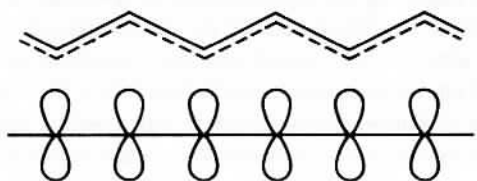
ORBITALS AND BANDS IN ONE DIMENSION

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 present in one dimension.

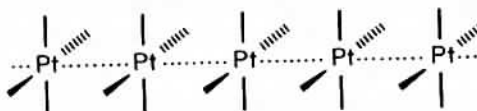
Let's begin with a chain of equally spaced H atoms, 1, or the isomorphic π system of a non-bond-alternating, delocalized polyene 2, stretched out for the moment. And we will progress to a stack of Pt(II) square planar complexes, 3, Pt(CN) $_4^{2-}$ or a model PtH $_4^{2-}$.



1



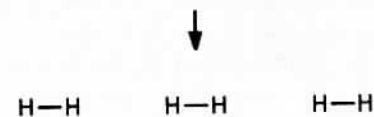
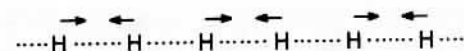
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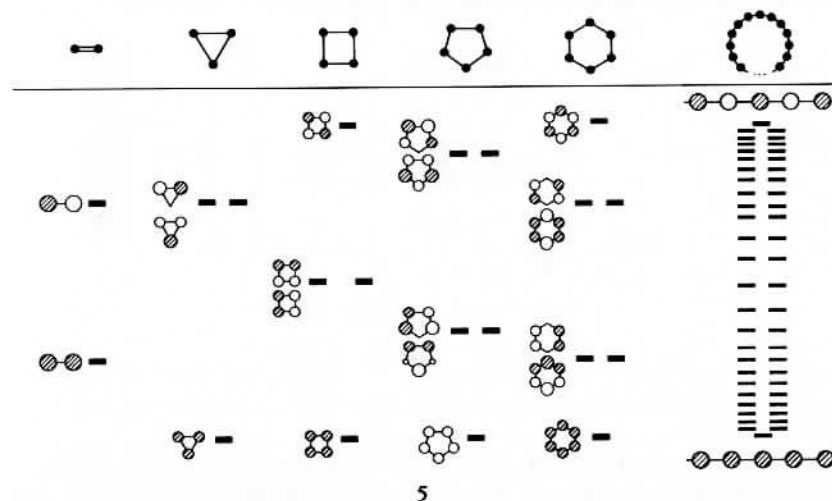
A digression here: every chemist would have an intuitive feeling for what that model chain of hydrogen atoms would do if released from the prison of its theoretical construction. At ambient pressure, it would form a chain of hydrogen molecules, 4. This simple bond-forming process would be analyzed by 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 repeatedly throughout this book, 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 and remains 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).



4

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.

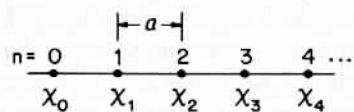


5

BLOCH FUNCTIONS, k , BAND STRUCTURES

There is a better way to write out all these orbitals by making use of the translational symmetry. If we have a lattice whose points are labeled by an index $n = 0, 1, 2, 3, 4 \dots$ 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 that translation is as good a symmetry operation as any other we know) are given in 6. Here a is the lattice spacing, the unit cell in one dimension, and k is an index that 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 as a, e_1, e_2 in C_5 are labels.

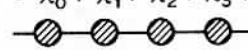


$$\psi_k = \sum_n e^{ikna} \chi_n$$

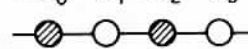
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In the solid state physics trade, the process of symmetry adaptation is called "forming Bloch functions."^{6,8-11} To reassure chemists that one is getting what one expects from 6, let's see what combinations are generated for two specific values of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

$$k=0 \quad \psi_0 = \sum_n e^{i0n} \chi_n = \sum_n \chi_n$$

$$= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots$$


$$k=\frac{\pi}{a} \quad \psi_{\frac{\pi}{a}} = \sum_n e^{i\pi n} \chi_n = \sum_n (-1)^n \chi_n$$

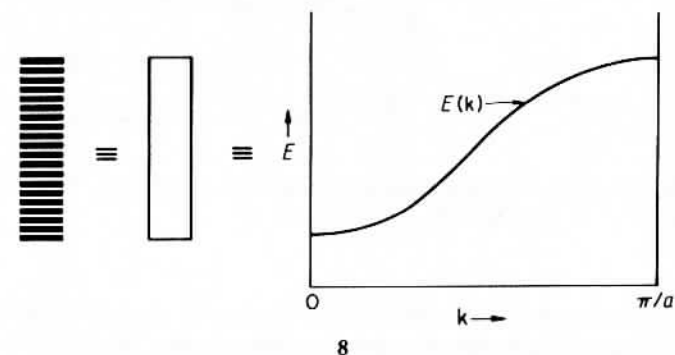
$$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$$


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 rather 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 $k = 2\pi/\lambda$ and momentum derives from the de Broglie relationship $\lambda = h/p$. Remarkably, 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. However, no matter how complicated they are, they can still be understood.

BAND WIDTH

One very important feature of a band is its *dispersion*, or *bandwidth*, 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

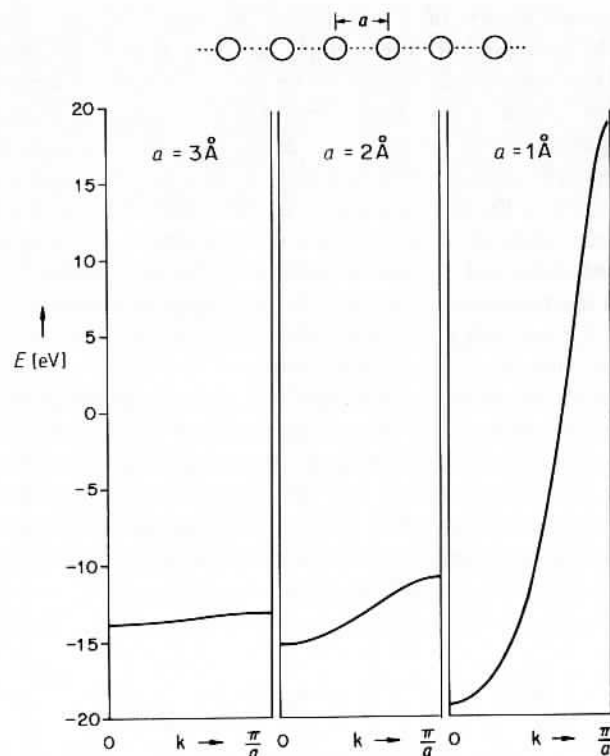


Figure 1 The band structure of a chain of hydrogen atoms spaced 3, 2, and 1 Å apart. The energy of an isolated H atom is -13.6 eV.

splitting of levels in a dimer (ethylene or H^2), 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. Figure 1 illustrates this in detail for a chain of H atoms spaced 3, 2, and 1 Å apart. That the bands extend unsymmetrically around their "origin," the energy of a free H atom at -13.6 eV, 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 four-electron repulsions and steric effects in one-electron theories.¹¹ A similar effect is responsible for the bands "spreading up" in Fig. 1.

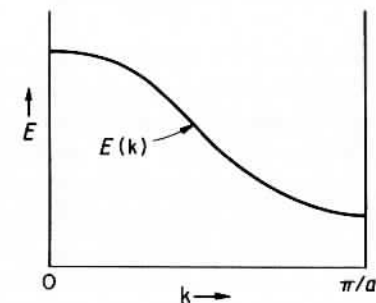
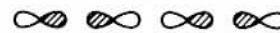
SEE HOW THEY RUN

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 as for the H case are given to us by the translational symmetry, but now it is clearly $k = 0$ that is high energy, the most antibonding way to put together a chain of p orbitals.

$$\psi_0 = \chi_0 + \chi_1 + \chi_2 + \chi_3 + \dots$$



$$\psi_{\pi/a} = \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$$



9

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 that 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 threefold 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 , $\chi_1 + \chi_2 + \chi_3$; for e (one choice of an infinity), $\chi_1 - 2\chi_2 + \chi_3$, $\chi_1 - \chi_3$, where χ_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.



10

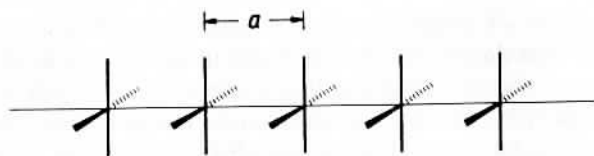


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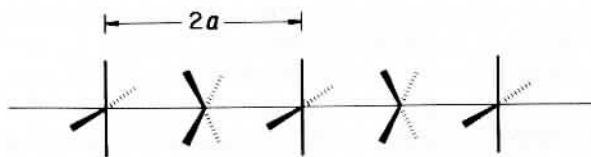
To summarize: band width is set by inter-unit-cell overlap, and the way bands run is determined by the topology of that overlap.

AN ECLIPSED STACK OF Pt(II) SQUARE PLANAR COMPLEXES

Let us test the knowledge we have acquired on an example slightly 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 $\sim 3.3 \text{ \AA}$. More exciting are the partially oxidized materials, such as $K_2Pt(CN)_4Cl_{0.3}$ and $K_2Pt(CN)_4(FHF)_{0.25}$. These are also stacked, but staggered, 13, with a much shorter $Pt \cdots Pt$ contact of $2.7 \rightarrow 3.0 \text{ \AA}$. The $Pt-Pt$ distance had been shown to be inversely related to the degree of oxidation of the material.¹²



12



13

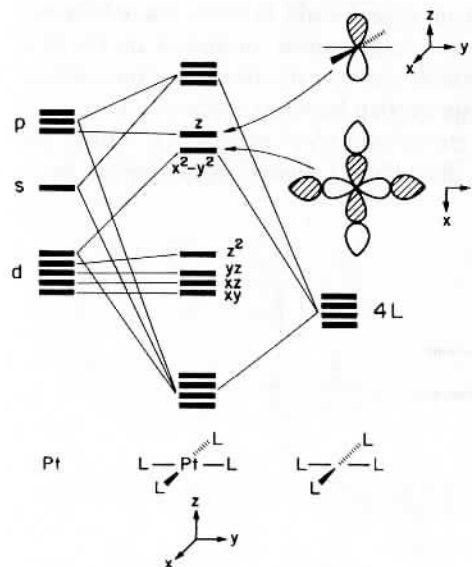


Figure 2 Molecular orbital derivation of the frontier orbitals of a square planar PtL_4 complex.

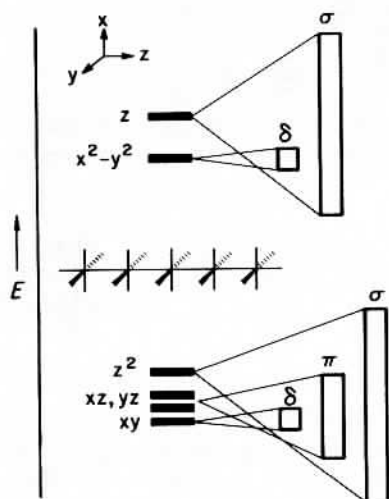
The real test of understanding is prediction. So let's try to predict the approximate band structure of 12 and 13 without a calculation, just using the general principles at hand. Let's not worry about the nature of the ligand; it is usually CN^- , but since it is only the square planar feature that is likely to be essential, let's imagine a theoretician's generic ligand H^- . We'll begin with 12 because its unit cell is the chemical PtL_4 unit, whereas the unit cell of 13 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 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 molecular orbitals (MOs) are of the same symmetry). However, ignoring that secondary mixing and just developing a band from each monomer level independently represents a good start.

First, here is 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, as shown in 14. This characterization follows from the realization that the first set of interactions (z , z^2) is σ type, and 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 (of course, the latter has a ligand admixture, but that doesn't change its symmetry) are δ .



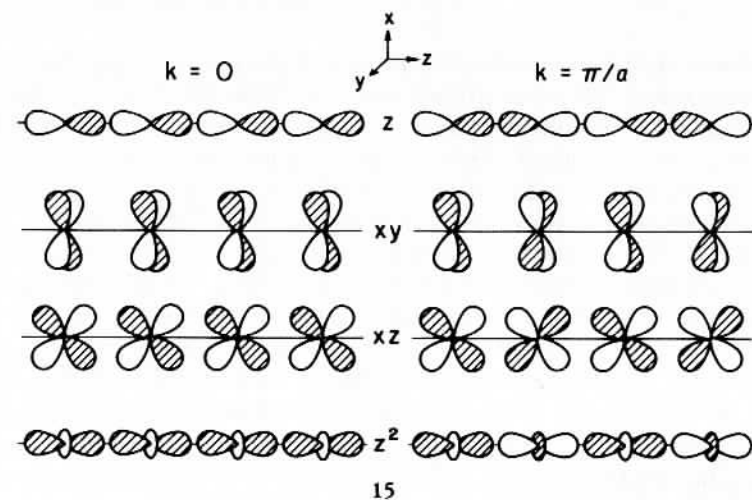
14

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) whereas the z and xz bands will run down (the $k = 0$ combination is the most antibonding).

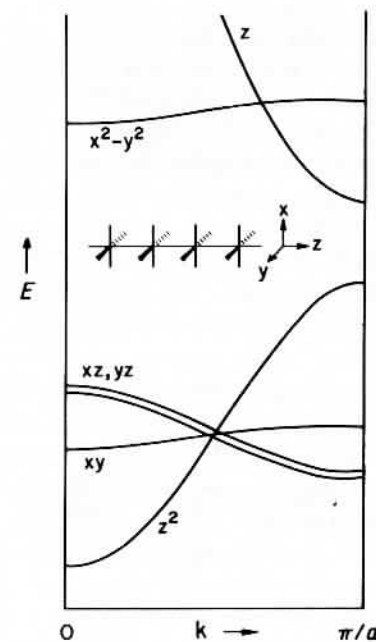
The predicted band structure, merging considerations of band width and orbital topology, is that of 16. To make a real estimate, one would need an actual calculation of the various overlaps, and these in turn would depend on the Pt...Pt separation.

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.

Here we can 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



15



16

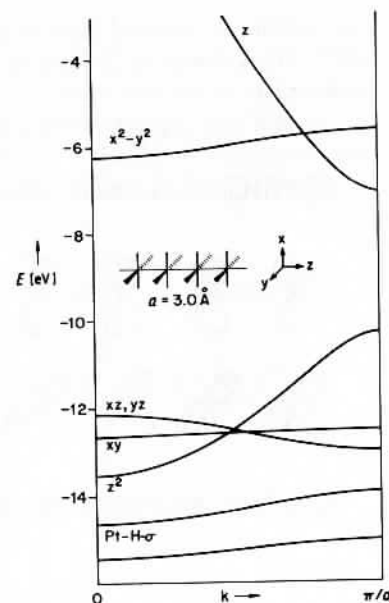
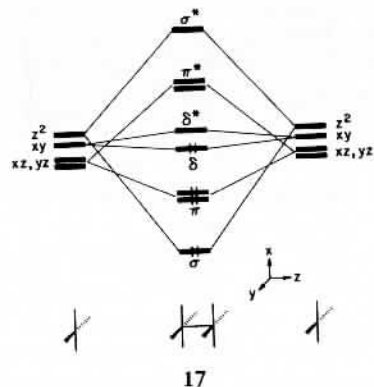


Figure 3 Computed band structure of an eclipsed PtH_4^{2-} stack, spaced at 3 Å. The orbital marked xz, yz is doubly degenerate.

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, e.g., 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 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 are 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 semiconductors,⁹ 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 yet introduced 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 , and think of the sequence $\text{N}_2, \text{O}_2, \text{F}_2, \text{Ne}_2$), 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 $\text{Pt} \cdots \text{Pt}$ separation decreases on oxidation. A typical degree of oxidation is 0.3 electron 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 platino-cyanides 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

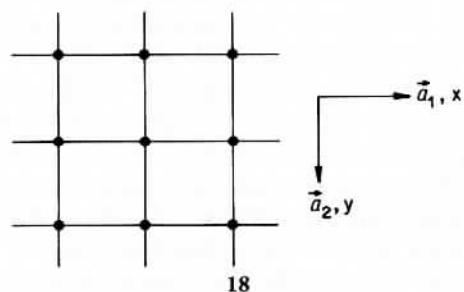
the Fermi level cut one or more bands (soon we will use the language of density of states to say this more precisely). One must beware, however, of (1) distortions that open up gaps at the Fermi level and (2) very narrow bands cut by the Fermi level because these will lead to localized states, not to 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}

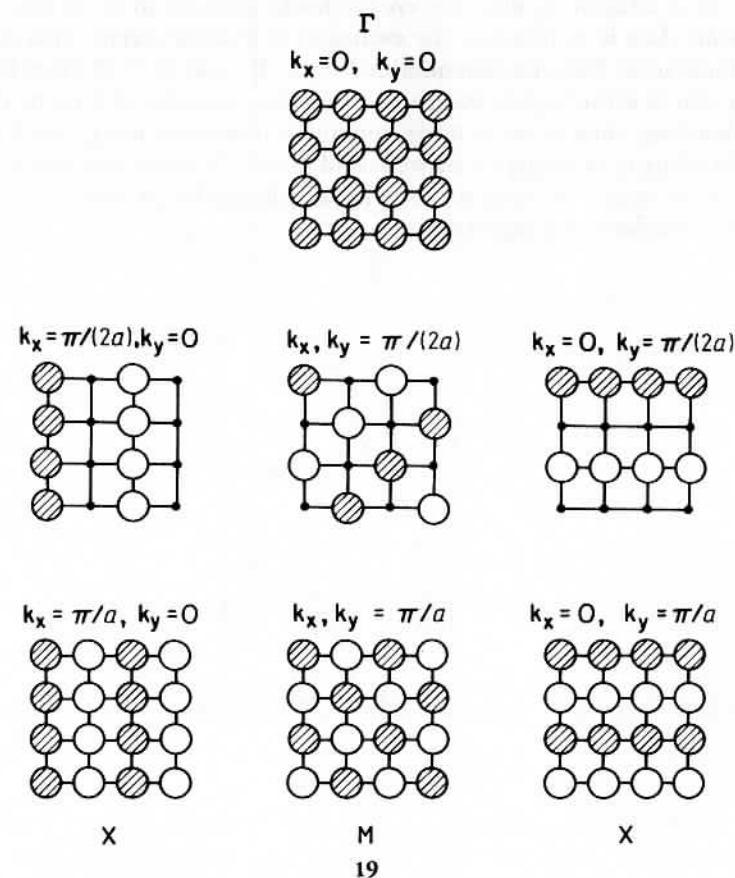
To introduce some of these ideas, let's begin with a square lattice, 18, defined by the translation vectors \vec{a}_1 and \vec{a}_2 . Suppose there is an H 1s orbital on each lattice site. It turns out that the Schrödinger equation in the crystal factors into separate wave equations along the x and y 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 in 19.

The construction of these is obvious. What the construction also

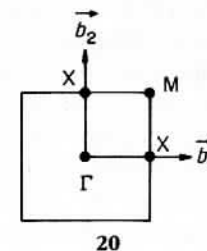


shows, very clearly, is the vector nature of k . Consider the $(k_x, k_y) = (\pi/2a, \pi/2a)$ and $(\pi/a, \pi/a)$ solutions. A look at them reveals that they are waves running along a direction that is the vector sum of k_x and k_y , i.e., on a diagonal. The wavelength is inversely proportional to the magnitude of that vector.

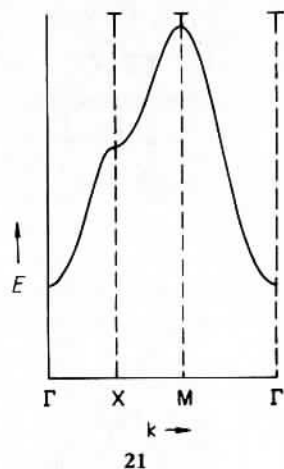
The space of k here is defined by two vectors \vec{b}_1 and \vec{b}_2 , and the range



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 , and M were so labeled in 19.



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 for a hydrogen lattice with $a = 2.0 \text{ \AA}$ (Fig. 4) confirms our expectations.



21

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.)

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. 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, since 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

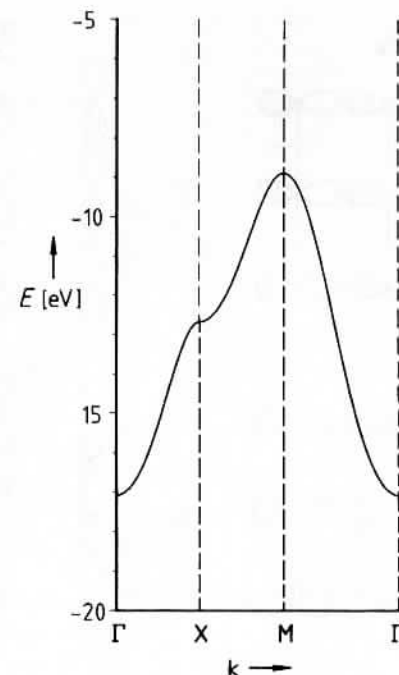


Figure 4 The band structure of a square lattice of H atoms, H-H separation 2.0 \AA .

p_x, p_y 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 nondegenerate 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 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 GdPS,¹⁶ a square overlayer of S atoms adsorbed on Ni(100),¹⁷ the oxygen and lead nets in litharge,¹⁸ or a Si layer in BaPdSi₃,¹⁹—will have these orbitals.

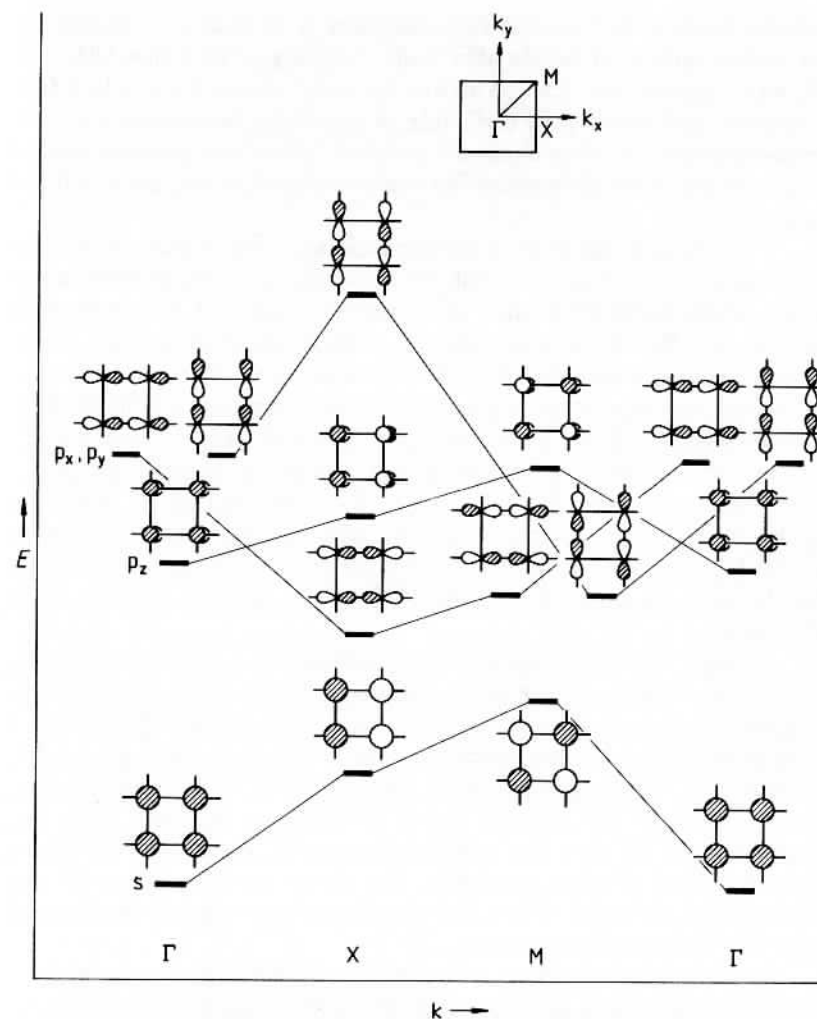
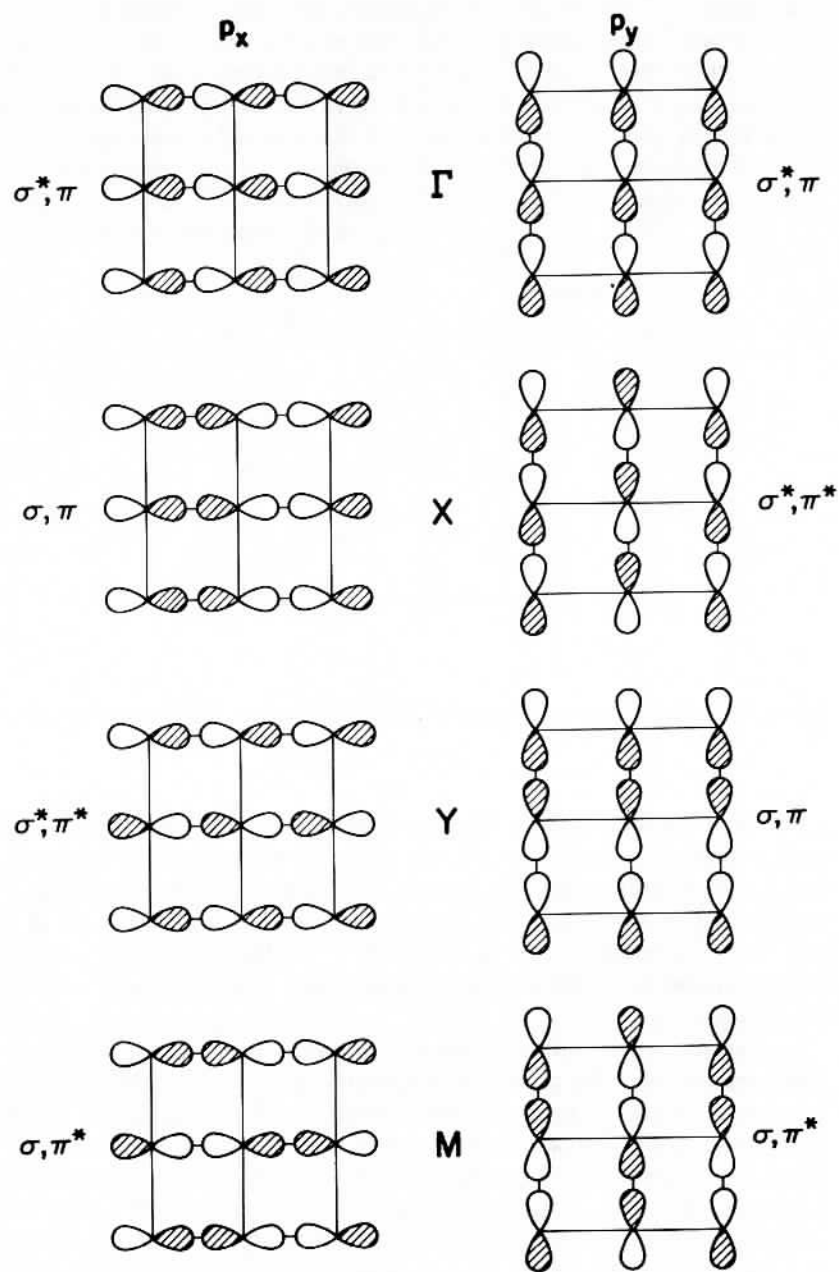
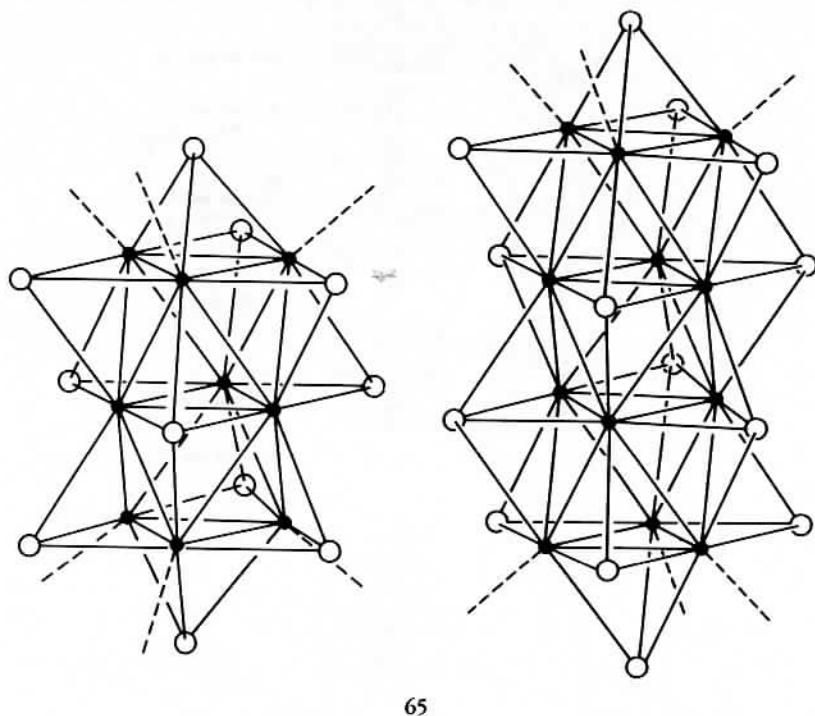


Figure 5 Schematic band structure of a planar square lattice of atoms bearing ns and np orbitals. The s and p levels have a large enough separation that the s and p band do not overlap.

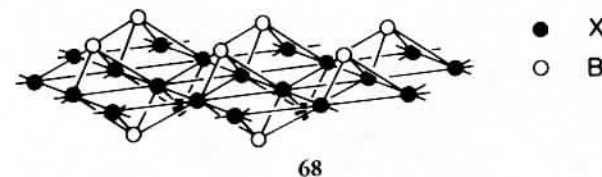
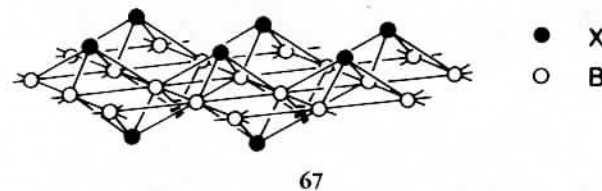
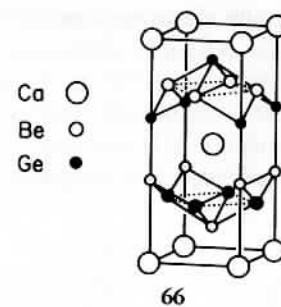
SETTING UP A SURFACE PROBLEM

The strong incentive for moving to at least two dimensions is that obviously one needs this for studying surface-bonding problems. Let's begin to set these up. The kind of problems we want to investigate, for example, are how CO chemisorbs on Ni; how H_2 dissociates on a metal surface; how

question, of e_g symmetry, is made up of Mo d functions that 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 substantial DOS at the Fermi level, one of several requirements 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 $\text{X}\cdots\text{X}$ contact in the AB_2X_2 ThCr_2Si_2 structure. There the entire transition metal or B sublattice, made up of square nets, acts as a donor or acceptor, a reducing or oxidizing agent, for the X sublattice, made up of $\text{X}\cdots\text{X}$ 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.

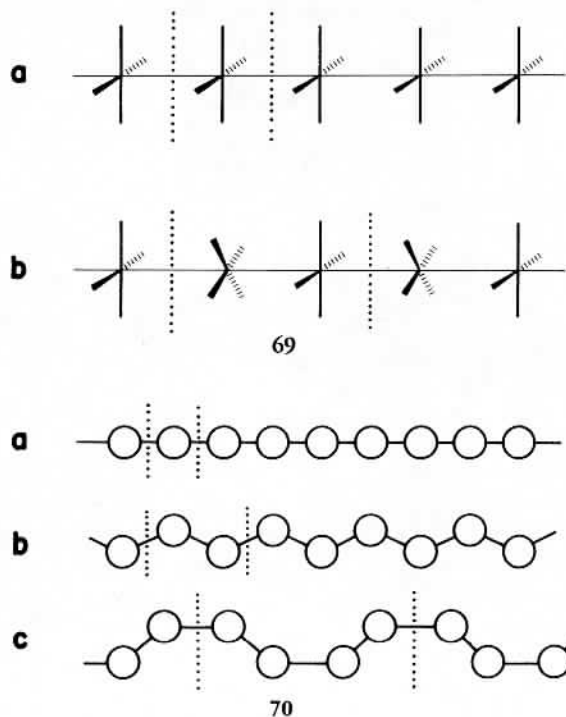


MORE THAN ONE ELECTRONIC UNIT IN THE UNIT CELL. FOLDING BANDS

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 four CH units per unit cell. A physicist might say that 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 geometric 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.

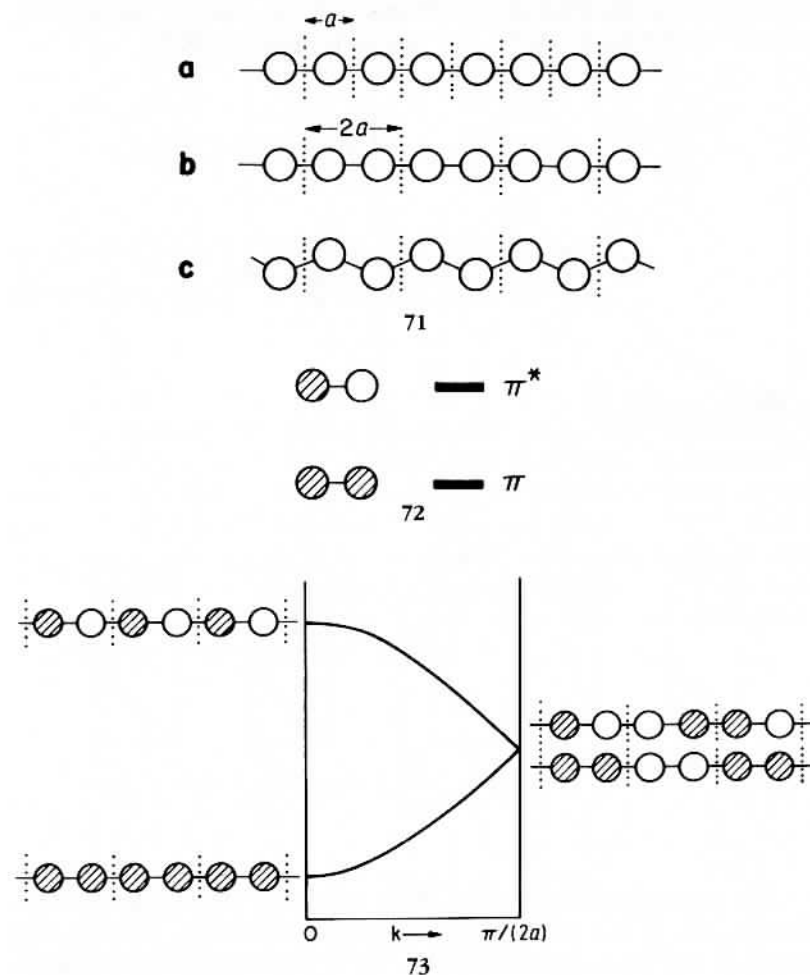


The number of bands in a band structure is equal to the number of molecular orbitals in the unit cell. So if the unit cell contains 17 times as many atoms as the basic unit, it will contain 17 times as many bands. The band structure may look messy. The chemist's feeling that the 17-mer is a small perturbation 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.

Conformation 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 MOs in unit cell, (2) form Bloch functions from them. Within the unit cell the MOs of the dimer are π and π^* , 72. Each of these spreads out into a band, that of the π "running

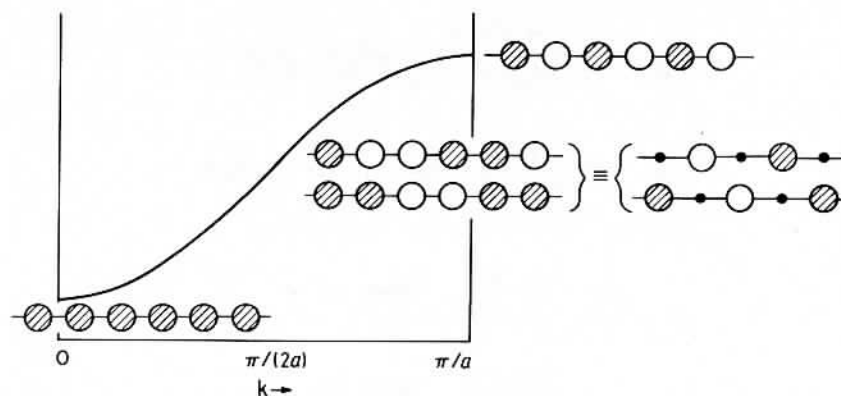
up," that of the π^* "running down," 73. The orbitals are written out explicitly at the zone boundaries. This allows one to see that the top of the π band and the bottom of the π^* band, both at $k = \pi/2a$, are precisely degenerate. There is no bond alternation in this polyene (yet), and the two orbitals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



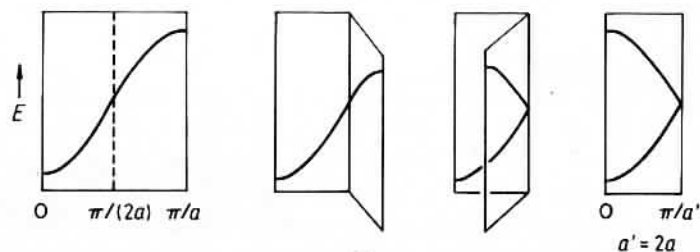
If we now detach ourselves from this viewpoint and go back and construct the orbitals of the one CH per unit cell linear chain 71a, we get 74. The Brillouin zone in 71b (73) is half as long as it is here because the unit cell is twice as long.

At this point, we are hit by the realization 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, two 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



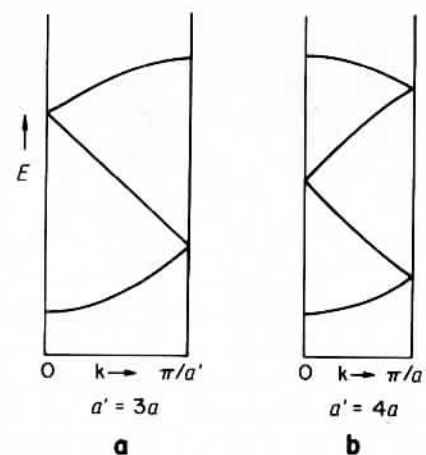
74



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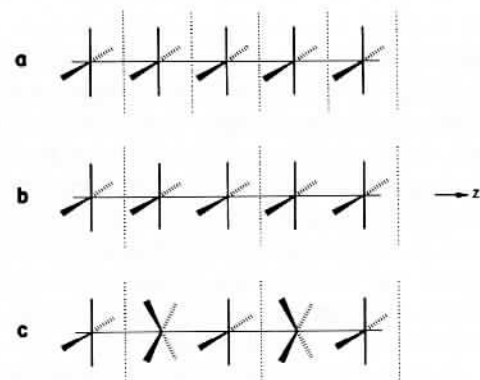
The process can be continued. If the unit cell is tripled, the band will fold as in 76a. If it is quadrupled, we get 76b, and so on. However, the point of all this is not just redundancy, seeing the same thing in different ways. There are two important consequences or utilizations of this folding. First, 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 → 73 → 76a → 76b), allows a chemist to simplify the analysis in his or her mind. 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.



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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 → b → c, i.e., doubling the unit cell in an eclipsed polymer and then rotating every other unit by 45° around the z axis.



77

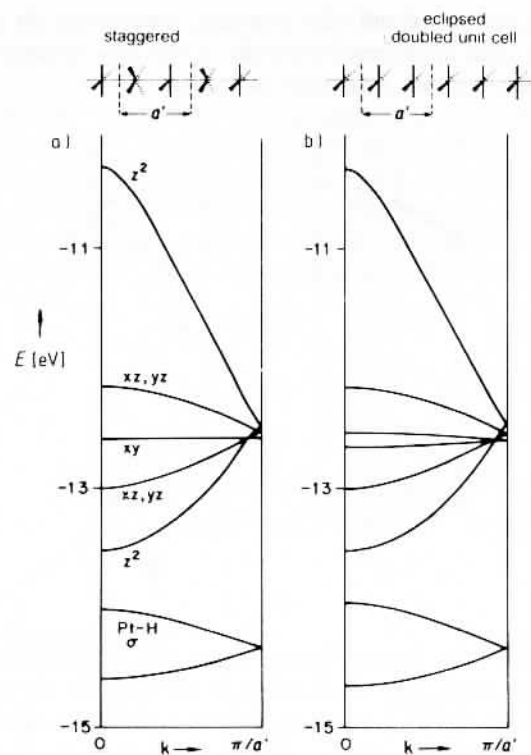
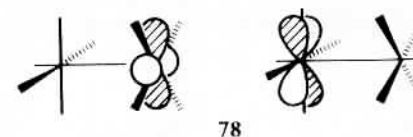


Figure 35 The band structure of a staggered PtH_4^{2-} stack (left), compared with the folded-back band structure of an eclipsed stack, two PtH_4^{2-} in a unit cell (right).

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. 35), but degenerate in the staggered polymer. What happened here could be stated in two 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 eightfold rotation-reflection axis. Higher symmetry means more degeneracies. It is easy to see that the two combinations, 78, are degenerate.

Except for this minor wrinkle, the band structures of the folded-back eclipsed polymer and the staggered one are extremely 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, not until the ligands start bumping into each other, and for such steric effects there can be, in turn, much further intuition. The band structures may look different, since 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. Figure 36, which compares the DOS of the staggered and eclipsed polymers, shows just how alike they are in their distribution of levels.

There is another reason to feel 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 \rightarrow 71b \rightarrow 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, but rather is a result of strain.

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

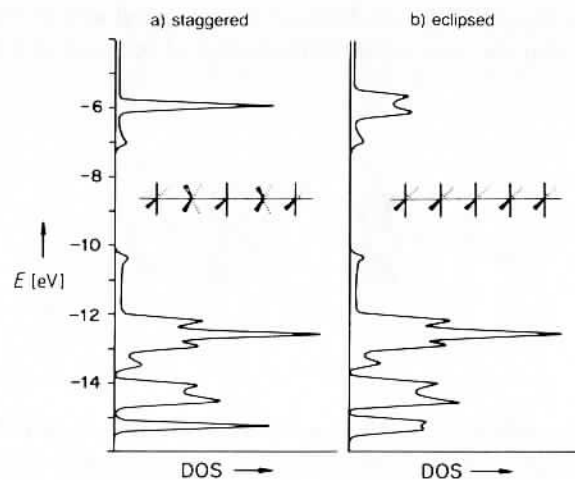
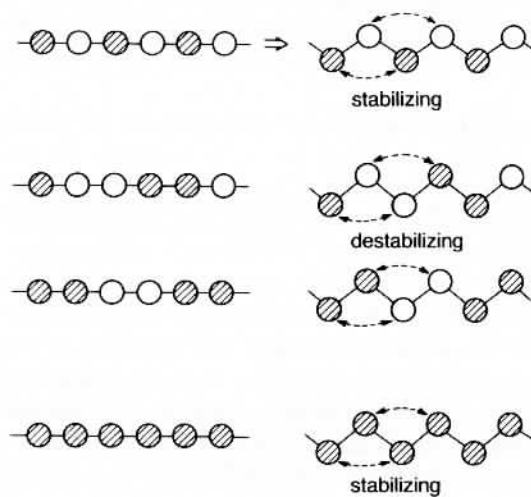


Figure 36 A comparison of the DOS of staggered (left) and eclipsed (right) PtH_4^{2-} stacks.



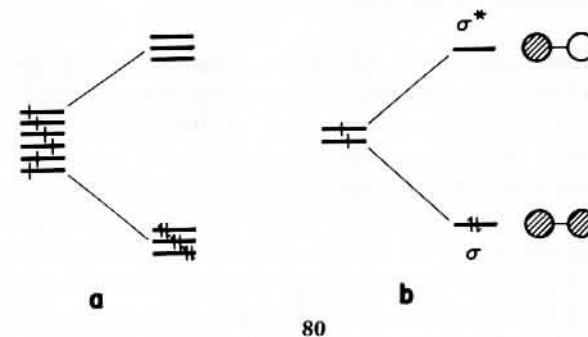
79

MAKING BONDS IN A CRYSTAL

When a chemist sees a molecular structure that contains several free radicals, orbitals with unpaired electrons, his or her inclination is to predict that such a structure will undergo a geometric change in which electrons will

pair up, forming bonds. It is this reasoning, so obvious as to seem almost subconscious, that 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 six) 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 had center stage, as it has in chemistry. The reasons for this are obvious: the most interesting developments in solid state physics have involved metals and alloys, and in these often close-packed or nearly close-packed substances, for the most part localized, chemical viewpoints have seemed irrelevant. For another large group of materials, ionic solids, it has 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 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 expect them. 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 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 to *maximize bonding*. There may be impediments to bonding. One such impediment might be electron repulsion, another steric effects, i.e., the impossibility of two radicals to reach within bonding distance of each other. Obviously, the

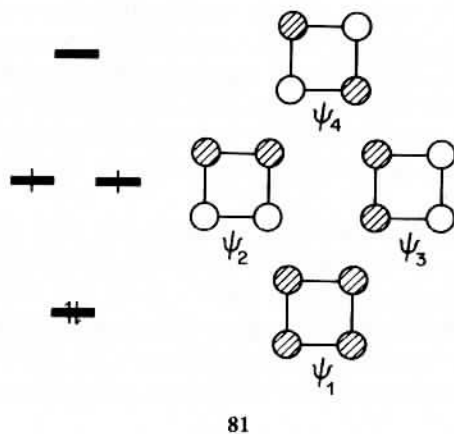
stable state is a compromise; some bonding may have to be weakened to strengthen some other bonding. But, in general, a system will distort so as to make bonds out of radical sites. Or, to translate this into the language of densities of states, *maximizing bonding in the solid state is connected to lowering the DOS at the Fermi level, moving bonding states to lower energy and 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 thinking of the solid state physicist. This is the Jahn–Teller effect,⁶⁷ and it's worthwhile to show how it works by a simple example.

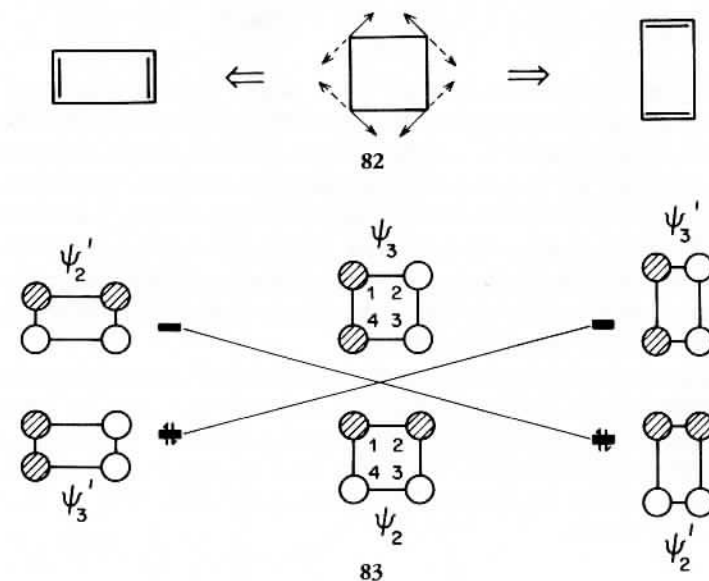
The Hückel π MOs of a square planar cyclobutadiene are well known. They are the one below two below one set shown in 81. We have a typical Jahn–Teller situation, i.e., two electrons in a degenerate orbital. (Of course, we need worry about the various states that arise from this occupation, and the Jahn–Teller 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 that 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.



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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.

The orbital workings of this Jahn–Teller distortion are easy to see. In 83, Ψ_2 is stabilized: the 1–2, 3–4 interactions that were bonding in the square are increased; the 1–4, 2–3 interactions that 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.

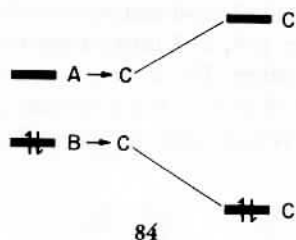


The essence of the Jahn–Teller theorem is revealed here: a symmetry-lowering deformation breaks an orbital degeneracy, stabilizing one orbital, destabilizing another. Note the phenomenological correspondence to 80 in the previous section.

One doesn't need a real degeneracy to benefit from this effect. Consider a nondegenerate 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, and 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

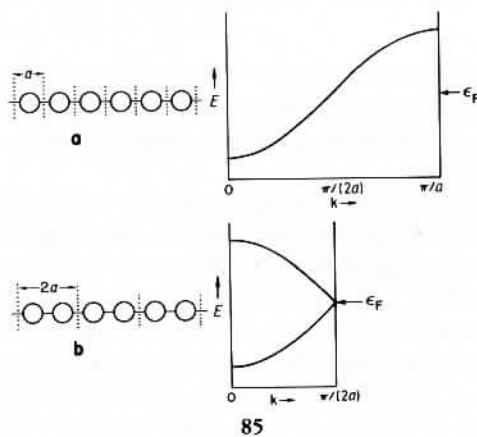
The essence of the first or second order Jahn–Teller effect is that a high-symmetry geometry generates a real or near degeneracy, which can be broken with stabilization by a symmetry-lowering deformation. Note a

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^{2+}).

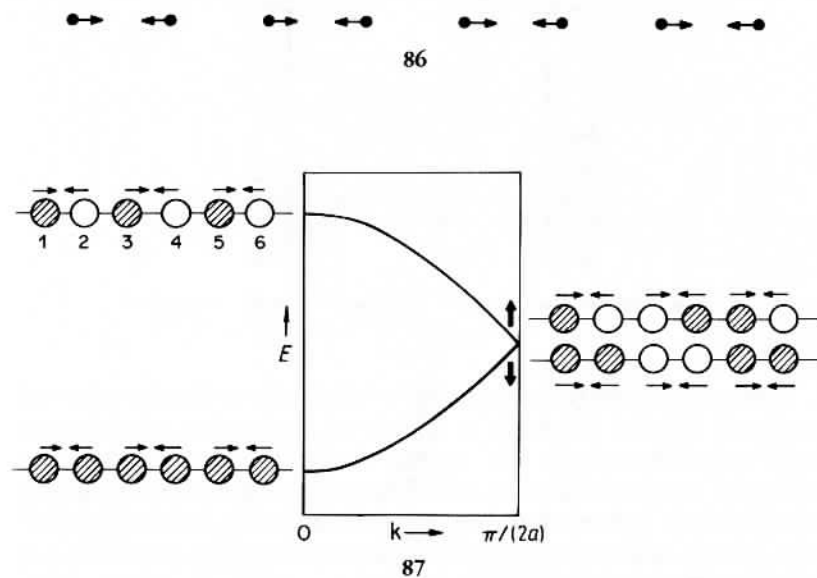


We can apply this framework to the solid. There is degeneracy and near degeneracy for any partially filled band. The degeneracy is that already mentioned, since $E(k) = E(-k)$ for any k in the zone. The near degeneracy is, of course, for k 's just above or just below the specified Fermi level. For any such partially filled band there is available, in principle, a deformation that 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 that opens up a gap just at the Fermi level. This is the Peierls distortion,⁶⁸ the solid state counterpart of the Jahn-Teller effect.

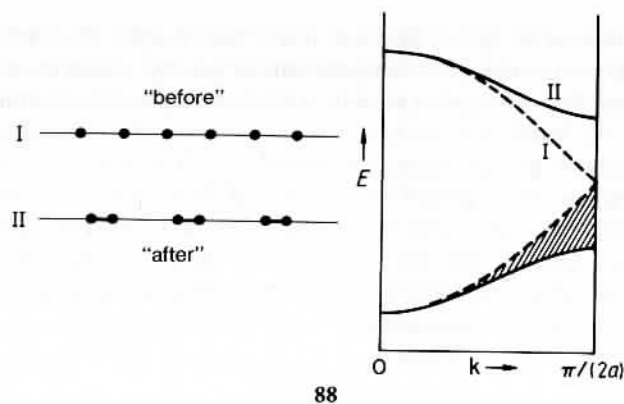
Let's see how this works on a chain of hydrogen atoms (or a polyene). The original chain has one orbital per unit cell, 85a, and an associated simple band. We prepare it for deformation by doubling the unit cell, 85b. The band is typically folded. The Fermi level is halfway up the band; the band has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



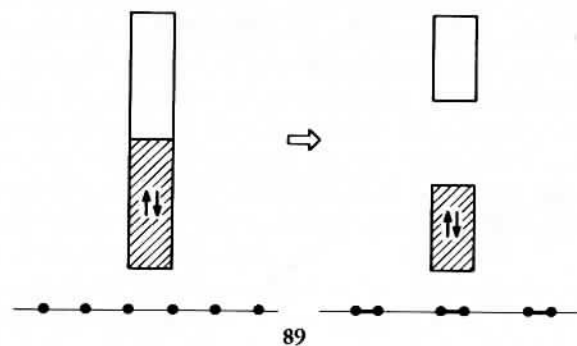
The phonon or lattice vibration mode that couples most effectively with the electronic motions is the symmetrical pairing vibration, 86. Let's examine what it does to typical orbitals at the bottom, middle (Fermi level), and top of the band, 87. At the bottom and top of the band nothing happens. What 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 just take place 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 E_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.

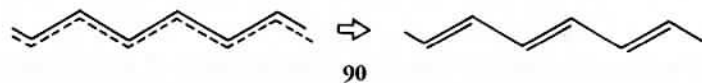


88



89

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.

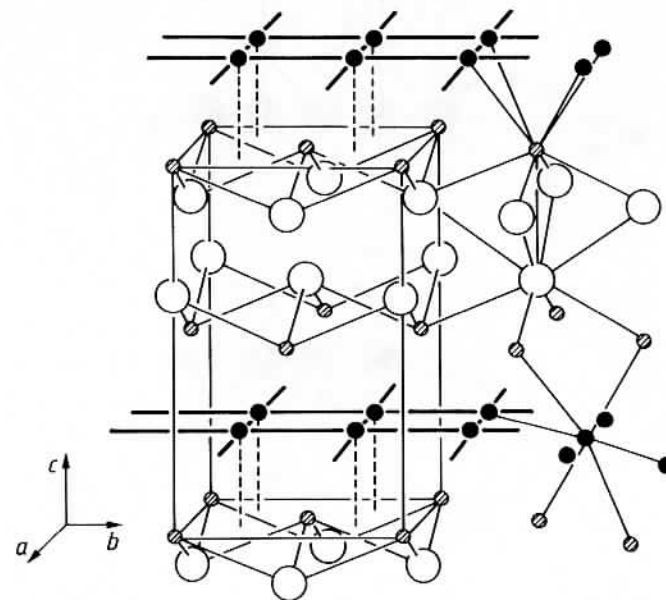


90

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 and the other components, A and B, are often main group elements. Diagram 91 shows one view of this structure, 92 another.



91

In the 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, and 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.