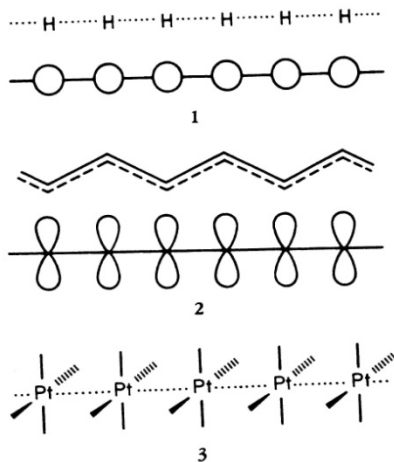**EXTRACT FROM „SOLIDS AND SURFACES" R. HOFFMANN, VCH 1988**

et'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 he moment. And we will progress to a stack of Pt(II) square planar omplexes, **3**, $Pt(CN)_4{}^{2-}$ or a model $PtH_4{}^{2-}$.

1

2

3

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
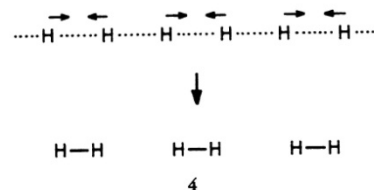
The orbitals of medium-sized rings on the way to that very large one are quite well known. They are shown in **5**. For a hydrogen molecule (or ethylene) there is bonding $\sigma_g(\pi)$ below an antibonding $\sigma_u{}^*(\pi^*)$. For cyclic H_3 or cyclopropenyl we have one orbital below two degenerate 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
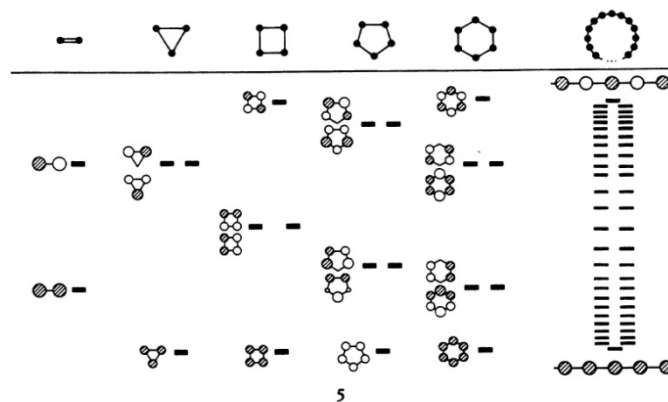
BLOCH FUNCTIONS, *k*, BAND STRUCTURES

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 $n = 0, 1, 2, 3, 4 \cdots$ 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.

$$n = \begin{array}{cccccc} \overset{\longmapsto a \longmapsto}{} \\ 0 & 1 & 2 & 3 & 4 \cdots \end{array}$$
$$\chi_0 \quad \chi_1 \quad \chi_2 \quad \chi_3 \quad \chi_4$$

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

6

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.

$$k = 0 \qquad \psi_0 = \sum_n e^0 \chi_n = \sum_n \chi_n$$
$$= \chi_0 + \chi_1 + \chi_2 + \chi_3 + \cdots$$

$$k = \frac{\pi}{a} \qquad \psi_{\frac{\pi}{a}} = \sum_n e^{\pi i n} \chi_n = \sum_n (-1)^n \chi_n$$
$$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \cdots$$

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 $-\pi/a \le k < \pi/a$ or $|k| \le \pi/a$. 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.

8
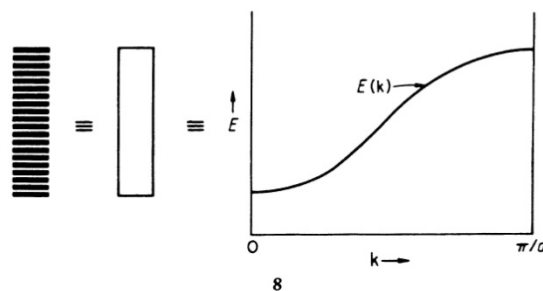
Graphs of $E(k)$ vs. k are called band structures. You can be sure that they can be much more complicated than this simple one. However, no matter how complicated they are, they can still be understood.

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
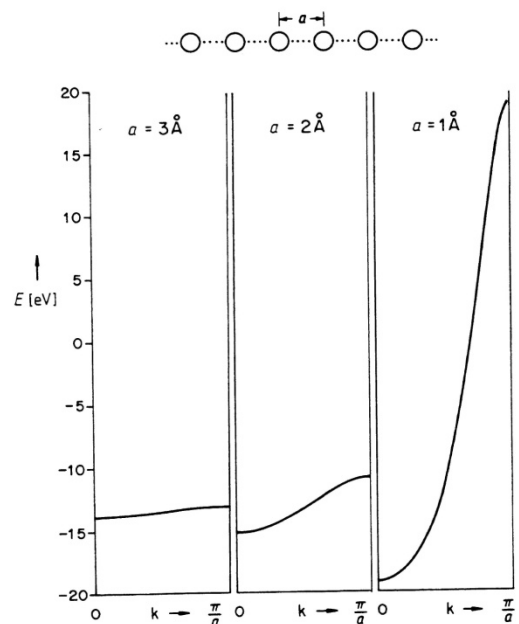
...O···O··O·O···O··O···

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.

9
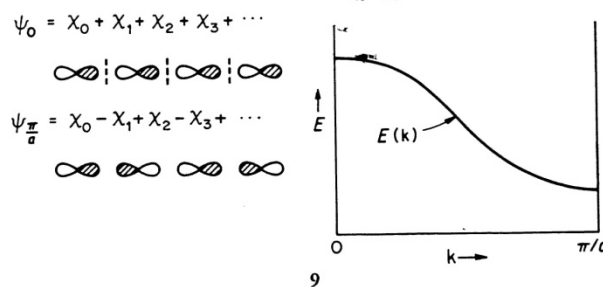
The band of s functions for the hydrogen chain "runs up," the band of p orbitals "runs down" (from zone center to zone edge). In general, it is the topology of orbital interactions that determines which way bands run.

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.
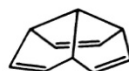
10

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 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$_2$Pt(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$_2$Pt(CN)$_4$Cl$_{0.3}$ and K$_2$Pt(CN)$_4$(FHF)$_{0.25}$. These are also stacked, but staggered, **13**, with a much shorter Pt$\cdots$Pt contact of $2.7 \rightarrow 3.0$ Å. The Pt–Pt distance had been shown to be inversely related to the degree of oxidation of the material.[12]
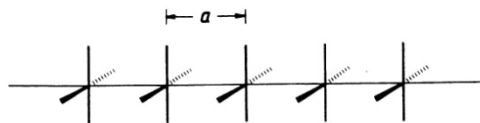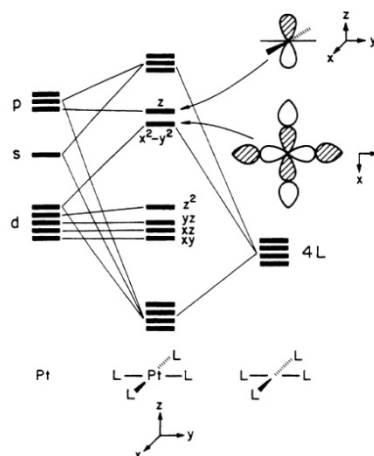

12
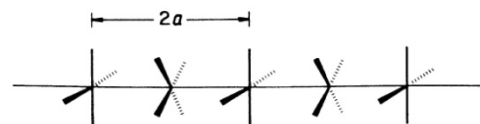
13

**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.
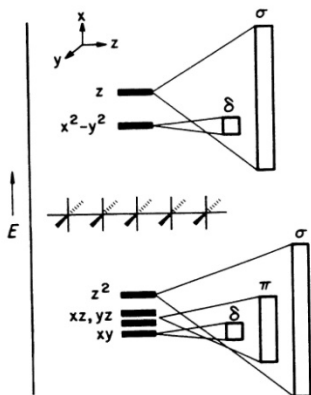

14

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$\cdots$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
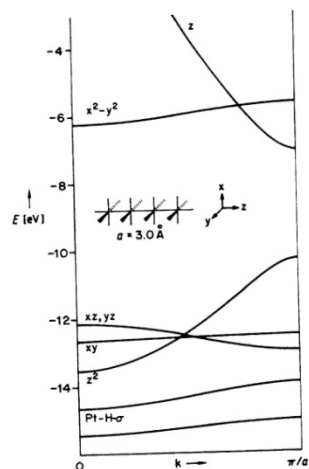
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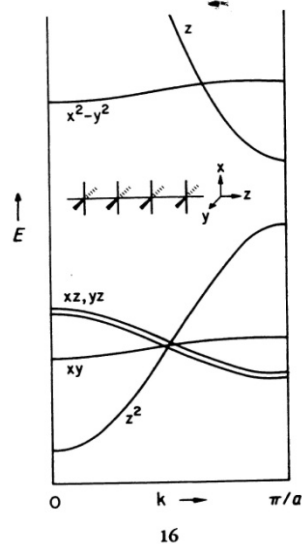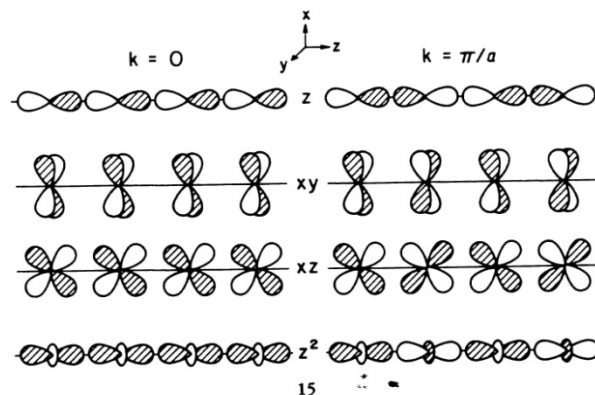
16

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 $Re_2Cl_8^{2-}$, 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.

17
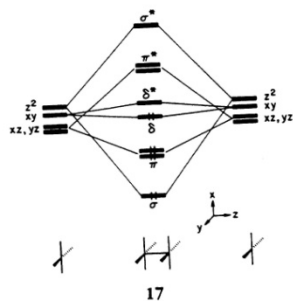
THE FERMI LEVEL

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 $Re_2Cl_8^{2-}$, 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 $[PtH_4^{2-}]_\infty$ 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 platinums in this $[PtH_4^{2-}]_\infty$ 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 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$\cdots$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 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 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

18
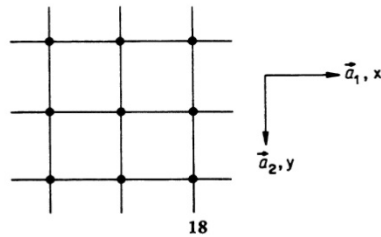
shows, very clearly, is the vector nature of k. Consider the $(k_x, k_y) = (\pi/2a, \pi/2a)$ and $(\pi/a, \pi/a)$ solutions. A look at them reveals that they are waves running along a direction that is the vector sum of k_x and k_y, i.e., on a diagonal. The wavelength is inversely proportional to the magnitude of that vector.

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

19
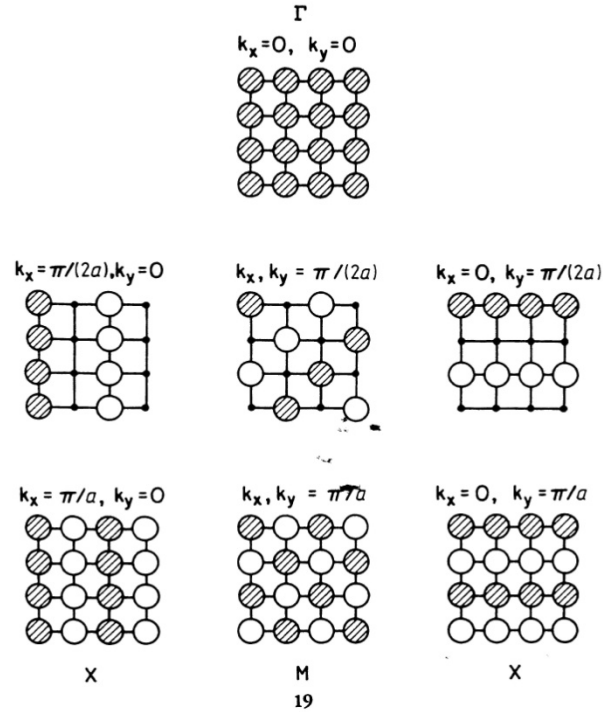
of allowed k, the Brillouin zone, is a square. Certain special values of k are given names: $\Gamma = (0, 0)$ is the zone center, $X = (\pi/a, 0) = (0, \pi/a)$, $M = (\pi/a, \pi/a)$. These are shown in **20**, and the specific solutions for Γ, X, and M were so labeled in **19**.

20
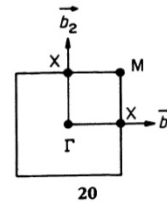
It is difficult to show the energy levels $E(\vec{k})$ for all $\vec{k}$. So what one typically does is to illustrate the evolution of E along certain lines in the Brillouin zone. Some obvious ones are $\Gamma \to X$, $\Gamma \to M$, $X \to M$. From **19** it is clear that M is the highest energy wave 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 $a = 2.0$ Å (Fig. 4) confirms our expectations.
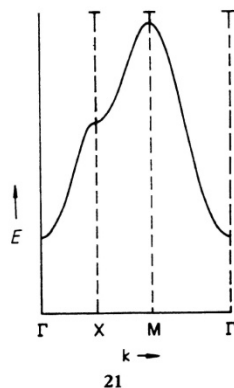
21

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
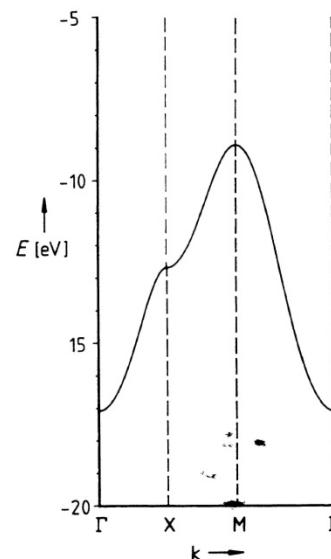
Figure 4 The band structure of a square lattice of H atoms, H–H separation 2.0 Å.

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 $\Gamma \to M$, but for that one needs a little group theory[15]) 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 absorbed on Ni(100),[17] the oxygen and lead nets in litharge,[18] or a Si layer in BaPdSi$_3$[19]—will have these orbitals.

p_x   **p_y**

σ^*, π Γ σ^*, π

σ, π X σ^*, π^*

σ^*, π^* Y σ, π

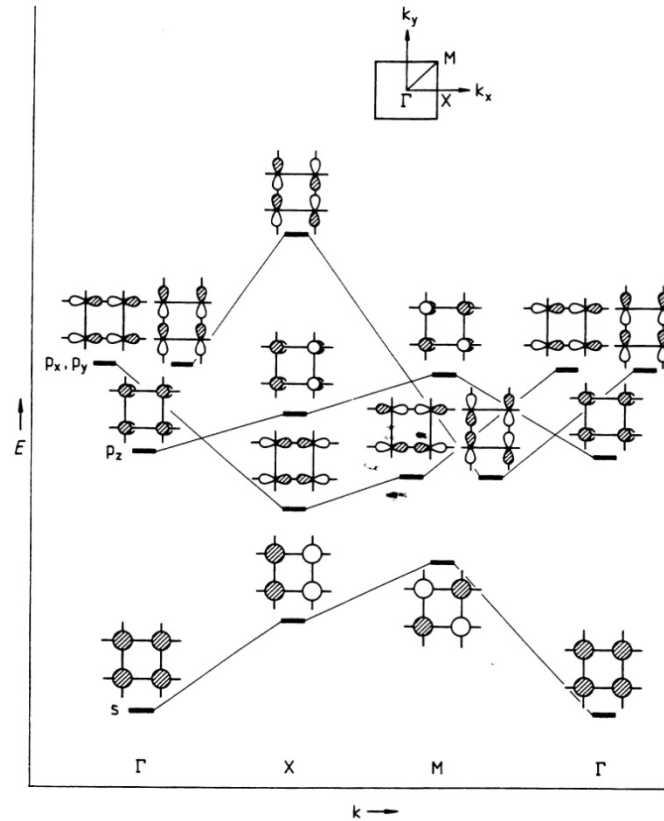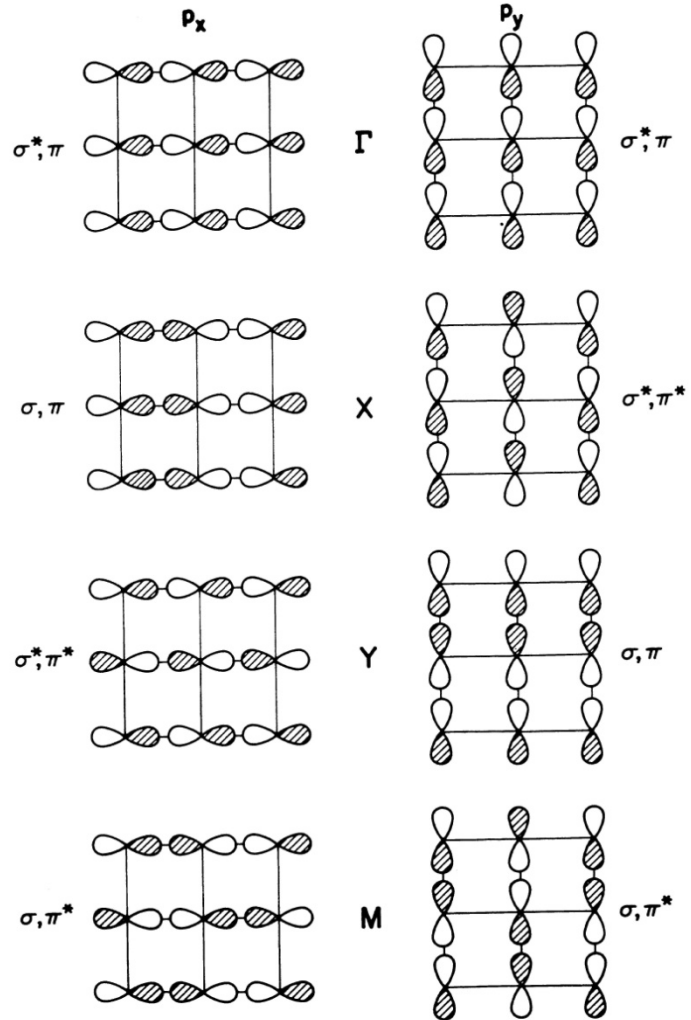σ, π^* M σ, π^*

22

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

orbital in the unit cell that 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:* This is 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 COs 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 4s, 4p.

(5) *Why 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, of course. 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, and 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 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 way is to look at all the levels in a given energy interval. The density

of states (DOS) is defined as follows:

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

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 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 say it in plain English, the flatter the band, the greater the density of states at that energy.

26
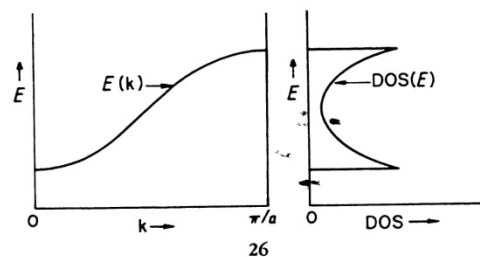
The shapes of DOS curves are predictable from the band structures. Figure 8 shows the DOS curve for the PtH_4^{2-} chain, Fig. 9 for a two-dimensional monolayer of CO. These could have been sketched from their respective band structures. In general, the detailed construction of these is a job best left to computers.

The DOS curve counts levels. The integral of DOS up to the Fermi level is the total number of occupied MOs. Multiplied by 2, it's the total number of electrons, so that the DOS curves plot the distribution of electrons in energy.

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, i.e., 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
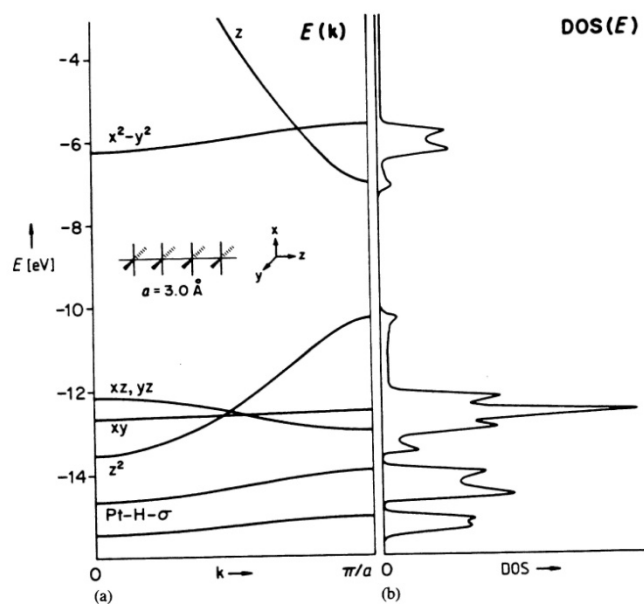
Figure 8 Band structure and density of states for an eclipsed PtH_4^{2-} stack. The DOS curves are broadened so that the two-peaked shape of the xy peak in the DOS is not resolved.

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

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_4^{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. Diagram **27** is a sketch of what we would expect. In **27** I haven't been careful to draw 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.

This was easy, because the polymer was built up of molecular monomer units. Let's try something inherently three-dimensional. The rutile structure of TiO_2 is a relatively common type. As **28** shows, the rutile
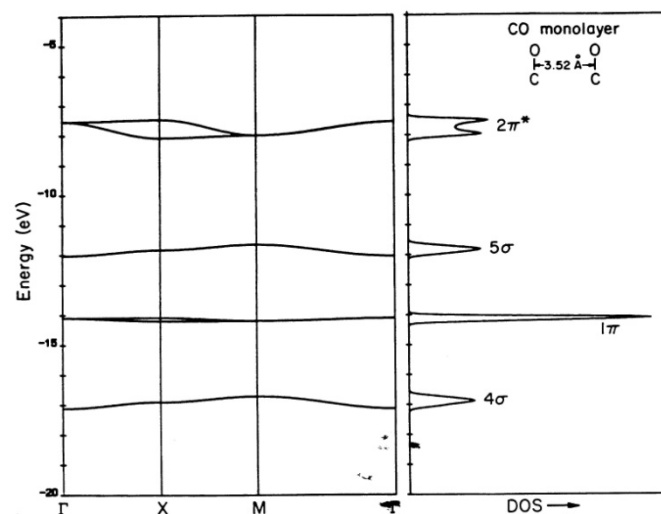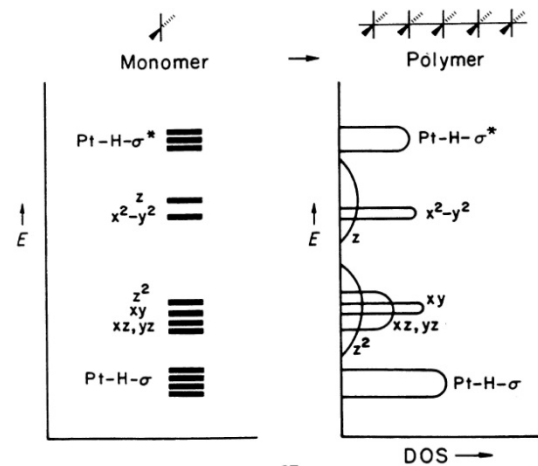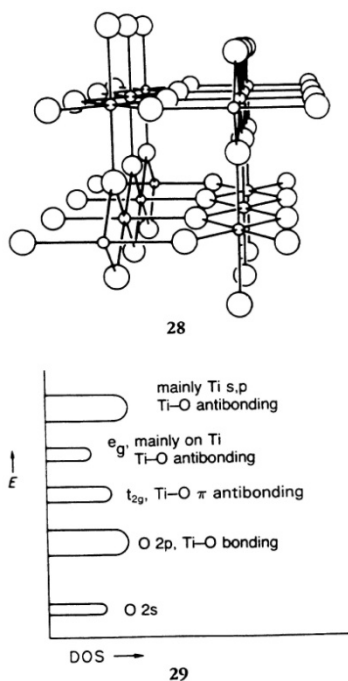

27

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···O or Ti···Ti interaction in this crystal. We expect something like **29**.

28

mainly Ti s,p
Ti–O antibonding

e_g, mainly on Ti
Ti–O antibonding

t_{2g}, Ti–O π antibonding

O 2p, Ti–O bonding

O 2s

DOS →

29

Note that the writing down of the approximate DOS curve *bypasses* 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
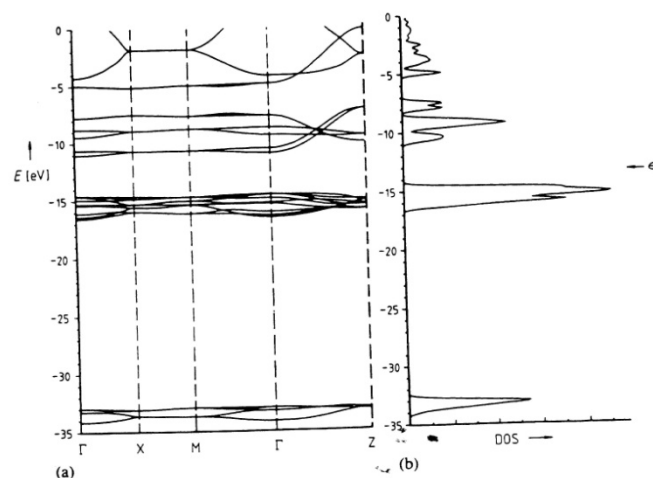
Figure 10 Band structure and density of states for rutile, TiO_2.

easy, in one or two dimensions. So the computed band structure in Fig. 10 will seem complex. The number is doubled (i.e., 12 O 2p, 6 t_{2g} 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.) that refer to directions in the three-dimensional Brillouin zone. If we glance at the DOS, we see that it does resemble the expectations of **29**. 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 $YBa_2Cu_3O_7$ 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 chemist's ability to write down approximate DOS curves should not be slighted. It gives us tremendous power, qualitative understanding, and 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 *Magnetism and Chemical Bonding*, just how good the chemist's approximate construction of band structures can be.[25]

However, in **27** and **29**, the qualitative DOS diagrams for PtH_4^{2-} and

TiO_2, there is 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 asks right away, 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:

$$\Psi = c_1\chi_1 + c_2\chi_2$$

where χ_1 is on center 1 and χ_2 on center 2. Let's assume that centers 1 and 2 are not identical, and that χ_1 and χ_2 are normalized but not orthogonal. The distribution of an electron in this MO is given by $|\Psi|^2$. Ψ should be normalized, so

$$1 = \int |\Psi|^2 \, d\tau = \int |c_1\chi_1 + c_2\chi_2|^2 \, d\tau = c_1^2 + c_2^2 + 2c_1c_2S_{12}$$

where S_{12} is the overlap integral between χ_1 and χ_2. This is how one electron in Ψ is distributed. Now it's obvious that c_1^2 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 somehow assign the "overlap density" $2c_1c_2S_{12}$ to the two centers. Mulliken suggested (and that's why we call this a Mulliken population analysis[20]) 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 be 1. It should be realized that the Mulliken prescription for partitioning the overlap density, while uniquely defined, is quite arbitrary.

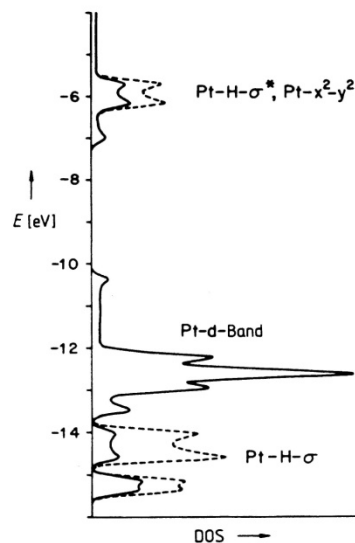What a computer does is just a little more involved, since it sums these

Figure 11 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.

contributions for each atomic orbital on a given center (there are several) over each occupied MO (there may be many). 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 (FMOs); i.e. the MOs 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.

Figures 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.

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
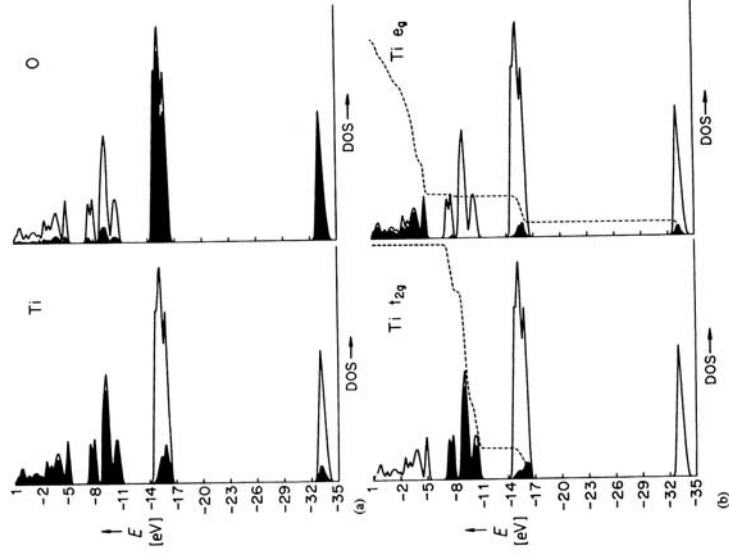
Figure 12 Contributions of Ti and O to the total DOS of rutile, TiO$_2$ are shown at top. At bottom, the t_{2g} and e_g Ti contributions are shown; their integration (on a scale of 0–100%) is given by the dashed line.

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).
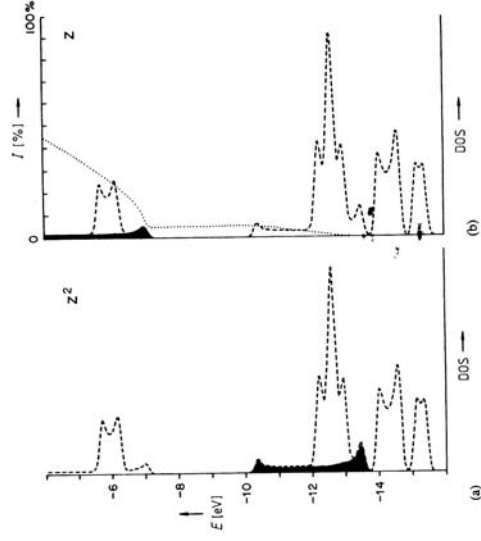
Figure 13 z^2 and z contributions to the total DOS of an eclipsed PtH$_4^{2-}$ stack. The dotted line is an integration of the z-orbital contribution.

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 most easily picked up by the integral in Fig. 13. The dotted line is a simple integration, like a nuclear magnetic resonance (NMR) integration. It counts, on a scale of 0–100%, what percentage of the specified orbital is filled at a given energy. At the Fermi level in unoxidized PtH$_4^{2-}$, 4% of the p$_z$ states are filled.

How does this come about? There are two ways to talk about it. Locally, the donor function of one monomer (z^2) can interact with the acceptor function (z) of its neighbor. This is shown in **30**. The overlap is good, but the energy match is 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 π/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 very 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.

$$z^2 \qquad z$$

30
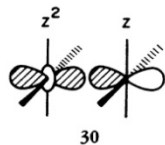
THE DETECTIVE WORK OF TRACING MOLECULE-SURFACE INTERACTIONS: DECOMPOSITION OF THE DOS

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 (Figs. 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 Figs. 7 and 9.[27] Some of the wriggles in the DOS curves also are not real, but a result of insufficient k-point sampling in the computation.

It's clear that the composite system $c(2 \times 2)$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 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, 0–100%, is to be read at top. The integration shows the total percentage of the 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 electron in the $2\pi^*$ levels together.
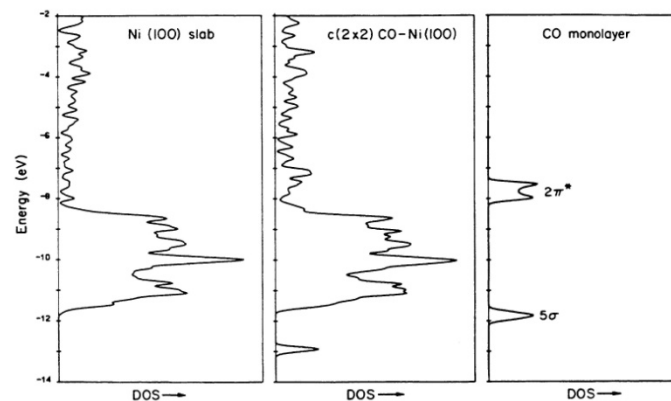
Figure 14 The total density of states of a model $c(2 \times 2)$CO-Ni(100) system (center), compared to its isolated four-layer Ni slab (left) and CO monolayer components.
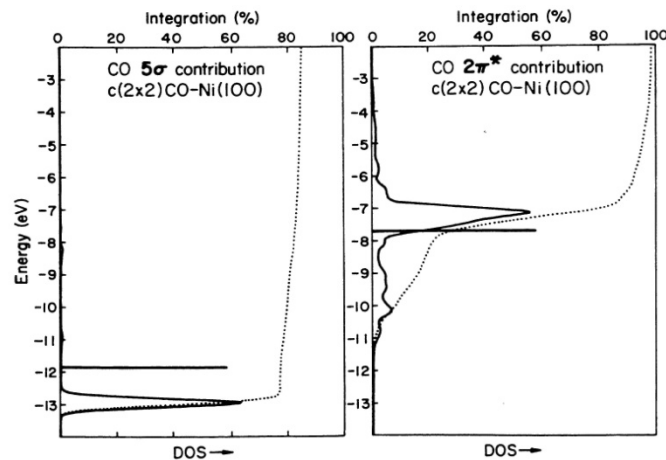

Figure 15 For the $c(2 \times 2)$CO-Ni(100) model this shows the 5σ and $2\pi^*$ contributions to the total DOS. Each contribution is magnified. The position of each level in isolated CO is marked by a line. The integration of the DOS contribution is given by the dotted line.

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 $2\pi^*$ of CO and a d_π orbital xz, yz of the metal. We would suspect that similar interactions are operative on the surface.
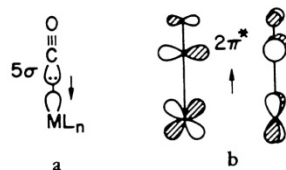
31

These can be looked for by setting side by side the $d_\sigma(z^2)$ and 5σ contributions to the DOS, and d_π(xz, yz) and $2\pi^*$ contributions. In Fig. 16 the π interaction is clearest: note 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 = 1/4. Consider one of these, the dibridged adsorption site alternative **25b** redrawn in **32**. The acetylene brings to the adsorption process a degenerate 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 into the π_σ and π_σ^* components that 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 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]
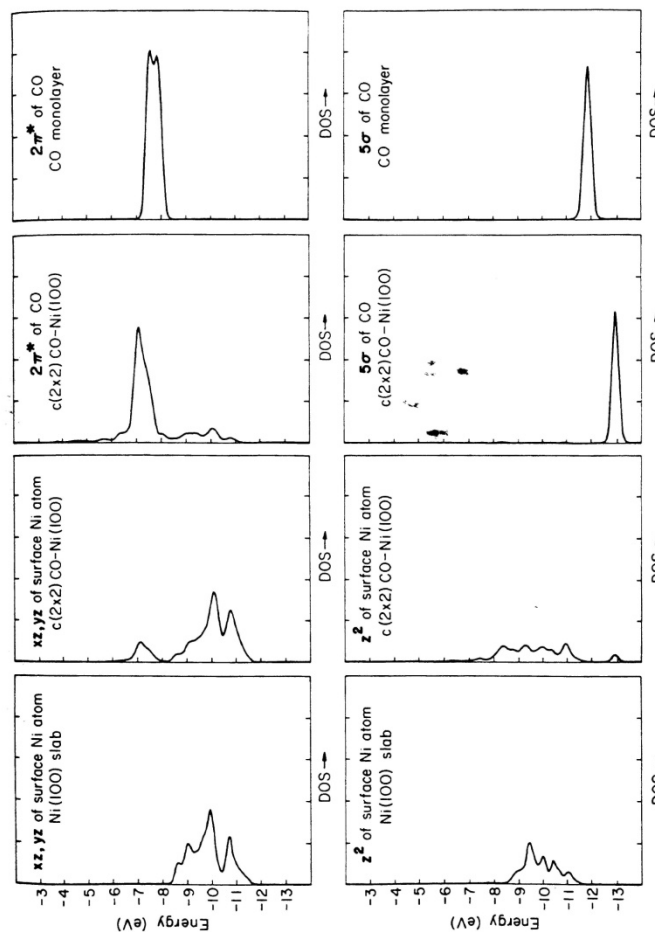

Figure 16 Interaction diagrams for 5σ and $2\pi^*$ of $c(2 \times 2)$C)–Ni(100). The extreme left and right panels in each case show the contributions of the appropriate orbitals (z^2 for 5σ, xz, yz for $2\pi^*$) of a surface metal atom (left) and of the corresponding isolated CO monolayer MO. The middle two panels then show the contributions of the same fragment MOs to the DOS of the composite chemisorption system.
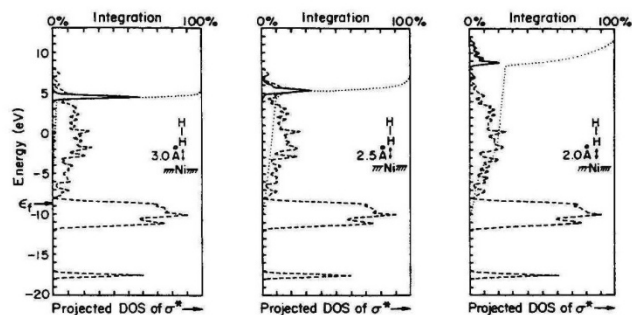
Figure 18 That part of the total DOS (dashed line) which is in the H$_2$ σ_u^* (solid line) at various approach distances of a frozen H$_2$ to a Ni(111) surface model. The dotted line is an integration of the H$_2$ density.

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 individuals, 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...

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 over all orbitals on the two atoms, over all occupied MOs) 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. Figure 19 shows the familiar energy levels of a diatomic, N$_2$, a density-of-states plot of these (just sticks proportional to the number of levels, of length 1 for σ, 2 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, $2\sigma_u$ and $3\sigma_g$ are essentially nonbonding. These are best characterized as lone pair combinations. π_u is bonding, π_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 seven 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, $2c_ic_jS_{ij}$. What we are defining is an overlap population-weighted density of states. The beginning of the obvious acronym (OPWDOS) has unfortunately 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 about 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 nonbonding, the top antibonding. The COOP curve obviously has the shape shown at 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 antibonding. That curve, the dashed 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 that are bonding, negative regions that are antibonding. The amplitudes of these curves depend on the number of states in that energy interval, the
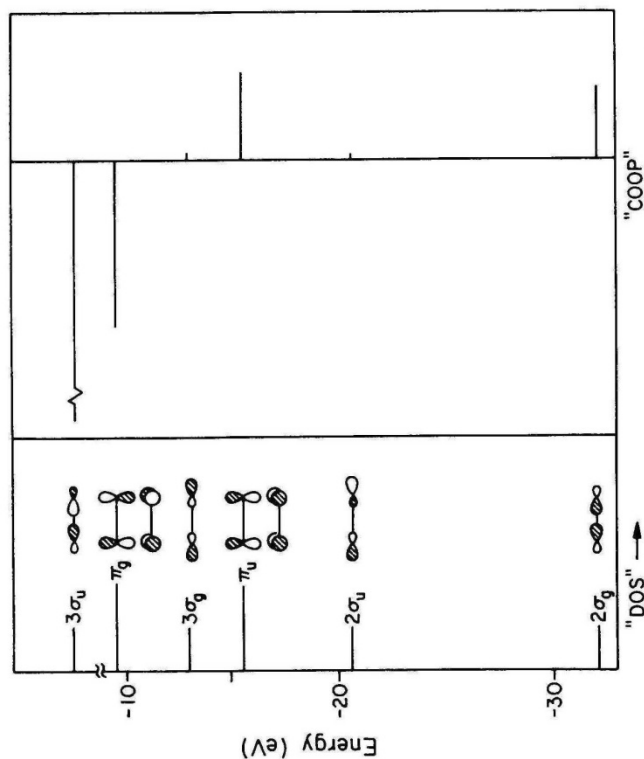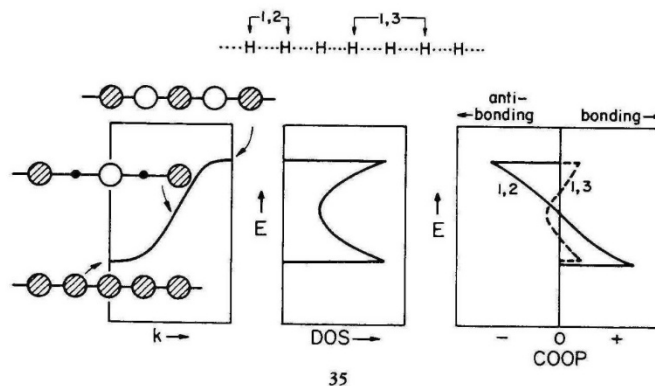
Figure 19 The orbitals of N_2 (left) and a "solid state way" to plot the DOS and COOP curves for this molecule. The $1\sigma_g$ and $1\sigma_u$ orbitals are out of the range of this figure.

magnitude of the coupling overlap, and the size of the coefficients in the MOs.

35

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. Figure 20 shows both the Pt–H and Pt–Pt COOP curves. 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, -15 eV are Pt–H σ bonding, the band at -6 eV 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 that are involved in Pt–Pt bonding. The rather complex structure of the -10 to -13-eV 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 antibonding (see 35 and Fig. 3).
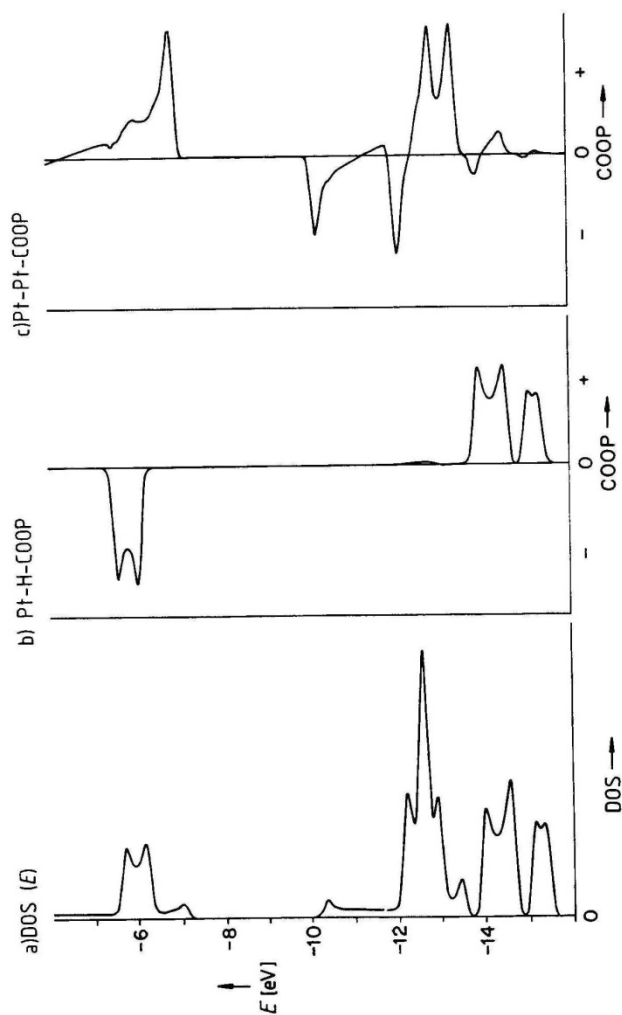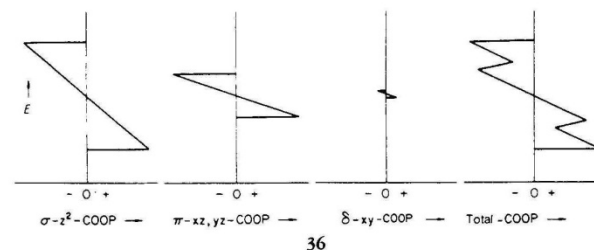
Figure 20 Total density of states (left), and Pt–H (middle) and Pt–Pt (right) crystal orbital overlap population curves for the eclipsed PtH_4^{2-} stack.

The δ contribution to the COOP is small because of the poor overlap involved. The large Pt–Pt bonding region at -7 eV is due to the bottom of the Pt z band.

$$\sigma\text{-}z^2\text{-COOP} \longrightarrow \qquad \pi\text{-}xz,yz\text{-COOP} \longrightarrow \qquad \delta\text{-}xy\text{-COOP} \longrightarrow \qquad \text{Total -COOP} \longrightarrow$$

36

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 -10 eV 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, nonstoichiometries 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.

Earlier we showed a band structure for rutile. The corresponding COOP curve for the Ti–O bond (Fig. 21) is extremely 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 antibonding.

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
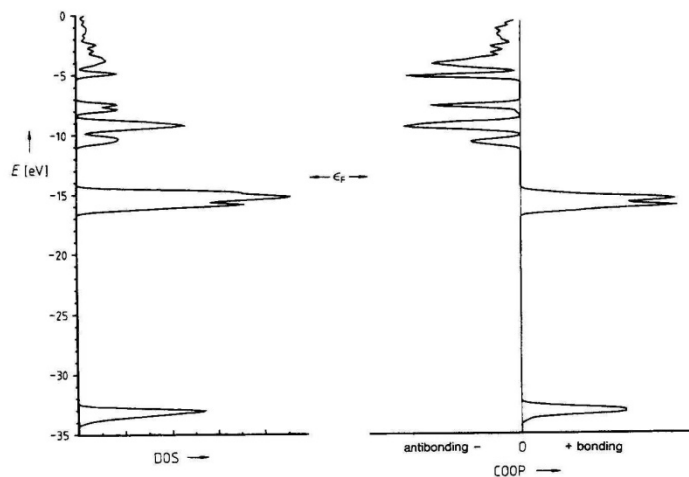
Figure 21 DOS and Ti–O COOP for rutile.

wide band will result. They also mix with each other 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 a d contribution. The general features of 37 are reproduced. At the Fermi level, a substantial part of the s band is occupied, so that the calculated[35] Ni configuration is $d^{9.15}s^{0.62}p^{0.23}$.

37

66

67

68
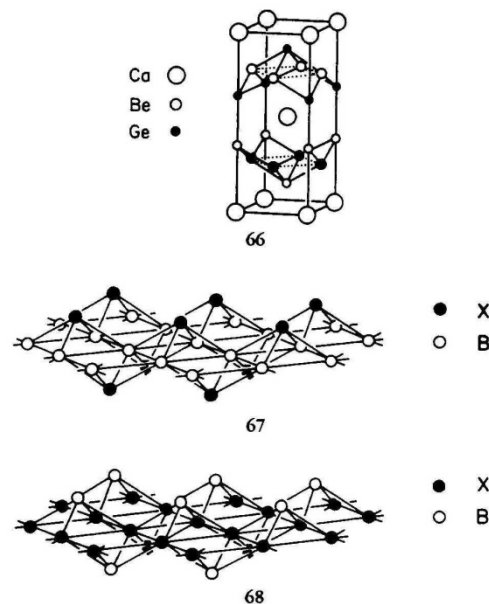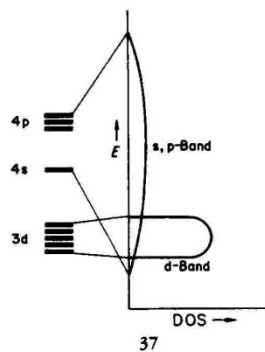
MORE THAN ONE ELECTRONIC UNIT IN THE UNIT CELL. FOLDING BANDS

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 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.
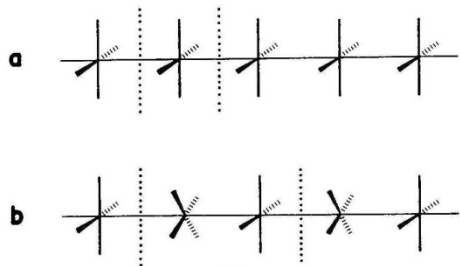

69
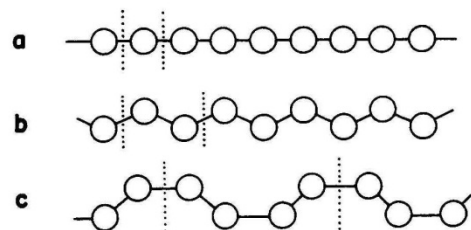
70

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.
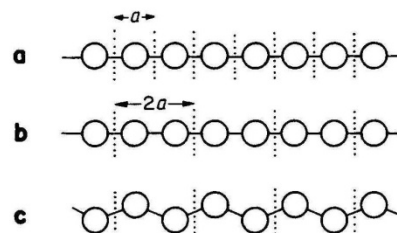

71

72
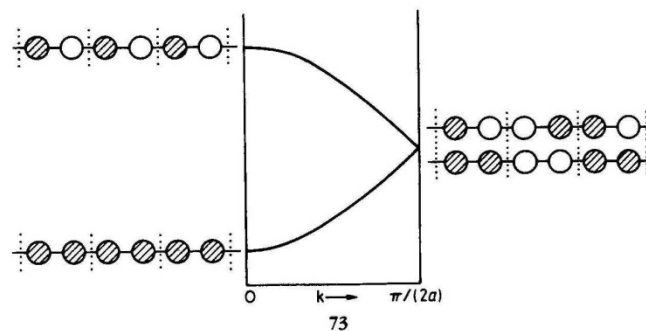
73

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 (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]
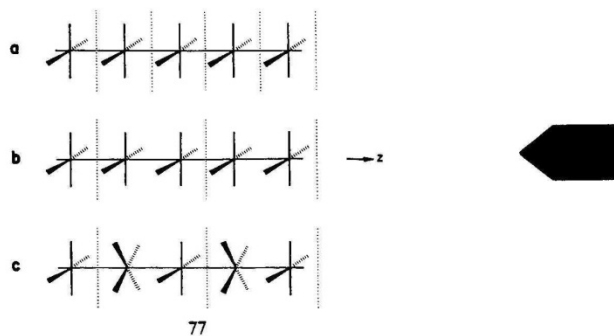

74

75
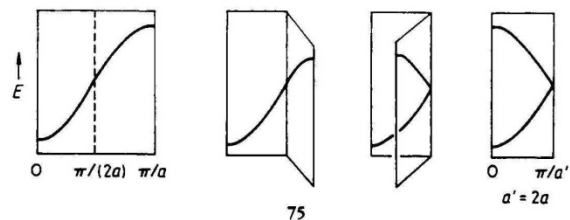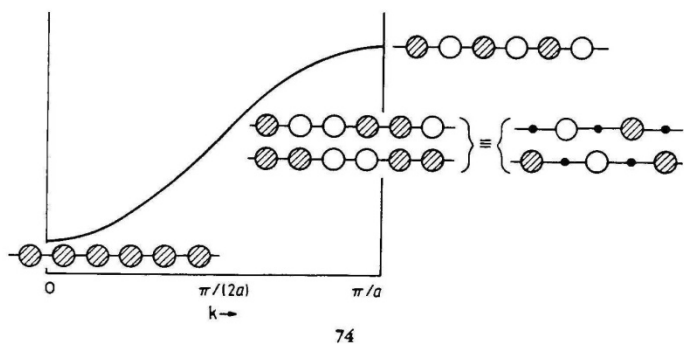
The process can be continued. If the unit cell is tripled, the band will fold as in 76a. If it is quadrupled, we get 76b, and so on. However, the point of all this is not just redundancy, seeing the same thing in different ways. There are two important consequences or utilizations of this folding. First, 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.

76
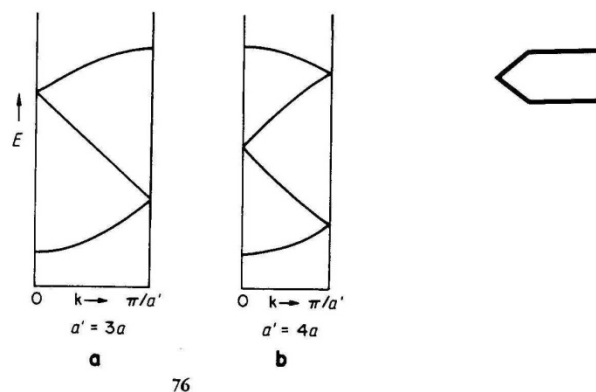
To illustrate this point, let me show the band structure of the *staggered* PtH_4^{2-} chain, 69b. This is done in Fig. 35, left. There are twice as many bands in this region as there are in the case of the eclipsed monomer (the xy band is doubly degenerate). This is no surprise; the unit cell of the staggered polymer is $[PtH_4^{2-}]_2$. 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.
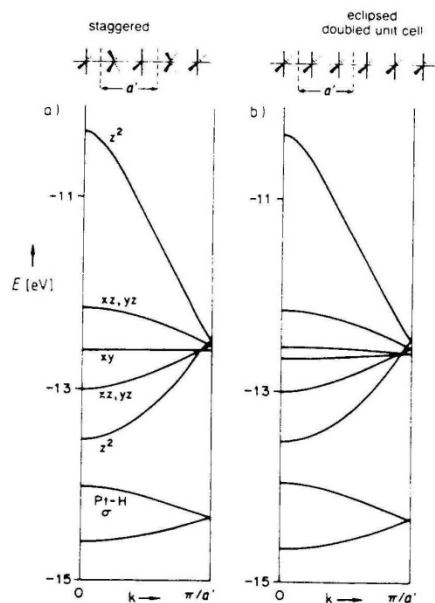

77

staggered

eclipsed
doubled unit cell

a)

b)

E [eV]

z^2

-11

-11

xz, yz

xy

-13

xz, yz

-13

z^2

Pt-H
σ

-15

-15

$0 \qquad k \longrightarrow \qquad \pi/a'$

$0 \qquad k \longrightarrow \qquad \pi/a'$

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.

78
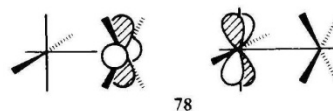
The chemist's intuition is that the eclipsed and staggered polymers *can't* be very different—at least, not until the ligands start bumping into each other, and for such steric effects there can be, in turn, much further intuition. The band structures may look different, since one polymer has one, the 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** → **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, 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.
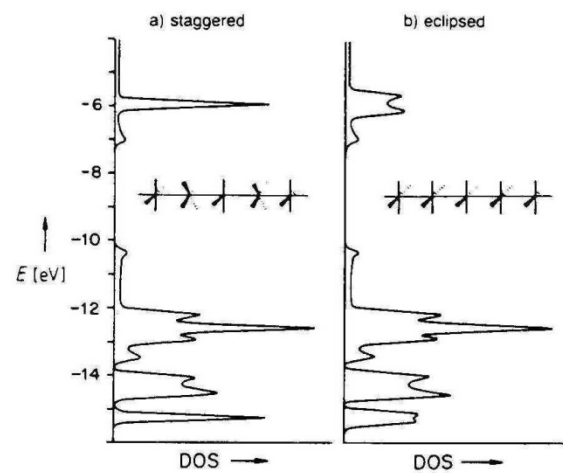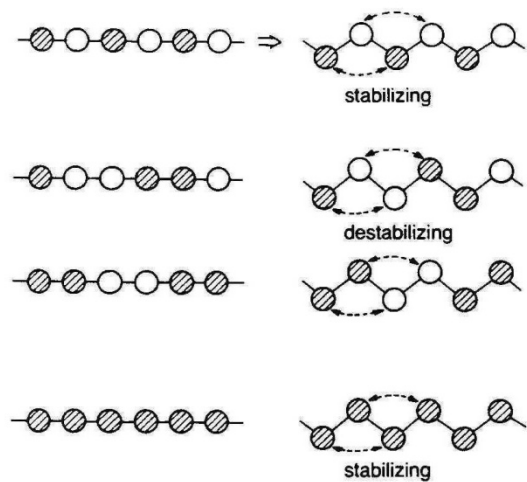
Figure 36 A comparison of the DOS of staggered (left) and eclipsed (right) $PtH_4{}^{2-}$ stacks.

stabilizing

destabilizing

stabilizing

79

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.
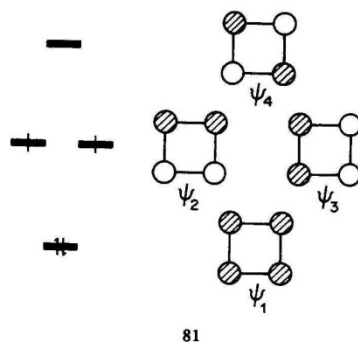
81

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.


82
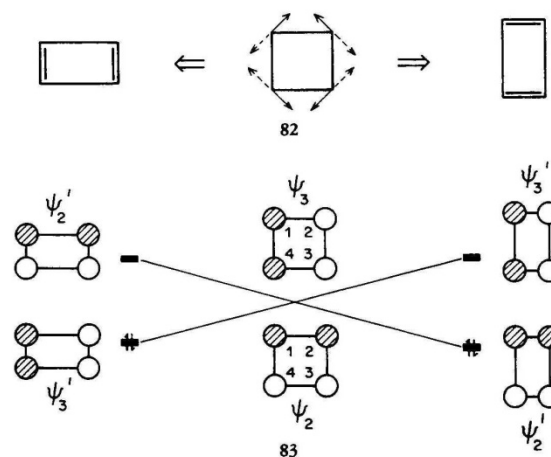
83

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 ($S_4{}^{2+}$).


84
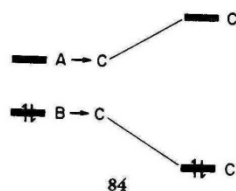
We can apply this framework to the solid. There is degeneracy and near degeneracy for any partially filled band. The degeneracy is that already mentioned, since $E(k) = E(-k)$ for any k in the zone. The near degeneracy is, of course, for k's just above or just below the specified Fermi level. For any 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.


85
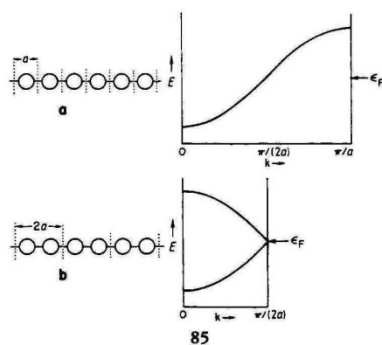
The phonon or lattice vibration mode that couples most effectively with the electronic motions is the symmetrical pairing vibration, **86**. Let's examine what it does to typical orbitals at the bottom, middle (Fermi level), and top of the band, **87**. At the bottom and top of the band nothing happens. 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.

86

87
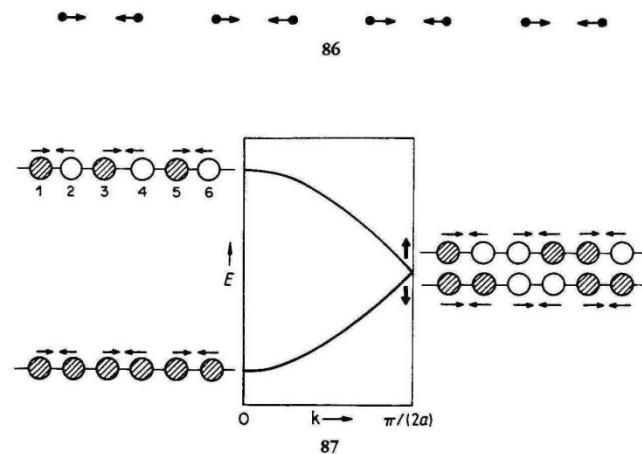
The action does not just take place at the Fermi level, but in a second order way the stabilization "penetrates" into the zone. It does fall off with k, a consequence of the way perturbation theory works. A schematic representation of what happens is shown in **88**. A net stabilization of the system occurs for any Fermi level, but obviously it is maximal for the half-filled band, and it is at that 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**.
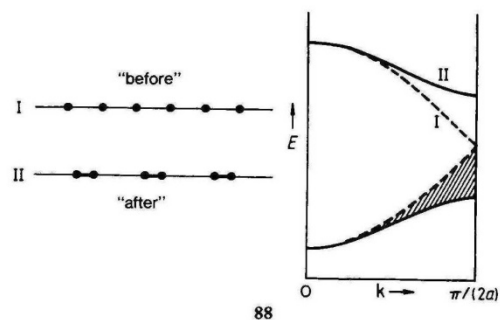
88
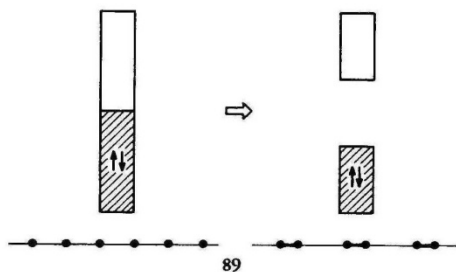
89

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.
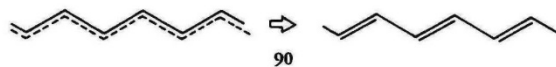

90

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.

95
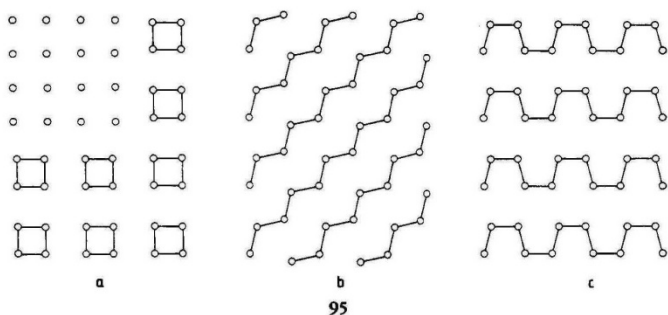
An interesting three-dimensional instance of a Peierls distortion at work (from one point of view) is the derivation of the observed structures of elemental arsenic and black phosphorus from a cubic lattice. This treatment is due to Burdett and coworkers.[6,74] The two structures are shown in their usual representation in **96**. It turns out that they can be easily related to a simple cubic structure, **97**.


P   As

96

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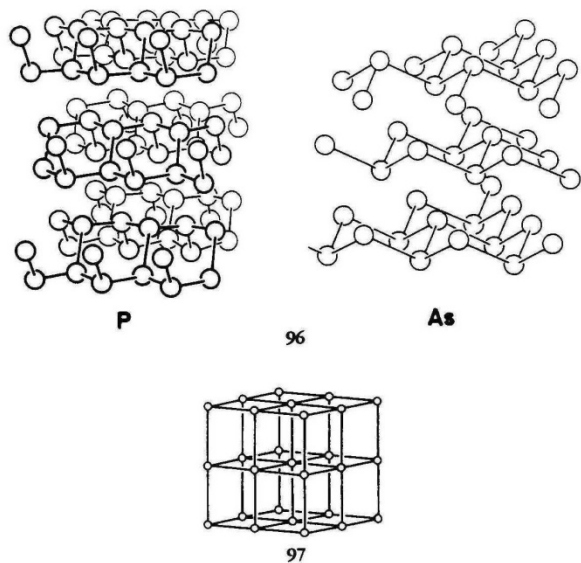
The DOS associated with the band structure of **97**, with one main group element of group 15 per lattice site, must have the block form **98**. There are five electrons per atom, so if the s band is completely filled, we have a half-filled p band. The detailed DOS is given elsewhere.[74] What is significant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

98

99
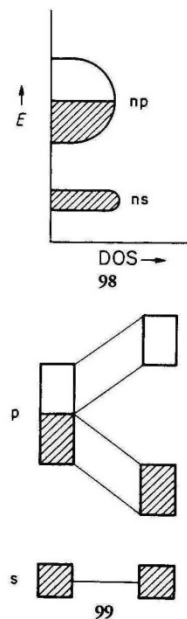
Burdett, McLarnan, and Haaland[74,a,c] showed that there are no less than 36 different ways to so distort. Two of these correspond to black phosphorus and arsenic, **100**. There are other possibilities as well.

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

100
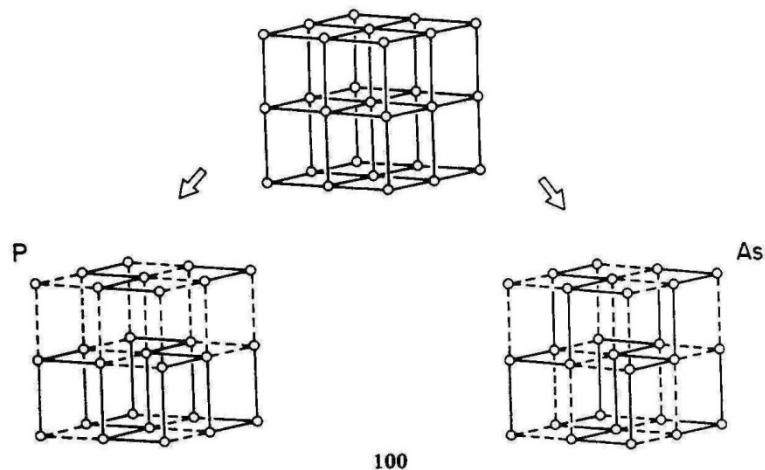
One final comment that is relevant to the $ThCr_2Si_2$ structure. The reader will note that we did not use a Peierls distortion argument in the resolution of the P–P pairing problem in that common structural type when we discussed it earlier. We could have done so, somewhat artificially, by choosing a structure in which the interlayer P···P separation was so large that the P–P σ and σ^* DOS came right at the Fermi level. Then a pairing distortion could have been invoked, yielding the observed bond. That, however, would have been a somewhat artificial approach. Peierls distortions are ubiquitous and important, but they're not the only way to approach bonds in the solid.