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A CHEMICAL AND THEORETICAL WAY TO LOOK AT BONDING ON  
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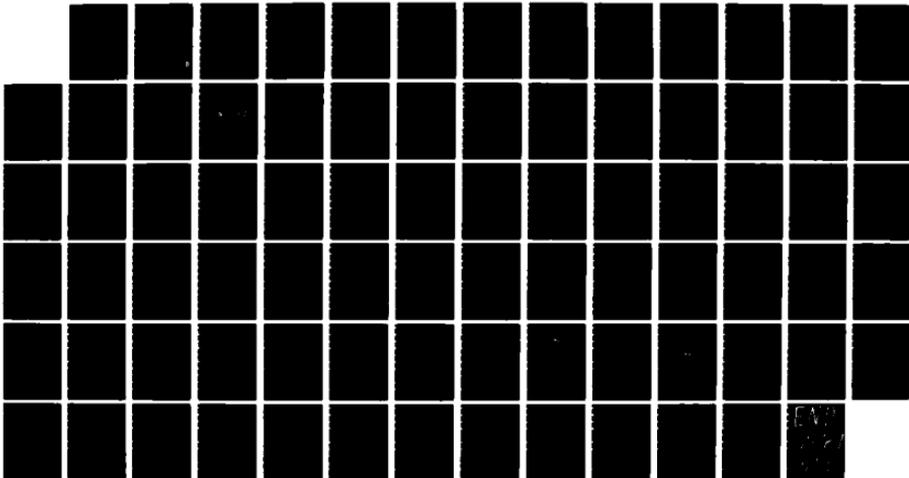
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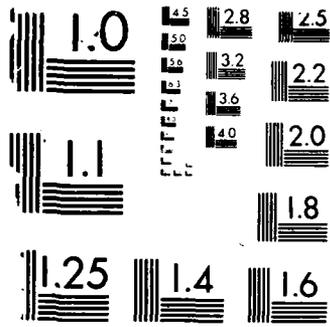
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TECHNICAL REPORT NO. 31

A CHEMICAL AND THEORETICAL WAY TO  
LOOK AT BONDING ON SURFACES

by

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July, 1987

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A CHEMICAL AND THEORETICAL WAY TO LOOK AT BONDING ON SURFACES

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Abstract. An account is given of a theoretical approach to surface structure and reactivity that is within the framework of solid state theory, yet strives for chemical ways of interpretation. One begins then from highly delocalized band structures, but introduces interpretational tools (density of states decompositions, crystal orbital overlap populations) that allow a tracing of local, chemical acts. It is quite feasible to construct interaction diagrams for surfaces, and to make frontier orbital arguments, just as for molecules. There are some interesting ways in which the surface-adsorbate interaction differs from simple molecular binding - in particular, in the way that two-orbital four- and zero-electron interactions can turn into bonding. The surface and bulk acting as a reservoir of electrons or holes at the Fermi level are important in this context. Chemisorption emerges as a compromise in a continuum of bonding whose extremes are dissociative adsorption and surface reconstruction.



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A surface - be it of a 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 resemblances to other forms of matter: bulk, discrete molecules in the gas phase and in solution, various aggregated states. And it will have differences. It is important to find the similarities and it is also important to note the differences - the similarities connect the chemistry of surfaces to the rest of chemistry; the differences are what make life interesting (and make surfaces economically useful).

Experimental surface science is a meeting ground of chemistry, physics, and engineering.<sup>1</sup> New spectroscopies have given us a wealth of information, be it sometimes fragmentary, on the ways that atoms and molecules interact with surfaces. The tools may come from physics, but the questions that are asked are very chemical - what is the structure and reactivity of surfaces by themselves, and of surfaces with molecules on them? In fact, a chemist who relaxes a little about the impressive spectroscopies will find an amusing phenomenological resemblance between current surface science studies and organic structure determinations by physical methods in the early days of the application of these methods, say the forties. Great stories, many of them true, are constructed about structures and reactions on the basis of a few evanescent bumps in an often hard-to-come-by spectrum.

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

There have been an extraordinary number of theoretical contributions to surface science.<sup>2</sup> These have come from physicists and chemists, they have ranged from semiempirical MO calculations to state-of-the-art Hartree-Fock self-consistent-field+CI and advanced density functional procedures. Some people have used atom and cluster models, some extended slab or film models for surfaces. I would like to present in this account some of the things my coworkers and I have learned about surface-molecule interactions from extended Hückel band calculations.<sup>3</sup> This computational method is a very approximate one (all other methods are superior to it), but its transparency and the applicability to it of the simplest perturbation theoretic reasoning makes the method well-suited to tracing origins and interactions. Our choice of a translationally extended system (i.e. two-dimensional film or slab model rather than a cluster) is intentional. The aim is to build a bridge to physics, to do the calculations in the framework or language with which most solid state physicists are likely to feel comfortable. The special feature, what makes these calculations more than the lowest quality band calculation, is that from the experience of chemistry and quantum chemistry we can construct the interpretational tools that will extract local, chemical actions from the delocalized orbitals. The calculations are mediocre, on some absolute scale; the analysis is, I hope, clever and chemical.

### Setting Up: The Surface and the Adsorbate

The kind of problem that we want to study is how CO chemisorbs on Ni, how H<sub>2</sub> dissociates on a metal surface, how acetylene bonds to Pt(111) and then rearranges to vinylidene or ethylidyne, how surface carbide or sulfide affects the chemistry of CO, how CH<sub>3</sub> and CH<sub>2</sub> bind, migrate, and react on an iron surface. It makes sense to look first at structure and bonding in the stable or metastable way points, the chemisorbed species. Then one could proceed to construct potential energy surfaces for motion of chemisorbed species on the surface, and eventually for reactions.

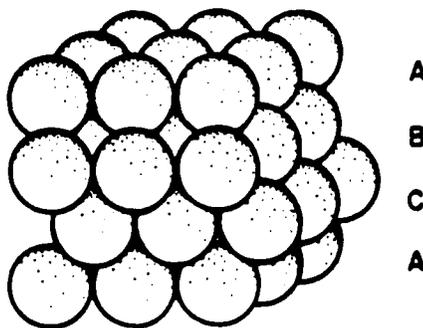
The very language I have used here conceals a trap. It puts the burden of motion and reactive power on the chemisorbed molecules, and not on the surface, which might be thought passive, untouched. Of course, this can't be so. We now know that exposed surfaces reconstruct, i.e. make adjustments in structure driven by their unsaturation.<sup>4</sup> They do so first by themselves, without any adsorbate. And they do it again, in a different way, in the presence of adsorbed molecules. The extent of reconstruction is great in semiconductors and extended molecules, small in molecular crystals and metals. The calculations I will discuss deal with metal surfaces. One is then reasonably safe (we hope) if one assumes no reconstruction. It will turn out, however, that the signs of eventual reconstruction are to be seen even in these calculations.

It might be mentioned here that reconstruction is not a phenomenon reserved for surfaces. In the most important development in theoretical inorganic chemistry in the seventies, Wade<sup>5a</sup> and Mingos<sup>5b</sup> have provided us with a set of skeletal electron pair counting rules. These rationalize the related geometries of borane and transition metal clusters. One aspect of their theory is that if the electron count increases or decreases from the

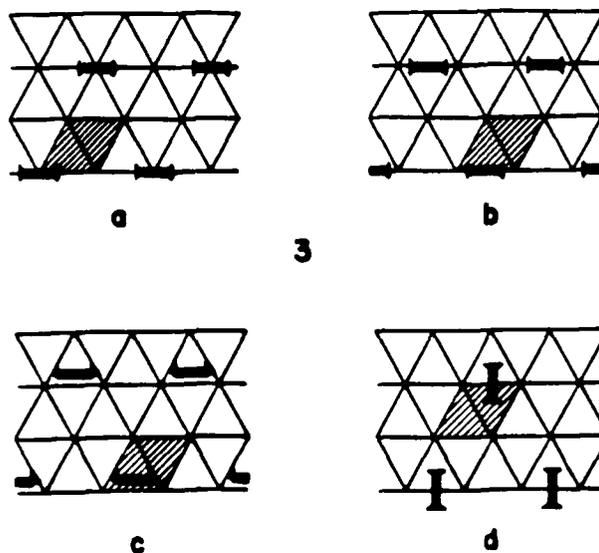
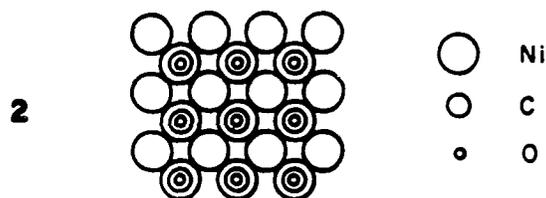
appropriate one for the given polyhedral geometry, that the cluster will adjust geometry - open a bond here, close one there - to compensate for the different electron count. Discrete molecular transition metal clusters and polyhedral boranes also reconstruct.

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

So one chooses a slab of finite depth. 1 shows a four-layer slab model of a Ni(111) surface, a typical close-packed hexagonal face. How thick should the slab be? Thick enough so that its inner layers approach the electronic properties of the bulk, the outer layers those of the true surface. In practice, it is more often economics which dictates the typical choice of three or four layers.



Molecules are then brought up to this slab. Not one molecule, for that would ruin the desirable two-dimensional symmetry, but an entire array or layer of molecules maintaining translational symmetry. This immediately introduces two of the basic questions of surface chemistry: coverage and site preference. 2 shows a  $c(2 \times 2)CO$  array on  $Ni(100)$ , on-top adsorption, coverage =  $\frac{1}{4}$ . 3 shows four possible ways of adsorbing acetylene in a coverage of  $\frac{1}{4}$  on top of  $Pt(111)$ . The experimentally preferred mode is the three-fold bridging one, 3c. Many surface reactions are coverage dependent.<sup>1</sup> And the position where a molecule sits on a surface, its orientation relative to the surface, is one of the things one wants to know.

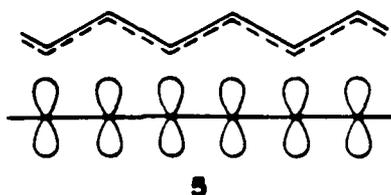
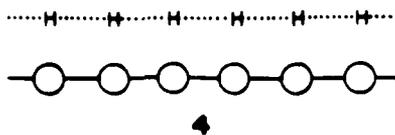


### How to Think About Many Orbitals

So: a slab, three or four atoms thick, of a metal, and a monolayer of adsorbed molecules. The thicker the layer and the smaller the coverage, the more atoms in a unit cell. And, there are lots of unit cells. If there are  $n$  valence orbitals in the unit cell ( $n$  might be  $\sim 100$ ), and  $N$  microscopic unit cells in the macroscopic crystal ( $N$  approaches Avogadro's number) then there are  $Nn$  orbitals in all. That's a large number, hence the title of this section. At first sight, one is set back by the prospect of that myriad of levels. A person addicted to frontier orbital arguments, such as the author, one who would like to find the causes of a geometrical preference or a stereochemical preference in the nature of one orbital, might be particularly discouraged. For there is no way in the world that one orbital out of so many has the power to control or steer.

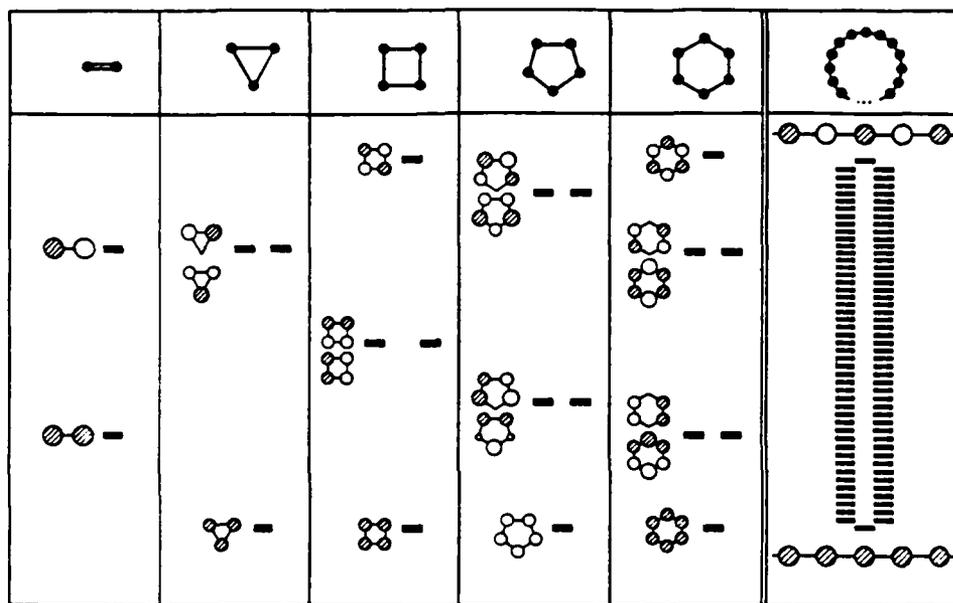
There is a way out of these quandaries. It is, first of all, symmetry, translational symmetry, leading to band structures and crystal orbitals, and, second, the language of densities of states.<sup>6,7</sup>

To introduce the idea of a band structure, let's begin with a simple one-dimensional system, a chain of equally spaced H atoms, 4, or the isomorphous  $\pi$ -system of a non-bond-alternating polyene, 5. Such infinite chains can be modeled as an imperceptibly bent part of a very large ring.



This is called applying cyclic boundary conditions.

The orbitals of the oligomers on the way to that very large ring are very well known, 6. In hydrogen (or ethylene) there is a bonding  $\sigma_g$  ( $\pi$ ) level below an antibonding  $\sigma_u^*$  ( $\pi^*$ ). In the three-membered ring (cyclic  $H_3$ , cyclopropenium) the pattern is 1 below 2; in cyclobutadiene we have 1 below 2 below 1. And so on. Levels come in pairs, except for the lowest



6

and, occasionally, the highest, and the number of nodes increases as one goes up in energy. We'd expect the same for an infinite polymer, in the chemist's representation of a band of levels that is given at right in 6.

There is a neat way to write out all those orbitals in the band, making use of the translational symmetry. If we have a lattice whose points are labeled by an index  $n=0,1,2,3,4$  as shown in 7, and if on each lattice point there is a basis function (an H 1s orbital),  $x_0, x_1, x_2$ , etc. then the appropriate symmetry adapted linear combinations are given in 7.

7

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

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  $\psi$  transforms as. We will see in a moment that  $k$  is much more, but for now  $k$  is just an index for an irreducible representation, just like  $a$ ,  $e_1$ ,  $e_2$  in  $C_5$  point group symmetry are labels.

The process of symmetry adaptation is called in the solid state physics trade "forming Bloch functions".<sup>6,7</sup> To reassure a chemist that one is getting what one expects from 6, let's see in 8 what combinations are generated for two specific values of  $k$ ,  $k=0$  and  $k=\pi/a$ .

8

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

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

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

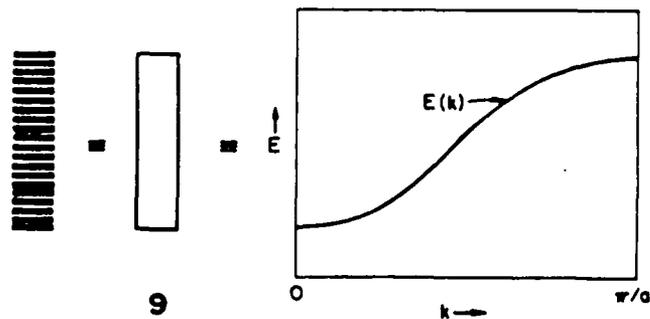
$$= \chi_0 - \chi_1 + \chi_2 - \chi_3 + \dots$$

Referring back to 6, we see that the wave function corresponding to  $k=0$  is the most bonding one, the one for  $k=\pi/a$  the top of the band. For other values of  $k$  we get a neat description of the other levels in the band. So  $k$  counts nodes as well. The larger the absolute value of  $k$ , the more nodes one has in the wave function. But one has to be careful - there is a range of  $k$  and if one goes outside of it one doesn't get a new wave function, but repeats an old one. The unique values of  $k$  turn out to be

in the interval  $-\pi/a < k \leq \pi/a$  or  $|k| \leq \pi/a$ . This is called the Brillouin zone, the range of  $k$ .

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 two for each  $k$  because there is an easily proved theorem that  $E(k) = E(-k)$ ). Most band structures do not draw the redundant  $E(-k)$ , but plot  $E(|k|)$  and label it as  $E(k)$ . The allowed values of  $k$  are equally spaced in the space of  $k$ , which is called reciprocal space. Remarkable  $k$  is not only a symmetry label and a node counter, but it is also a wave vector, and so related to momentum.<sup>6,7</sup>

What a chemist then draws as a band in 6, repeated at left in 9 (and the chemist tires and draws ~20 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 the curve looks continuous is that we have here a fine "dot matrix" printer at work - 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. For instance, if we refer back to the CO on Ni(100) surface of 2, the band structure of the CO monolayer by itself is given in Fig. 1, and that of the underlying four-layer Ni slab by itself is in Fig. 2.<sup>8-10</sup>

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Figures 1 and 2

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At first sight, these appear to be too complicated to be understood. Not so:

1) What is being plotted:  $E$  vs.  $\vec{k}$ . The lattice is two-dimensional.  $k$  is now a vector, varying within a two-dimensional Brillouin zone,  $\vec{k} = \vec{k} = (k_x, k_y)$ . Some of the special points in this zone are given canonical names:  $\Gamma$  (the zone center) =  $(0,0)$ ;  $X = (\pi/a, 0)$ ,  $M = (\pi/a, \pi/a)$ . What is being plotted is the variation of the energy along certain specific directions in reciprocal space connecting these points.

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

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

4) Why some bands are steep, others flat: because there is much inter-unit-cell overlap in one case, little in another. One very important feature of a band is its dispersion, or band width, the difference in

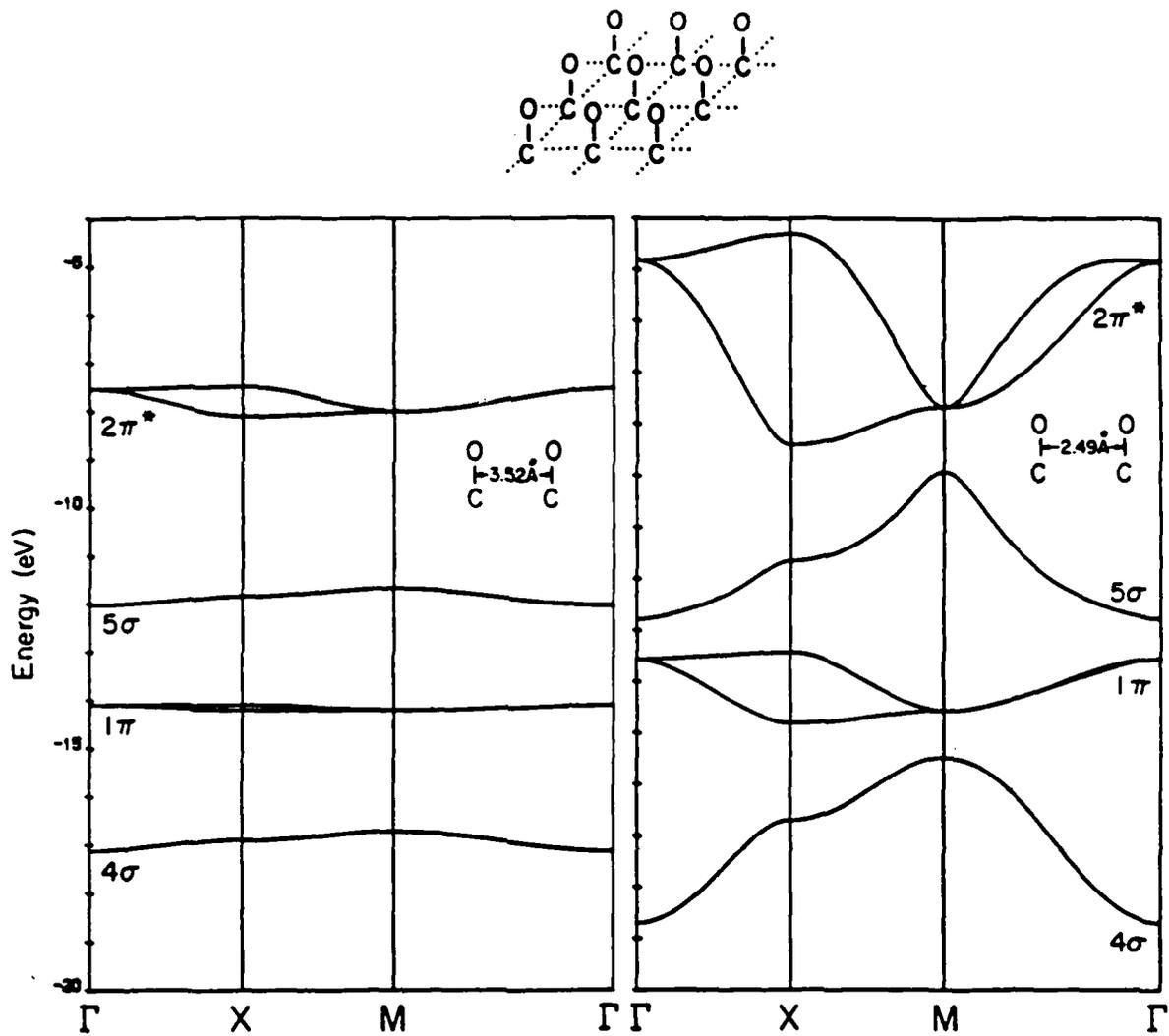


Figure 1. Band structures of square monolayers of CO at two separations: (a) left, 3.52 Å, (b) right, 2.49 Å. These would correspond to  $\frac{1}{2}$  and full coverage of a Ni(100) surface.

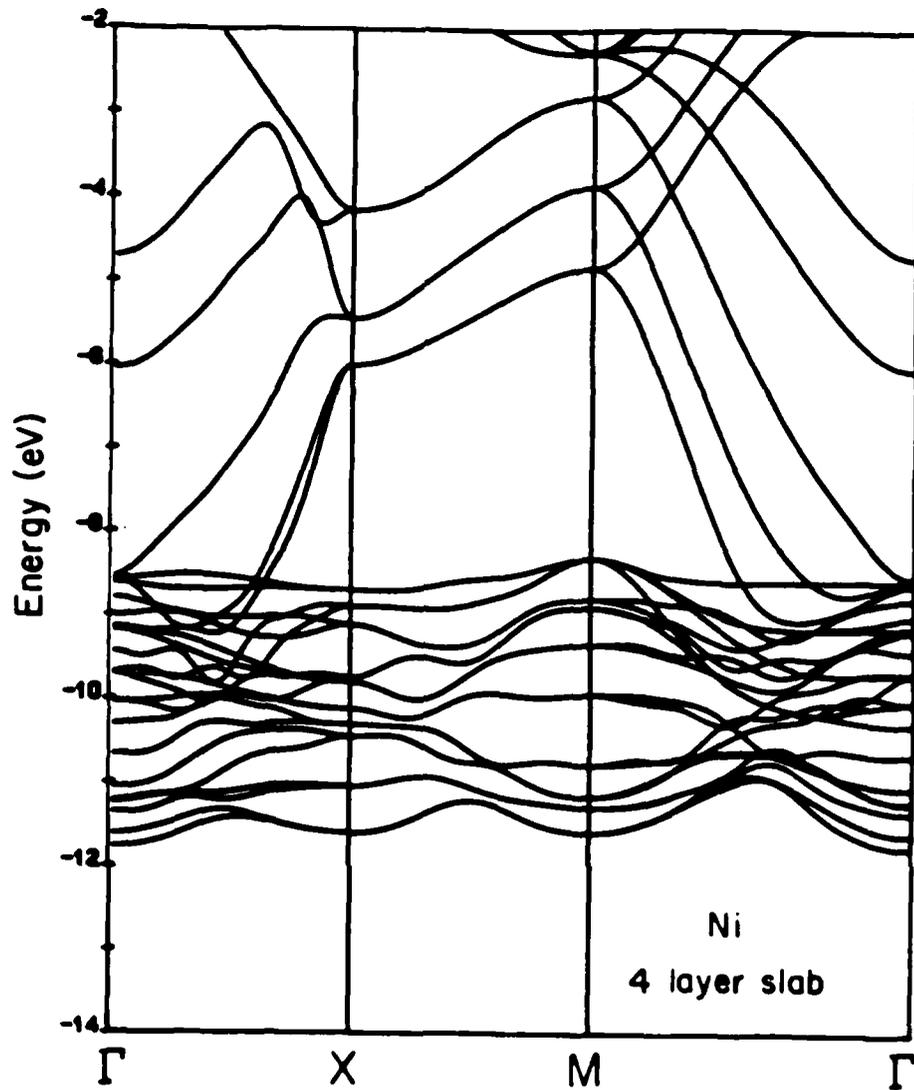


Figure 2. The band structure of a four-layer Ni slab that serves as a model for a Ni(100) surface. The flat bands are derived from Ni 3d, the more highly dispersed ones above these are 4s, 4p.

energy between the highest and lowest levels in the band. What determines the width of bands? The same thing that determines the splitting of levels in a dimer, ethylene, or  $H_2$ , 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.<sup>7</sup>

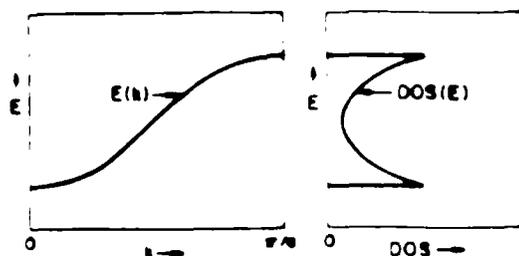
The CO monolayer bands in Fig. 1 are calculated at two different CO-CO spacings, corresponding to different coverages. It's no surprise that the bands are more dispersed when the CO's are closer together. In the case of the Ni slab, the s,p bands are wider than the d bands, because the 3d orbitals are more contracted, less diffuse than the s,p.

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

We still have the problem of how to talk about all these highly delocalized orbitals, how to retrieve a local, chemical, or frontier orbital language in the solid state. There is a way: perhaps we can talk about bunches of levels. There are many ways to group levels, but one pretty obvious one is to look at all the levels in a given energy interval. The density of states (DOS) is defined as follows:

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

For a simple band of a chain of hydrogen atoms, the DOS curve takes on the shape of 1)



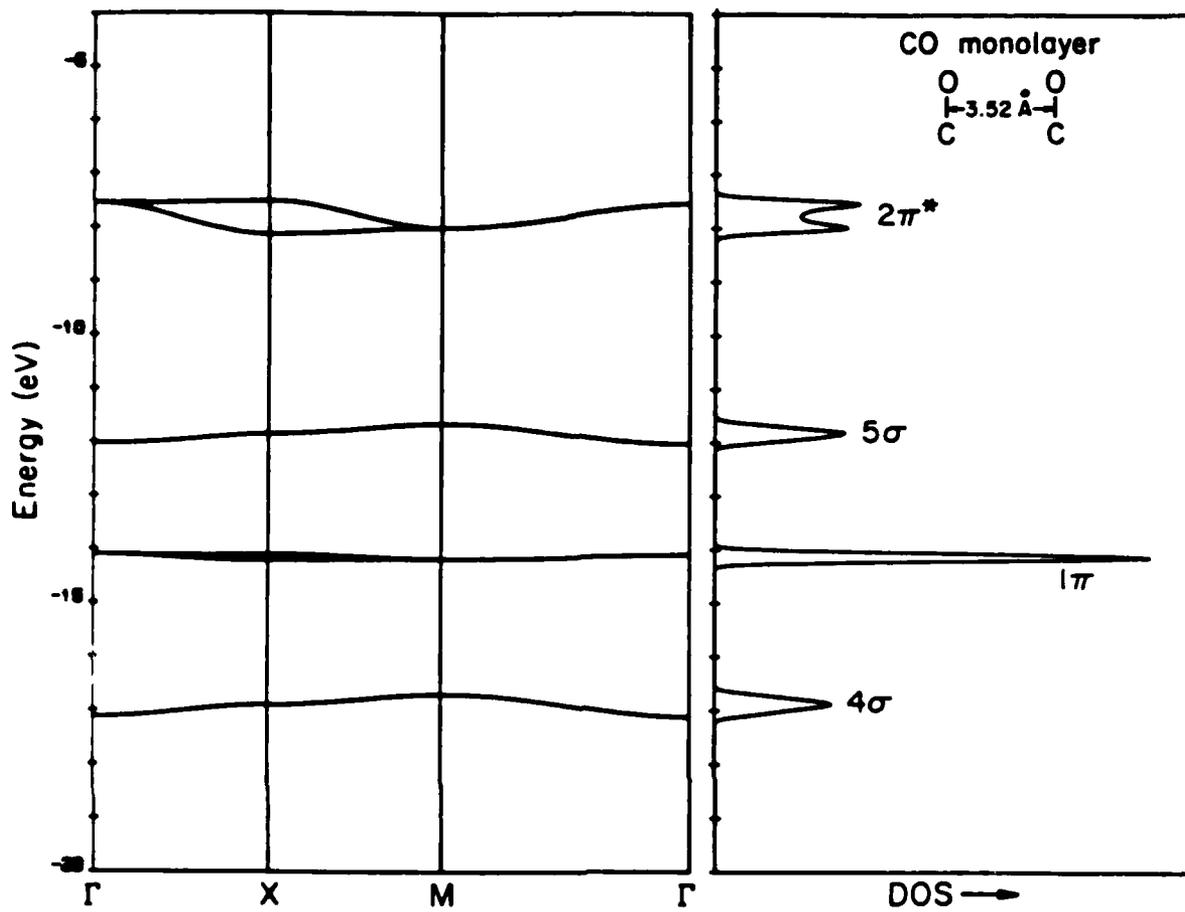


Figure 3. The density of states (right) corresponding to the band structure (left) of a square monolayer of CO's, 3.29 Å apart.

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, there are more states in a given energy interval at the top and bottom of this band. In general,  $DOS(E)$  is inversely proportional to the slope of  $E(k)$  vs.  $k$  or, to put it into plain English, the flatter the band, the greater the density of states at that energy.<sup>6,7</sup> An illustration of this point is provided by the DOS of a hypothetical array of non-interacting adsorbates, for instance an overlayer at very low coverage. The plot would show single lines ( $\delta$ -functions) at the energies of the MO's of one isolated adsorbate molecule.

The shapes of DOS curves are predictable from the band structures. Fig. 3 shows the DOS curve for one of the CO monolayers. It could have been sketched from the band structure at left. In general, the construction of these is a job best left for computers.

Figure 3

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

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

There is another aspect of the return to real space that is significant: chemists can sketch the DOS of any material, approximately, intuitively. All that's involved is a knowledge of the atoms, their approximate ionization potentials and electronegativities, and some judgment as to the extent of inter-unit-cell overlap (usually apparent from the structure). For an elaboration of this point, the reader is referred to another article discussing the general aspects of a theoretical and chemical approach to the solid state.<sup>7c</sup>

To summarize: we go from orbitals in the unit cell (real space) to band structures (reciprocal space) to densities of states (back in real space). In the remainder of the paper, I will be showing only densities of states, and we will draw chemical arguments from these. Occasionally the crystal orbitals at certain  $k$  points will be required.

We still need two concepts - the solid state analogue of a charge distribution, and some bond index. But to introduce these, we will use a specific surface problem.

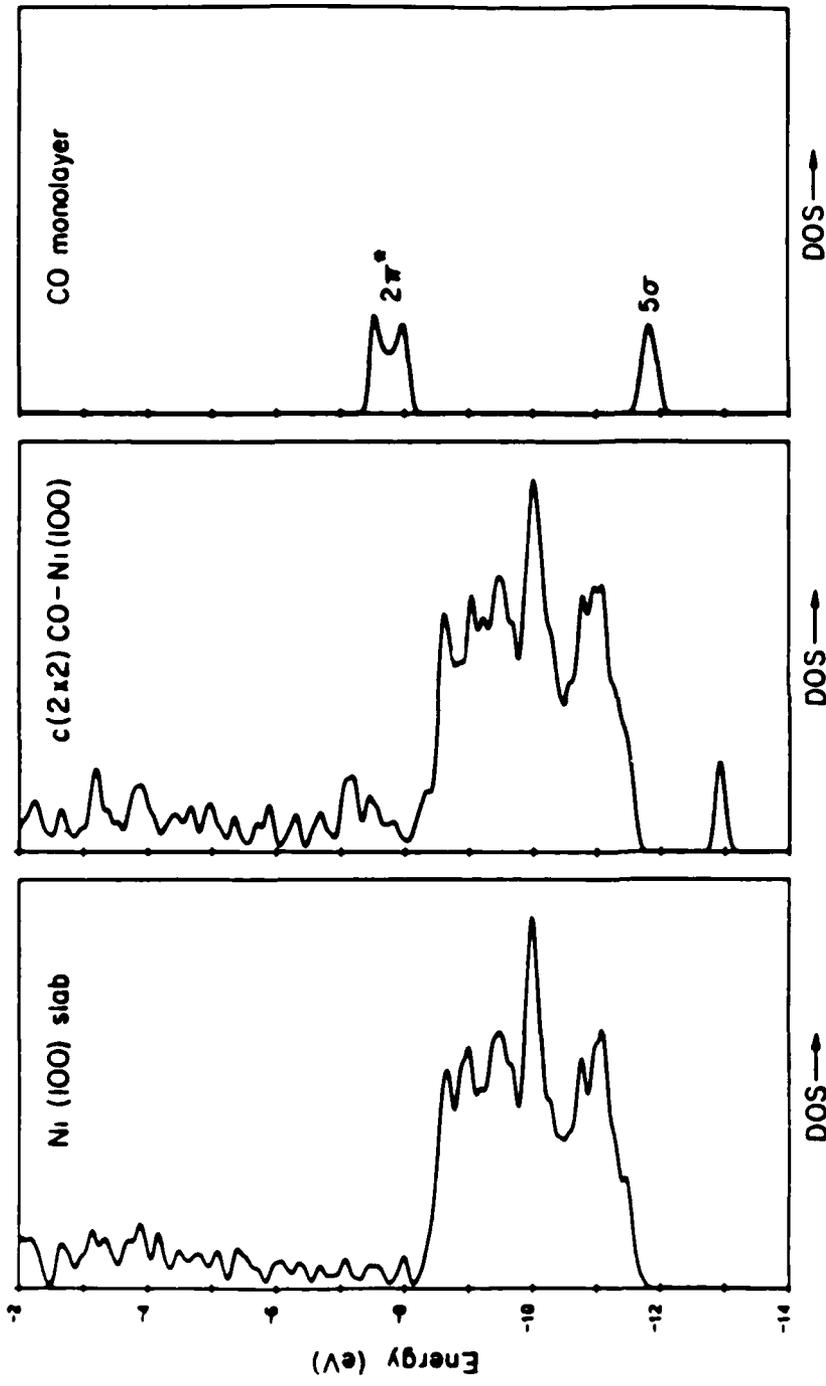


Figure 4. The total density of states of a model  $c(2 \times 2)CO-Ni(100)$  system (center), compared to its isolated 4-layer Ni slab (left) and CO monolayer components.

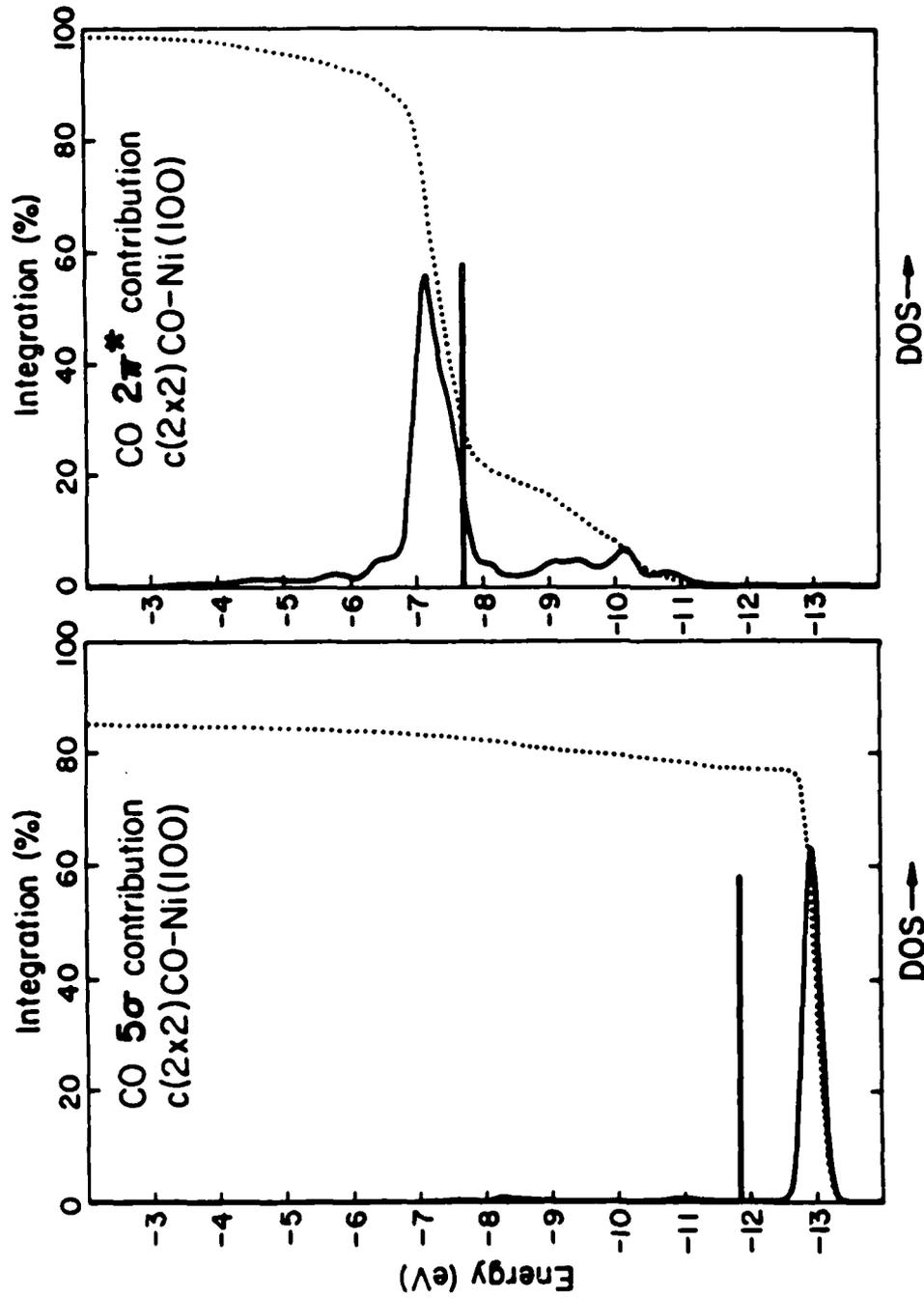


Figure 5. For the c(2x2)CO-Ni(100) model this shows the  $5\sigma$  and  $2\pi^*$  contributions to the total DOS. Each contribution is magnified. The position of each level in isolated CO is marked by a line. The integration of the DOS contribution is given by the dotted line.

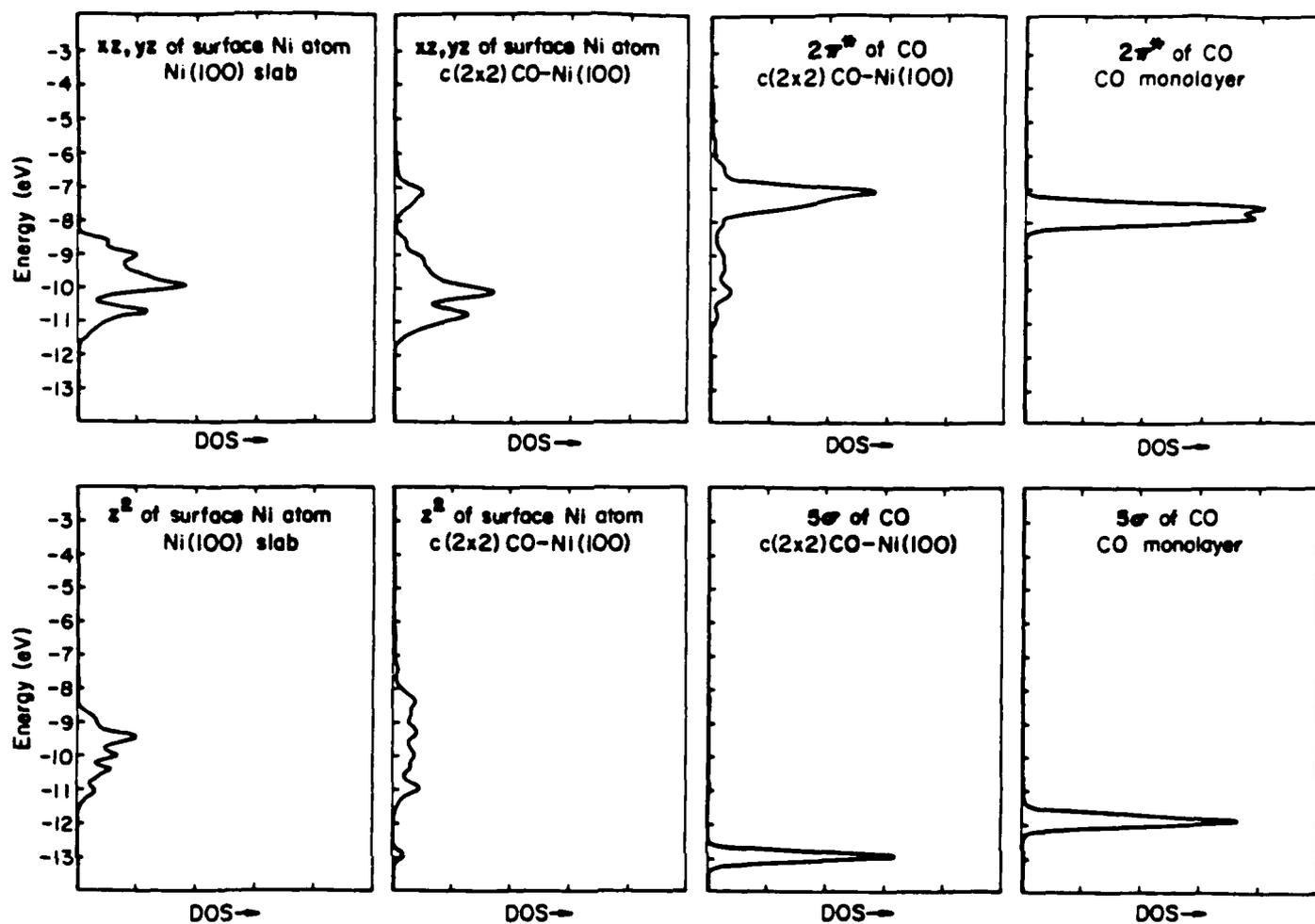


Figure 6. "Interaction Diagrams" for  $5\sigma$  and  $2\pi^*$  of  $c(2 \times 2)\text{CO-Ni}(100)$ . The extreme left and right panels in each case show the contributions of the appropriate orbitals ( $z^2$  for  $5\sigma$ ,  $xz, yz$  for  $2\pi^*$ ) of a surface metal atom (left), and of the corresponding isolated CO monolayer MO. The middle two panels then show the contributions of the same fragment MO's to the DOS of the composite chemisorption system.

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

We saw in the previous section the band structures and DOS of the CO overlayer and the Ni slab separately (Fig. 1-3). Now let's put them together in Fig. 4. The adsorption geometry is that shown in 2, with Ni-C 1.8 Å

Figure 4

It's clear that the composite system c(2x2)CO-Ni(100) is roughly a superposition of the slab and CO layers. Yet things have happened. Some of them are clear - the  $5\sigma$  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?

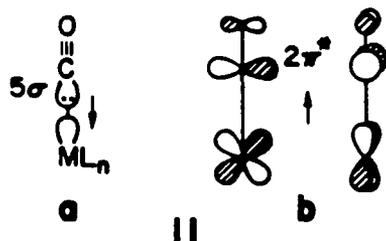
These questions are basically ones of the location of electrons in space, a matter of abiding interest to chemists. Given a molecular orbital, we want to know how the electrons in that orbital are distributed. It's possible to do this for the highly delocalized Bloch functions as well, though not without a computer. Orbital by orbital, atom by atom, band by band, the computer partitions the electron density among the contributing orbitals or atoms. The procedure is called a Mulliken population analysis.<sup>11</sup> It is repeated for several k points in the Brillouin zone, and then returns to real space by averaging over these points. These decompositions of the DOS are often called "projections of the DOS" or "local DOS" in the solid state trade. The integral of these projections up to the Fermi level then gives the total electron density in a given atom or in a specified orbital.

Let's see how this decomposition helps us to trace down the bonding in the chemisorbed CO system. Figure 5 shows the  $5\sigma$  and  $2\pi^*$  contributions to the DOS. The dotted line is a simple integration of the DOS of the

Figure 5

fragment of contributing orbital. The relevant scale, 0 to 100%, is to be read at top. This integration shows the total percent of the given orbital that's occupied at a specified energy. It is clear that the  $5\sigma$  orbital, though pushed down in energy, remains quite localized. Its occupation (the integral of this DOS contribution up to the Fermi level) is 1.62 electrons. The  $2\pi^*$  orbital obviously is much more delocalized. It is mixing with the metal d band, and, as a result, there is a total of 0.74 electrons in the  $2\pi^*$  levels together.

Which levels on the metal surface are responsible for these interactions? In discrete molecular systems we know that the important contributions to bonding are forward donation, 11a, from the carbonyl lone pair,  $5\sigma$ , to some appropriate hybrid on a partner metal fragment, and back donation, 11b, involving the  $2\pi^*$  of CO and a  $d_{\pi}$  orbital,  $xz,yz$ , of the metal. We would



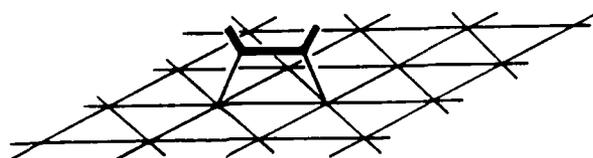
suspect that similar interactions are operative on the surface.

These can be looked for by setting side by side the  $d_{\sigma}(z^2)$  and  $5\sigma$  contributions to the DOS, and  $d_{\pi}(xz,yz)$  and  $2\pi^*$  contributions, in Fig. 6 the  $\pi$  interaction is clearest: note how  $2\pi^*$  picks up density where the  $d_{\pi}$  states are, and vice versa, the  $d_{\pi}$  states have a "resonance" in the  $2\pi^*$  density.

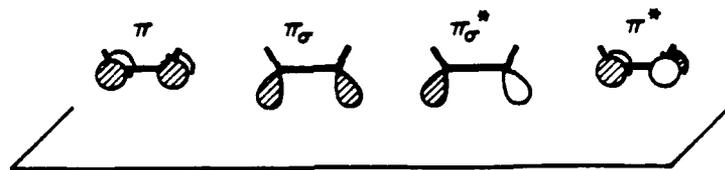
Figure 6

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  $5\sigma$  and  $2\pi^*$ . The reader can confirm at least that  $5\sigma$  does not pick up density where  $d_\pi$  states are, nor  $2\pi^*$  where  $d_\sigma$  states are mainly found.<sup>9</sup>

Let's consider another system in order to reinforce our comfort with these fragment analyses. In 3 we drew several acetylene-Pt(111) structures with coverage =  $\frac{1}{4}$ . Consider one of these, the dibridged adsorption site alternative 3b redrawn in 12. The acetylene brings to the adsorption process two  $\pi$  and two  $\pi^*$  orbitals. These are sketched in 13. If the acetylene is



12



13

bent, as it is in all molecular and surface complexes known, the degeneracy of  $\pi$  and  $\pi_\sigma$ , and of  $\pi_\sigma^*$  and  $\pi^*$  is broken. We jump right away to the contributions of the various acetylene orbitals to the total DOS of 3b, shown in Fig. 7. The sticks show the positions of the acetylene orbitals in the isolated

Figure 7

molecule. It is clear that  $\pi$  and  $\pi^*$  interact less than  $\pi_\sigma$  and  $\pi_\sigma^*$ . And the overlap reasons behind that differential are obvious. Note the large effect on  $\pi_\sigma^*$ , analogous to what we saw for  $2\pi^*$  of CO.

A third system: in the early states of dissociative  $H_2$  chemisorption, it is thought that  $H_2$  approaches perpendicular to the surface, as in 14. Consider Ni(111), related to the Pt(111) surface we have discussed earlier.

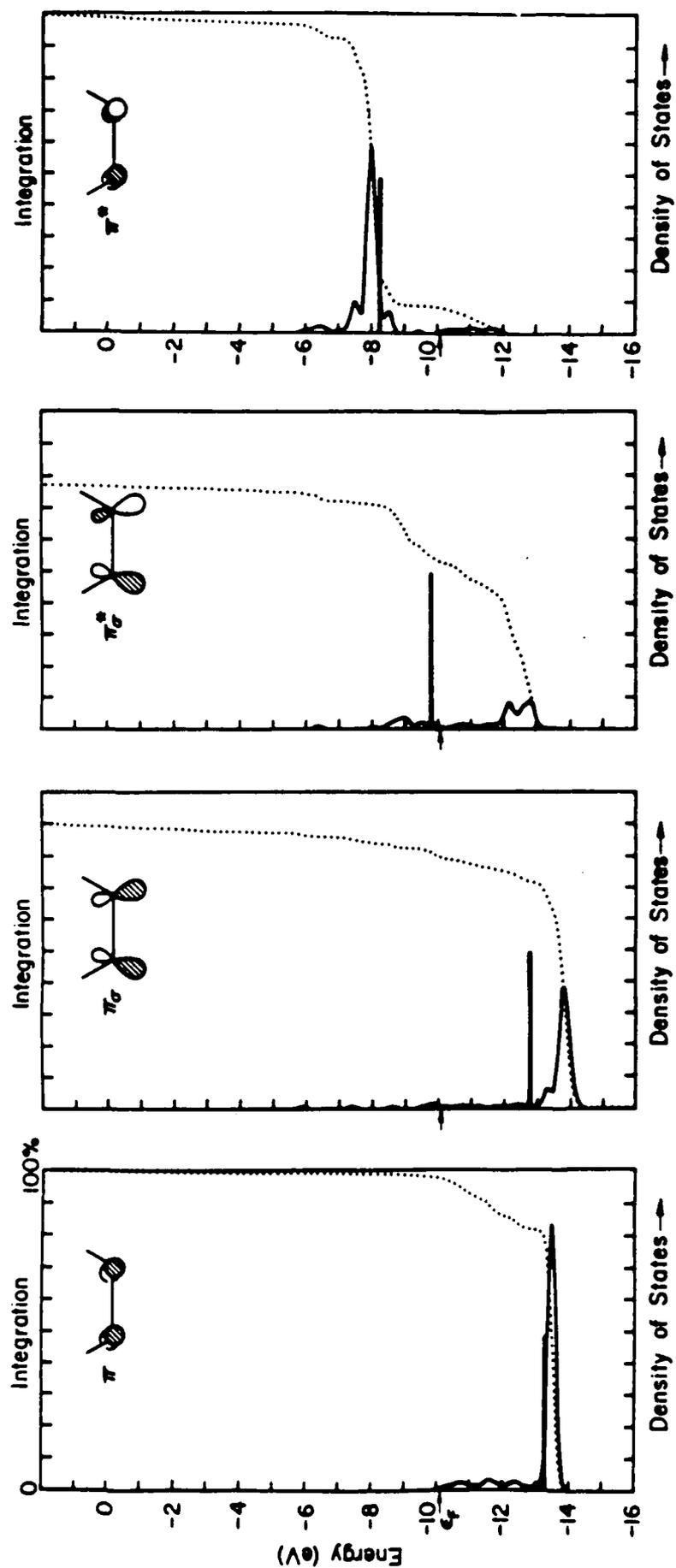
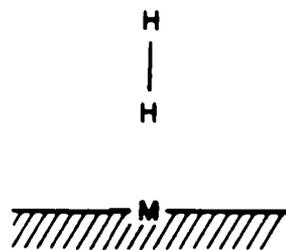


Figure 7. From left to right: contributions of  $\pi$ ,  $\pi_G$ ,  $\pi_G^*$  and  $\pi^*$  to the DOS of C<sub>2</sub>H<sub>2</sub> in a two-fold geometry on Pt(111). The lines mark the positions of these levels in a free bent acetylene. The integrations of the DOS contributions are indicated by the dotted line.



14

Fig. 8 shows a series of three snapshots of the total DOS and its  $\sigma_U^*(H_2)$  projection.<sup>13</sup> These are computed at separations of 3.0, 2.5 and 2.0 Å from

Figure 8

the nearest H of  $H_2$  to the Ni atom directly below it. The  $\sigma_g$  orbital of  $H_2$  (the lowest peak in the DOS in Fig. 8) remains quite localized. But the  $\sigma_U^*$  interacts, is strongly delocalized, with its main density pushed up. The primary mixing is with the Ni s,p band. As the  $H_2$  approaches some  $\sigma_U^*$  density comes below the Fermi level.

Why does  $\sigma_U^*$  interact more than  $\sigma_g$ ? The classical perturbation theoretic measure of interaction

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

helps one to understand this.  $\sigma_U^*$  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  $\sigma_g$ , 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  $\sigma_U^*$  coefficients are substantially greater than those in  $\sigma_g$ . This has been pointed out by many people, but in the present context importantly emphasized by Shustorovich and Baetzold.<sup>2,14,15</sup>

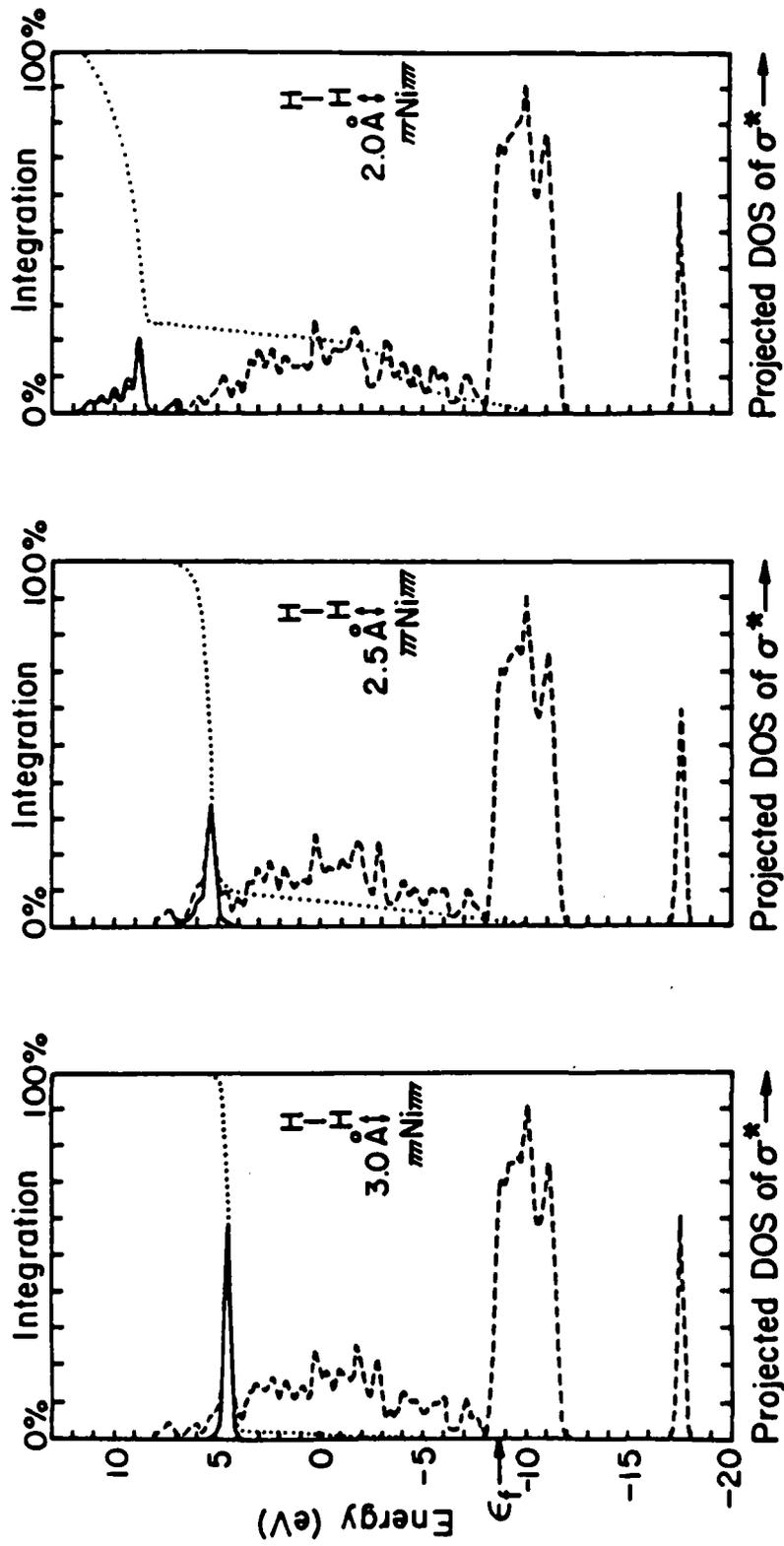


Figure 8. That part of the total DOS (dashed line) which is in the H<sub>2</sub> σ<sub>U</sub>\* (solid line) at various approach distances of a frozen H<sub>2</sub> to a Ni(111) surface model. The dotted line is an integration of the H<sub>2</sub> density.

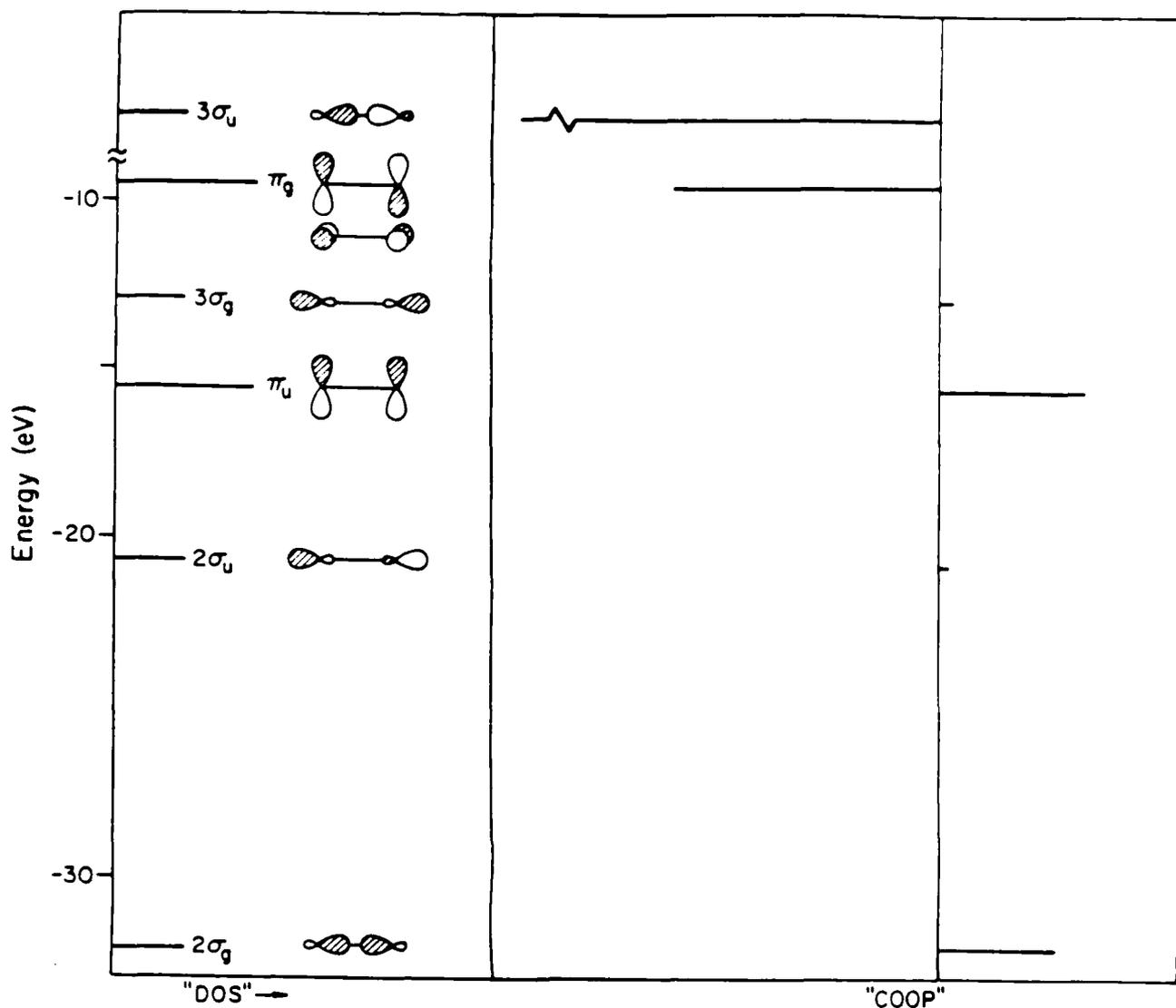


Figure 9. The orbitals of  $N_2$  (left) and a "solid state way" to plot the DOS and COOP curves for this molecule.

where are the bonds?

When CO or acetylene chemisorb partial bonds are formed to the surface. Bonds within the adsorbed molecule weaken, and we see the evidence for that directly in the diminished frequencies for specific vibrational modes, e.g. the CO stretch. It behooves us to look for a theoretical index of that bonding. This index, a COOP curve, which we will define, will allow us to push our detective investigation further, and it will help to restore a local, chemical viewpoint in an analysis of chemisorption.

The problem is how to find bonds in the highly delocalized bands. The idea is to extend the Mulliken population analysis to the crystal. Consider a two-center orbital:

$$\psi = c_1\phi_1 + c_2\phi_2$$

We want  $\psi$  to be normalized:

$$\int \psi^2 d\tau = 1 = \int (c_1\phi_1 + c_2\phi_2)^2 d\tau = c_1^2 + c_2^2 + 2c_1c_2S_{12}$$

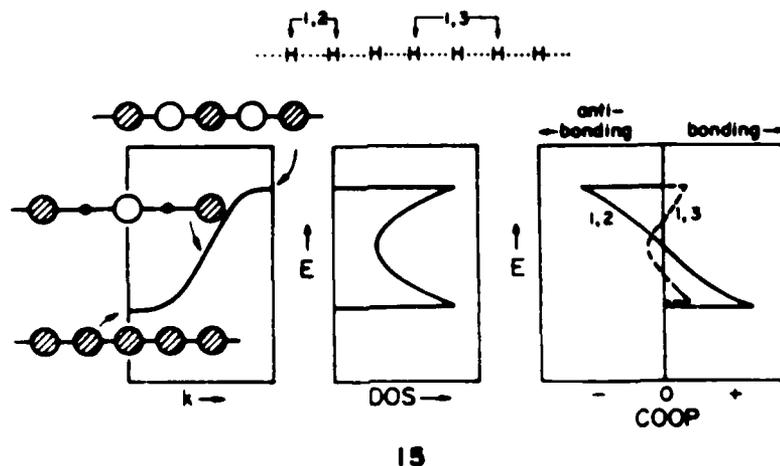
Another way to think about the normalization is that it also gives the distribution of an electron in  $\psi$ . It is clear that the overlap term  $2c_1c_2S_{12}$  is a characteristic of bonding. If the overlap integral  $S_{12}$  is taken as positive (and it can always be arranged so) then this quantity 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 this Mulliken "overlap population", for that is what  $2c_1c_2S_{12}$  (summed over all orbitals on the two atoms, over all occupied MO's) is called, depends on  $c_i, c_j, S_{ij}$ .<sup>22</sup>

Before we move into the solid, we might take a look at how these overlap populations might be used in a molecular problem. Fig. 9 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 one for  $\sigma$ , two for  $\pi$ ) and the contributions of these levels to the overlap population.  $1\pi_g$  and  $1\pi_u$  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 non-bonding. These are best characterized as lone pair combinations.  $\pi_u$  is bonding,  $\pi_g$  antibonding,  $3\sigma_u$  the  $\sigma^*$  level. The right-hand side of Fig. 9 characterizes the bonding in  $N_2$  at a glance. It tells us that maximal bonding is there for 7 electron pairs; more or fewer electrons will lower the N-N overlap population. It would be nice to have something like this for extended systems.

A bond indicator is easily constructed for the solid. An obvious procedure is to take all the states in a certain energy interval and interrogate them as to their bonding proclivities, measured by the Mulliken overlap population,  $2c_i c_j S_{ij}$ . What we are defining is an overlap population weighted density of states. The beginning of the obvious acronym (OPWDOS) unfortunately has been preempted by another common usage in solid state physics. For that reason, we have called this quantity COOP, for crystal orbital overlap population.<sup>16</sup> It's also nice to think of the suggestion of orbitals working together to make bonds in the crystal, so the word is pronounced "co-op".

To get a feeling for this quantity, let's think what a COOP curve for a hydrogen chain looks like. The simple band structure and DOS were given earlier, 10; they are repeated with the COOP curve in 15.



15

To calculate a COOP curve, one has to specify a bond. Let's take the nearest neighbor 1,2 interaction. The bottom of the band is 1,2 bonding, the middle non-bonding, the top antibonding. The COOP curve obviously has the shape shown at right in 23. 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 non-bonding. That curve, the dotted line in the drawing is different in shape. And, of course, its bonding and antibonding amplitude is much smaller because of the rapid decrease of  $S_{ij}$  with distance.

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

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

Let's see how the COOP curve can be used to support the picture of CO chemisorption that was described above. The relevant curve is in Fig. 10. The solid line describes Ni-C bonding, the dotted line C-O bonding. Note

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Figure 10

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the major contribution to Ni-C bonding in both the 5 $\sigma$  peak and the bottom of the d band. The 5 $\sigma$  contribution is due to  $\sigma$  bonding, 11a. But the bottom of the d band contributes through  $\pi$ -bonding, 11b. This is evident from the "mirroring" C-O antibonding in the region. The antibonding component of that d- $\pi^*$  interaction is responsible for the Ni-C and C-O antibonding above the Fermi level.

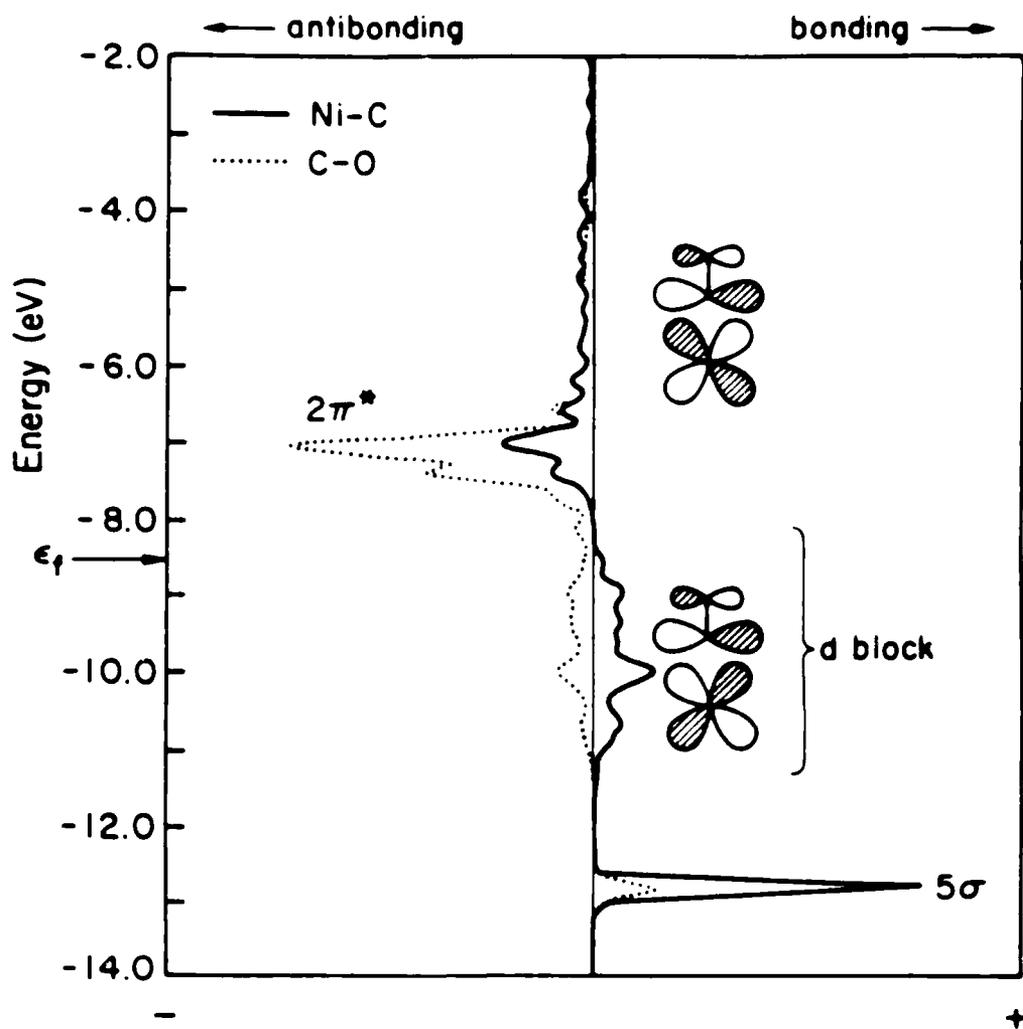
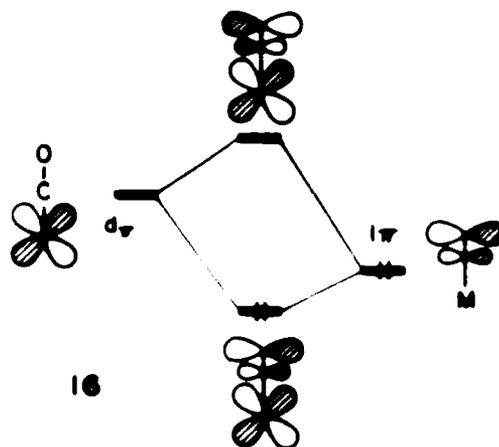


Figure 10. Crystal orbital overlap population for CO, on-top, in a  $c(2 \times 2)$ CO-Ni(100) model. Representative orbital combinations are drawn out.

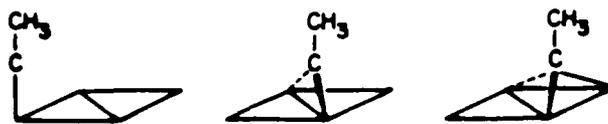
It may be useful to emphasize that these curves are not only descriptive, but also form a part of the story of tracing down interaction. For instance, supposing we were not so sure that it is the  $d_{\pi}-2\pi^*$  interaction which is responsible for a good part of the bonding. Instead, we could have imagined  $\pi$  bonding between  $1\pi$  and some unfilled  $d_{\pi}$  orbitals. The interaction is indicated schematically in 16. If this mixing were impor-



tant, the  $d$  block orbitals, interacting in an antibonding way with  $1\pi$  below them, should become in part Ni-C antibonding and C-O bonding. Nothing of this sort is seen in Fig. 9. The C-O antibonding in the  $d$  block region is, instead, diagnostic of  $2\pi^*$  mixing being important.

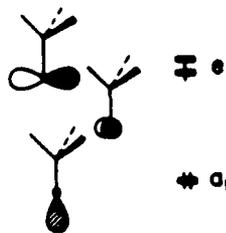
Incidentally, the integrated overlap populations up to the Fermi level are Ni-C 0.84, C-O 1.04. In free CO the corresponding overlap population is 1.21. The bond weakening is largely due to population of  $2\pi^*$  on chemisorption.

Another illustration of the utility of OCF curves is provided next by a question of chemisorption site preference. In many surfaces, including Pt(111), a particularly stable dead end in the surface chemistry of acetylene is ethynidyne,  $\text{CCH}_3$ .<sup>17</sup> How that extra hydrogen is picked up is a fascinating question. But let's bypass that and think about where the  $\text{CCH}_3$  wants to be. 17 shows three alternatives - 1-fold on-top, 2-fold on-bridging, and 3-fold on-capping. Experiment and theory show a great preference for the capping site. Why



17

The important frontier orbitals of a carbyne, CR, are shown in 18. The C 2p orbitals, the e set, are a particularly attractive acceptor set,



18

certain to be important in any chemistry of this fragment. We could trace its involvement in the three alternative geometries 17 via DOS plots, but instead we choose to show in Fig. 11 the Pt-C COOP curve for 1-fold and 3-fold adsorption.

Figure 11

In both on-top and capping sites the carbyne e set finds metal orbitals to interact with. Bonding and antibonding combinations form. The coupling overlaps are much better in the capping site. The result is that the carbon-metal e-type antibonding combinations do not rise above the Fermi level in the 1-fold case, but do so in the 3-fold case. Figure 11 clearly shows this - the bonding and antibonding combinations are responsible for recognizable positive and negative COOP peaks. The total surface-CCH, overlap populations are 0.777 in the 1-fold case, 1.600 in the 3-fold case. The total energy follows these bonding considerations; the capping site is much preferred.<sup>12</sup>

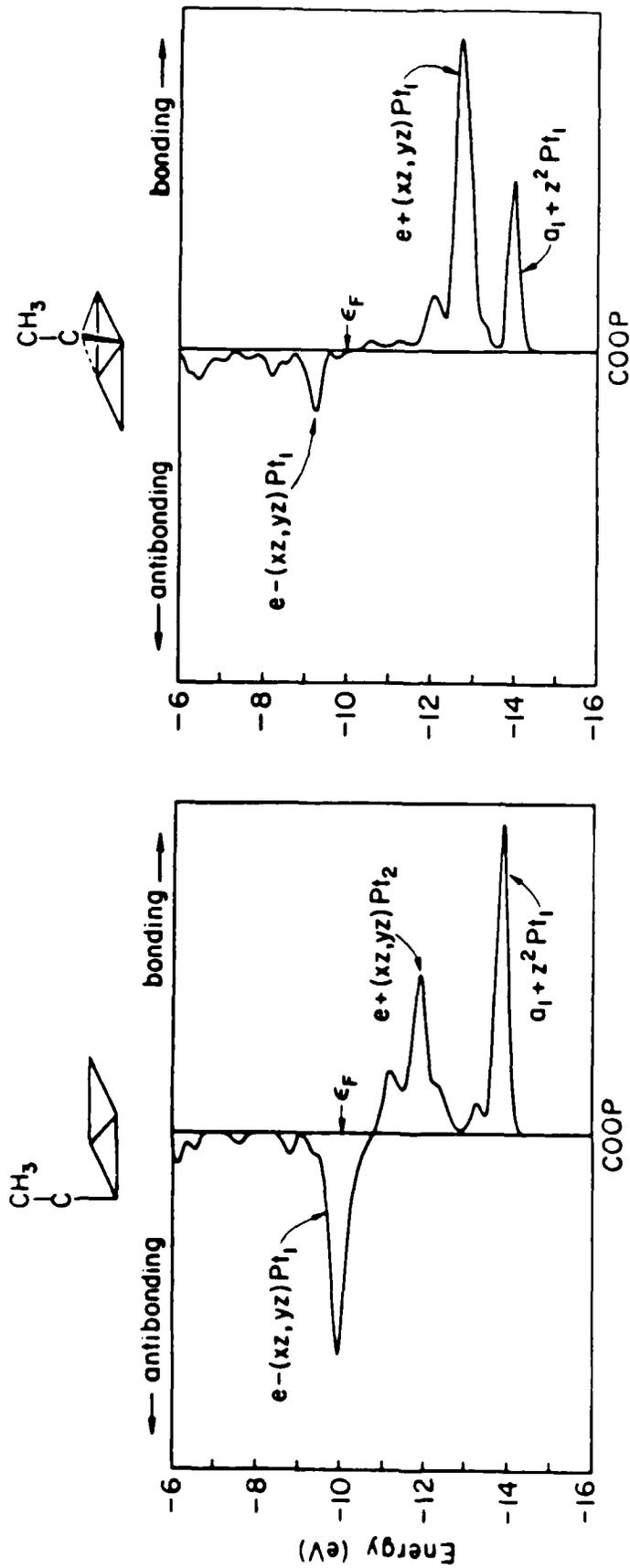
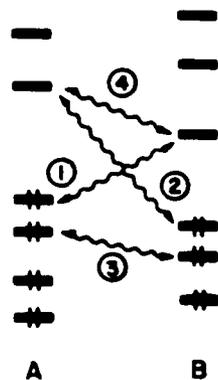


Figure 11. COOP curve for the  $\alpha$ -carbon- $Pt_1$  bond in the 1-fold (left) and 3-fold (right) geometry of ethylidyne,  $\text{CCH}_3$ , on  $Pt(111)$ .

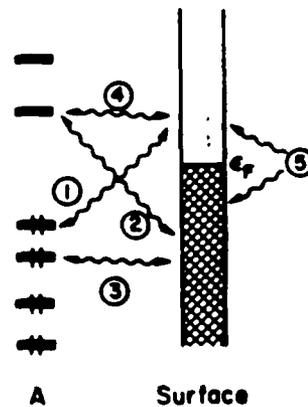
### Orbital Interactions in the Solid

The apparatus of densities of states and crystal orbital overlap populations has restored to us a frontier orbital or interaction diagram way<sup>18</sup> of thinking about the way molecules bond to surfaces. Whether it is  $2\pi^*$  CO with  $d_{\pi}$  of Ni(100), or e of CR with some part of the Pt(111) band, in either case we can describe what happens in terms of local action. The only novel feature so far is that the interacting orbitals in the solid often are not single orbitals localized in energy or space, but bands.

A side-by-side comparison of orbital interactions in discrete molecules and of a molecule with a surface is revealing. 19 is a typical molecular interaction diagram, 20 a molecule-surface one. Even though a molecule is,



19



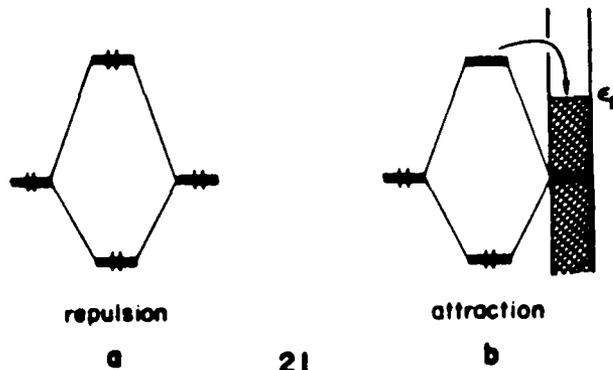
20

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

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

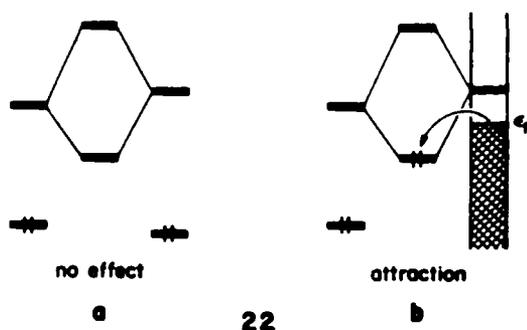
(i) The controlling interactions are likely to be the two-orbital, two-electron stabilizing interaction ① and ②. Depending on the relative energy of the orbitals and the quality of the overlap, each of these interactions will involve charge transfer from one system to the other. In interaction ①, A is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

(ii) Interaction ③ is a two-orbital, four-electron one. It is destabilizing, repulsive, as 21a shows. In one-electron theories, this is where steric effects, lone pair repulsions, etc. are to be found.<sup>18</sup> These interactions may be important. They may prevent bonding, interactions ①, ② from being realized. There is a special variant of this interaction which may occur in the solid, but is unlikely in discrete molecules. This is sketched in 21b - the antibonding component of a four-electron, two-orbital interaction may rise above the Fermi level. It will dump its electrons at the Fermi level, and can no longer destabilize the system. Only the intersystem bonding combination remains filled.



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

(iii) Interaction ④ involves two empty orbitals. In general, it would be discounted as having no energetic consequences. This is strictly true in molecular cases, 22a. But in the solid, where there is a continuum of levels, the result of such interaction may be that the bonding combination of the two interacting levels may fall below the Fermi level (22b). Becoming occupied, it will enhance fragment A - surface bonding. Again,



there may be an effect on the surface, because it has to supply the electrons for the occupation of that level.

(iv) Interaction ⑤ is something special to the metallic solid, that comes from the states of the metal surface forming a continuum. The interaction describes the second order energetic and bonding consequences of shifts of electron density around the Fermi level. First order interactions ①, ②, ③ and ④ all will move metal levels up and down. These metal levels, the ones that move, will belong to the atoms on the surface interacting with the adsorbate. The Fermi level remains constant - the bulk and surface are a nice reservoir of electrons. So electrons (holes) will flow in the surface and in the bulk underneath it, in order to compensate for the primary interactions. These compensating electrons or holes are, however,

not innocent of bonding themselves. Depending on the electron filling, they may be bonding or antibonding in the bulk, between surface atoms not involved with the adsorbate, even in surface atoms so involved, but in orbitals that are not used in bonding to the chemisorbed molecule.

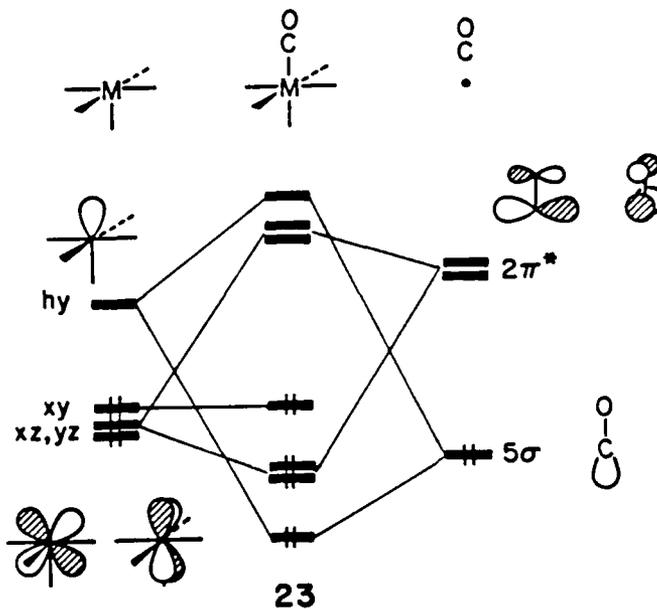
Before I leave this section, I should like to say quite explicitly that there is little novel in the use my coworkers and I have made of interaction diagrams and perturbation theory applied to surfaces. A. B. Anderson<sup>2</sup> has consistently couched his explanations in that language, and so have Shustorovich and Baetzold<sup>2</sup> - Shustorovich's account of chemisorption is based on an explicit perturbation-theoretic model. There is a very nice, quite chemical treatment of such a model in the work of Gadzuk<sup>19a</sup>, based on earlier considerations by Grimley<sup>19b</sup> and van Santen<sup>19c</sup> draws interaction diagrams quite analogous to ours. Salem and his coworkers<sup>19d</sup> have developed a related perturbation theory based on a way of thinking about catalysis that includes a discussion of model finite Hückel crystals, privileged orbitals, generalized interactions diagrams, and the dissolution of adsorbate into catalyst bands.

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

A Case Study: CO on Ni(100)

The Ni(100)-CO system already discussed<sup>9</sup> seemed to provide an excellent example of the primary two-electron interactions at work. We found charge transfer from  $5\sigma$  (its population going from 2.0 in the free CO to 1.62 in the CO-surface complex) and back donation from the surface to  $2\pi^*$  (whose population rose from 0 to 0.74). Actually, there is an interesting wrinkle here, in that the 4 and 0 electron interactions mentioned in point (3), above, manifest themselves.

To set a basis for what we will discuss, let's prepare a model molecular system for comparison. We'll build a metal-carbonyl bond between a  $d^6ML_5$  system and a carbon monoxide. The interaction diagram, 23, should certainly be familiar; the acceptor function of the  $ML_n$  fragment is provided by a low-lying  $dsp$  hybrid.<sup>20</sup> The two-electron bonding interactions are quite



explicit. They result ( $M = Ni^{++}$ ,  $L = H^-$ ,  $M - H$  1.7 Å,  $M - CO$  1.9 Å) in a depopulation of  $5\sigma$  by 0.41, and a population of  $2\pi^*$  by 0.51 electrons.

Table 1. Some Electron Densities in a Model  $H_5NiCO^-$  and the  $c(2 \times 2)CO-Ni(100)$  System

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

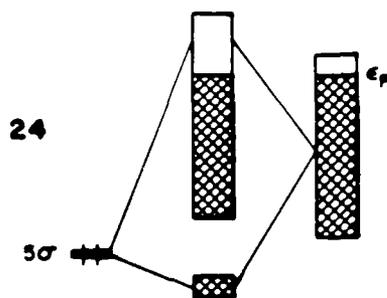
a) for those surface atoms which have CO on them.

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

The metal functions involved in these interactions react correspondingly: so  $xz, yz$  loses 0.48 electrons, and the hybrid orbital gains 0.48. The net charge drifts are pretty well-described by the sum of what happens in these orbitals: CO as a whole gains  $0.01e^-$ , and the  $ML_n$  fragment loses the same. The information is summarized in Table 1.

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

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



above the Fermi level (see 24 for a schematic). The net result is some loss of  $z^2$  density and concomitant bonding.<sup>21</sup>

Where do those "lost" electrons go? Table 1 indicates that some, but certainly not all, go to the CO. Many are "dumped" at the Fermi level into orbitals that are mainly metal  $d$  band, but on the inner metal atoms, or on

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

Before leaving this instructive example, I trust the point is not lost that the primary bonding interactions ① and ②, are remarkably alike in the molecule and on the surface. These forward and back donations are, of course, the consequence of the classical Dewar-Chatt-Duncanson model of ethylene or another fragment bonding in an organometallic molecule.<sup>22</sup> In the surface case, this is often termed the Blyholder model, the reference being to a perceptive early suggestion of such bonding for CO on surfaces.<sup>21b</sup> More generally, interactions ① and ② are the fundamental electronic origins of the cluster-surface analogy. This is a remarkably useful construction of a structural, spectroscopic and thermodynamic link between organometallic chemistry and surface science.<sup>23</sup>

### Barriers to Chemisorption

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

Consider a model molecule, simplified here to a single occupied level, approaching a surface. Some schematic level diagrams and an associated total energy curve are drawn in Fig. 12. The approach coordinate trans-

Figure 12

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

This simple picture was first given, to my knowledge, by E.L. Garfunkel and by C. Minot and their coworkers.<sup>24</sup> In reality, the repulsion at large metal adsorbate distances will be mitigated and, in some cases overcome, by attractive two-electron interactions of type ① or ② (see 20). But the presence of the interaction, I think, is quite general. It is responsible, in my opinion, for some of the large kinetic barriers to CO chemisorption and CH<sub>4</sub> decomposition measured in the elegant beam experiments of S.T. Ceyer and coworkers.

In reality, what we are describing is a surface crossing. And there may be not one, but several such, for it is not a single level, but groups of levels which are "pushed" above the Fermi level. There may be several metastable minima, precursor states, as a molecule approaches a surface.<sup>25</sup>

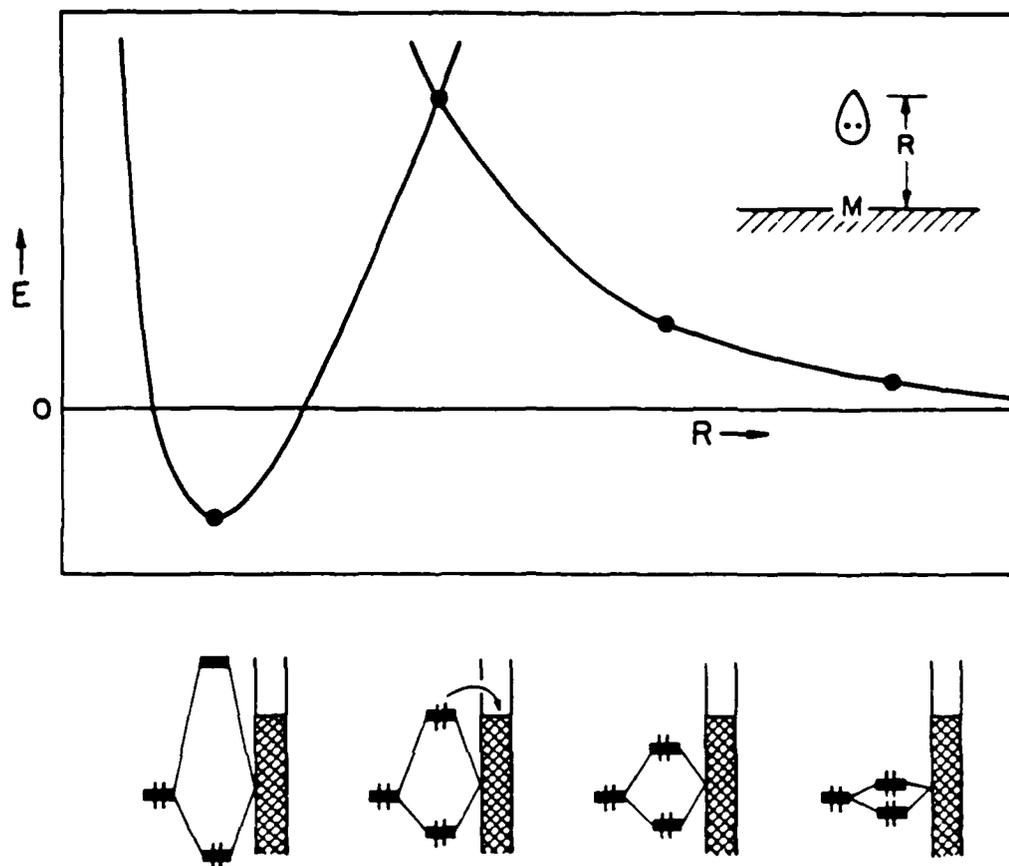
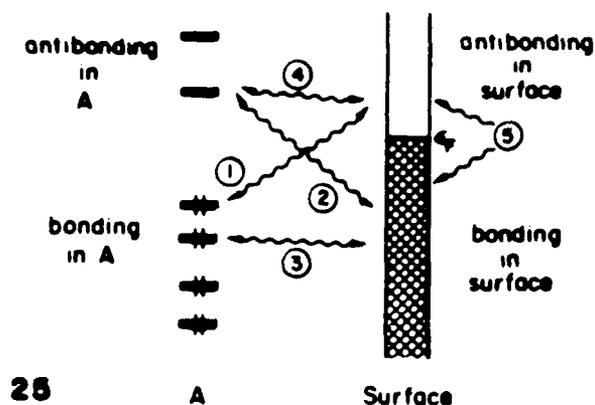


Figure 12. A schematic drawing showing how the interactions of levels (bottom) can lead to a potential energy curve (top) which has a substantial barrier to chemisorption.  $R$  measures the approach of a molecule, symbolized by a single interacting electron pair, to a surface. At large  $R$  repulsive four-electron interactions dominate. At some  $R$  (second point from left), the antibonding combination crosses the Fermi level, and dumps its electrons. At shorter  $R$  there is bonding.

In this section we have mentioned, for the second time, the bonding consequences of emptying, at the Fermi level, molecular orbitals delocalized over adsorbate and surface, and antibonding between the two. Salahub<sup>27</sup> and Anderson<sup>28</sup> stress the same effect. There is a close relationship between this phenomenon and a clever suggestion made some time ago by Mango and Schachtschneider<sup>9</sup> on the way in which metal atoms (with associated ligands) lower the activation barriers for forbidden concerted reactions. They pointed out that such electrons, instead of proceeding on to high antibonding levels, can be transferred to the metal. We, and others, have worked out the details of this kind of catalysis for some specific organometallic reactions, such as reductive elimination.<sup>29</sup> It's quite a general phenomenon, and we will return to it again in a subsequent section.

Chemisorption is a Compromise

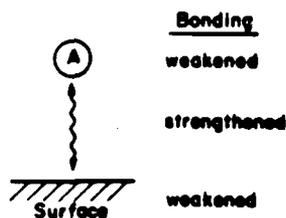
Consider again the basic molecule-surface interaction diagram 25, now drawn specifying the bonding within each component. The occupied orbitals



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

What is the effect of the various interactions on bonding within and between the adsorbate and the surface? Interactions (1) and (2) are easiest to analyze - they bind the molecule to the surface, and in the process they transfer electron density from generally bonding orbitals in the component

to antibonding orbitals in the other. The net result: a bond is formed between the adsorbed molecule A and the surface. But bonding within the surface and within A is weakened.



Schematically this is indicated in 26. What about interactions (3) and (4)? For moderate interaction (3) is repulsive and (4) has no effect. Neither does anything to bonding within A or the surface. When interaction grows, and antibonding ((3)) or bonding ((4)) states are swept past the Fermi level, these interactions provide molecule-surface bonding. At the same time, they weaken bonding in A, transferring electron density into antibonding levels and out of bonding ones. What the effect of such strong interaction of type (3) or (4) or, more generally, of second order electron shifts, type (5), is on bonding within the surface - that depends on the position of the Fermi level and the net electron drift.

The sum total of these interactions is still the picture of 26: metal-adsorbate bonding is accomplished at the expense of bonding within the metal and the adsorbed molecule. This is the compromise alluded to in the heading of this section.

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

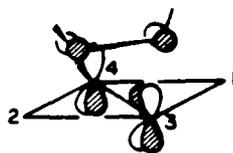
Earlier we drew four possible geometries for a layer of acetylene, coverage =  $\frac{1}{2}$ , on top of Pt(111), 3. Table 2 shows some of the indices

of the interaction in the four alternative geometries, in particular the occupations of the four acetylene fragment orbitals ( $\pi, \pi_\sigma, \pi_\sigma^*, \pi^*$ ), the various overlap populations, and calculated binding energies.

Table 2

The three-fold bridging geometry (3c) is favored, in agreement with experiment and other theoretical results.<sup>12</sup> One should say right away that this may be an accident - the extended Hückel method is not especially good at predicting binding energies. The two-fold (3b) and four-fold (3d) sites are slightly less bound, but more stable than the one-fold site, 3a. But this order of stability is not a reflection of the extent of interaction. Let's see how and why this is so.

The magnitude of interaction could be gauged by looking at the acetylene fragment orbital populations, or the overlap population. In the detailed discussion of the two-fold site in an earlier section, we saw  $\pi$  and  $\pi^*$  more or less unaffected,  $\pi_\sigma$  depopulated,  $\pi_\sigma^*$  occupied. As a consequence, Pt-C bonds are formed, the C-C bond weakened, and (interaction ⑤) some Pt-Pt bonds on the surface weakened. A glance at the fragment MO populations and overlap populations in Table 2 shows that all this happens much more in the four-fold site 3d - note that even  $\pi$  and  $\pi^*$  get strongly involved. The most effective interaction here is that shown in 27. Note that it is primarily of type ④.



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

Adsorbate induced surface reconstruction and dissociative chemisorption are merely natural extremes of this delicate balance. In each case, strong surface-adsorbate interactions direct the course of the transformation, either breaking up bonding in the surface so that it reconstructs, or disrupting the adsorbed molecules. An incisive discussion of the latter situation, for the case of acetylene on iron and vanadium surfaces has been provided by A. B. Anderson.<sup>30</sup>

Table 2. Bonding Characteristics of Several Acetylene Adsorption Sites on Pt(111).

	C <sub>2</sub> H <sub>2</sub>	Bare Surface				
Binding energy <sup>a</sup> (eV)			3.56	4.68	4.74	4.46
Overlap population	1.703					
C-C			1.405	1.319	1.206	1.080
Pt <sub>1</sub> -Pt <sub>2</sub>		0.136	0.126	0.077	0.088	-0.024
Pt <sub>2</sub> -Pt <sub>3</sub>		0.136	0.139	0.126	0.067	0.062
Pt <sub>1</sub> -Pt <sub>4</sub>		0.136	0.130	0.126	0.149	0.062
Pt <sub>1</sub> -C <sup>b</sup>			0.295	0.543	0.517	0.330
Pt <sub>3</sub> -C			0.001	0.005	0.193	0.266
Occupations						
π*	0.0		0.078	0.166	0.330	0.533
π <sub>σ</sub> *	0.0		0.811	1.059	1.028	0.893
π <sub>σ</sub>	2.0		1.733	1.588	1.591	1.566
π	2.0		1.959	1.956	1.731	1.530

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

<sup>b</sup> The carbon atom here is the closest to the particular Pt atom under consideration.

### Qualitative Reasoning About Orbital Interactions on Surfaces

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

Symmetry and perturbation theory make such a forward construction relatively simple, as they do for molecules. First, in extended systems the wave vector  $k$  is also a symmetry label, classifying different irreducible representations of the translation group. In molecules, only levels belonging to the same irreducible representation interact. Similarly, in the solid only levels of the same  $k$  can mix with each other.<sup>19</sup>

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

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

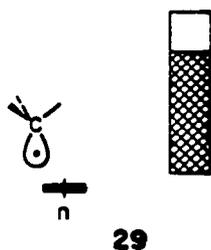
Overlap and separation in energy matter, and can be estimated.<sup>7d, 18, 19</sup>

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

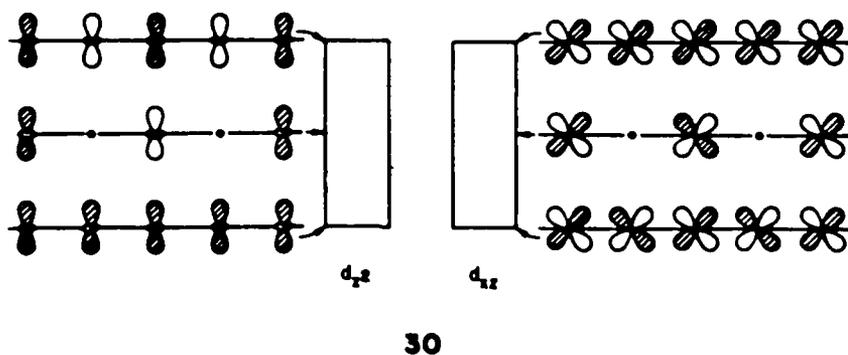
Consider the interaction of methyl,  $\text{CH}_3$ , with a surface, in on-top and bridging sites, 28.<sup>31</sup> Let's assume low coverage. The important methyl



orbital is obviously its lone pair  $n$ , for it will have the greatest overlap with any surface orbitals. The position of the lone pair relative to a metal  $d$  band is sketched in 29. How to analyze the interactions?

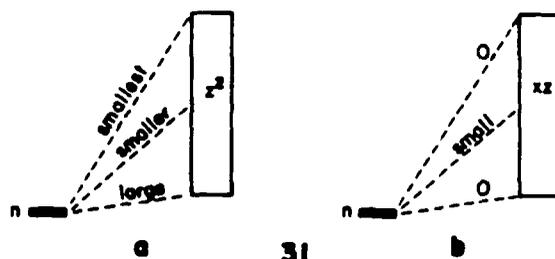


It's useful to take things apart and consider the metal levels one by one. 30, below, illustrates schematically some representative orbitals in the  $z^2$  and  $xz$  bands. The orbitals at the bottom of a band are metal-metal

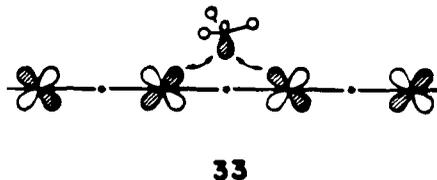
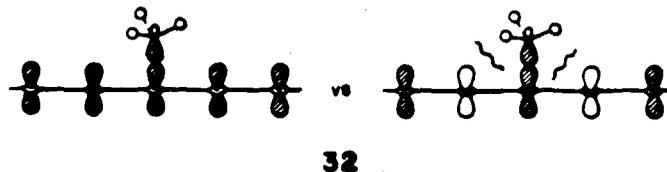


bonding, those in the middle non-bonding, at the top of the band antibonding. While things are assuredly more complicated in three dimensions, these one-dimensional pictures are indicative of what transpires.

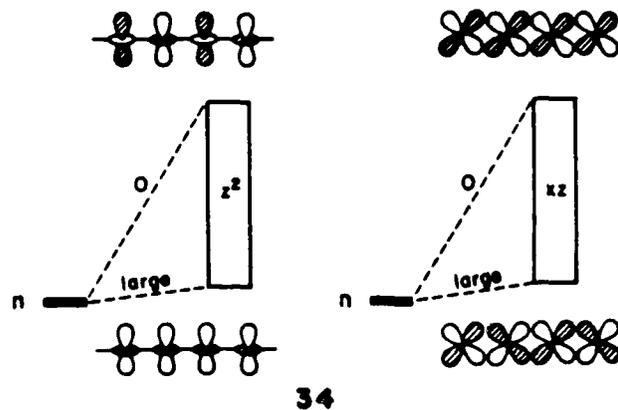
The methyl lone pair (it's really a band, but the band is narrow for low coverage) interacts with the entire  $z^2$  and  $xz$  bands of the metal, except at a few special symmetry-determined points where the overlap is zero. But it's easy to rank the magnitude of the overlaps, as I've done in 31 for on-top adsorption.



$n$  interacts with the entire  $z^2$  band, but because of the better energy match, more strongly so with the bottom of the band, as 32 shows. For interaction with  $xz$ , the overlap is zero at the top and bottom of the band, and never very efficient else-

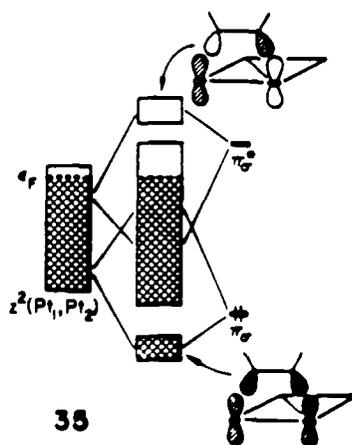


where (33). For adsorption in the bridge, as in 28b, we would estimate the



overlaps to go as 34. There is nothing mysterious in these constructions. The use of the perturbation theoretic apparatus and specifically the role of  $k$  in delimiting interactions on surfaces goes back to the work of Grimley<sup>19b</sup> and Gadzuk<sup>19c</sup>, and has been consistently stressed by Salem.<sup>19d</sup>

For a second example, let's return to acetylene on Pt(111), specifically in the two-fold and four-fold geometries.<sup>12</sup> In the two-fold geometry, we saw earlier (from the decomposition of the DOS) that the most important acetylene orbitals were  $\pi_\sigma$  and  $\pi_\sigma^*$ . These point toward the surface. Not surprisingly, their major interaction is with the surface  $z^2$  band. But  $\pi_\sigma$  and  $\pi_\sigma^*$  interact preferentially with different parts of the band, picking out those metal surface orbitals which have similar nodal patterns as the adsorbate. 35 shows this - in the two-fold geometry at hand the  $\pi_\sigma$  orbital interacts better with the bottom of the surface  $z^2$  band and the  $\pi_\sigma^*$  with



the top of that band.

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

We pointed out earlier that four-fold site chemisorption was particularly effective in weakening the surface bonding, and transferring electrons into  $\pi^*$  as well as  $\pi_{\sigma}^*$ , thus also weakening C-C bonding. The interaction responsible was drawn out in 27. Note that it involves the overlap of  $\pi^*$  specifically with the top of the  $xz$  band. Two formally empty orbitals interact strongly, and their bonding component (which is antibonding within the metal and within the molecule) is occupied.

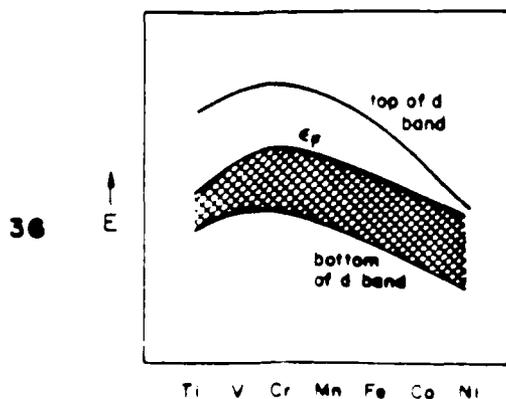
In general, it is possible to carry over frontier orbital arguments, the language of one-electron perturbation theory, to the analysis of surfaces.

### The Fermi Level Matters

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

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

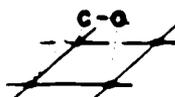
What actually happens is shown schematically in 36, perhaps the single most important diagram of metal physics. For a detailed discussion of



the band structure the reader is directed to the definite work of O. K. Andersen.<sup>32</sup> Roughly, what transpires is that the center of gravity of the d band falls as one moves to the right in the transition series. This is a consequence of the ineffective shielding of the nucleus for one d electron by all the other d electrons. The ionization potential of a single d electron increases to the right. The orbitals also become more contracted, therefore the less dispersed band at the right. At the same time, the band filling increases. The position of the band center of gravity and the filling compete; the former wins out. Thus the Fermi level falls at the right side of the transition series. What happens in the middle is a little more complicated.<sup>32</sup>

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

In general, early and middle transition metals break up carbon monoxide, late ones just bind it molecularly.<sup>33</sup> How the CO is broken up, in detail, is not known. Obviously, at some point the oxygen end of the molecule must come in contact with the metal atoms, even though the common coordination mode on surfaces, as in molecular complexes, is through the carbon. In the context of pathways of dissociation, the recent discovery of CO lying down on some surfaces, 37, is intriguing.<sup>34</sup> Perhaps such geometries intervene



37

on the way to splitting the diatomic to chemisorbed atoms.

Parenthetically, the discovery of  $\underline{37}$ , and of some other surface species bound in ways no molecular complex shows, should make inorganic and organo-metallic chemists read the surface literature not only to find references with which to decorate grant applications. The surface-cluster analogy, of course, is a two-way street. So far, it has been used largely to provide information (or comfort for speculations) for surface studies, drawing on known molecular inorganic examples of binding of small molecules. But now surface structural studies are better, and cases are emerging of entirely novel surface binding modes. Can one design molecular complexes inspired by structures such as  $\underline{37}$ ?

Returning to the problem of the metal surface influence on the dissociation of CO, we cannot study the reaction path, yet. But we can look at molecular chemisorption, C end bonded, and see if there are any clues. Table 3 shows one symptom of the bonding on several different surfaces,

Table 3

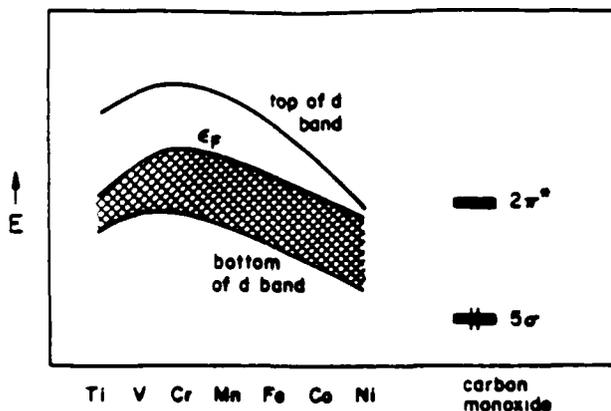
the population of CO  $5\sigma$  and  $2\pi^*$ .<sup>9</sup>

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

The reason for these bonding trends is obvious.  $\underline{38}$  superimposes the position of CO  $5\sigma$  and  $2\pi^*$  levels with the metal d band.  $5\sigma$  will interact more weakly as one moves to the left, but the dramatic effect is on  $2\pi^*$ .

Table 3. Some Orbital Populations in CO Chemisorbed on First Transition Series Surfaces (From Ref. 9)

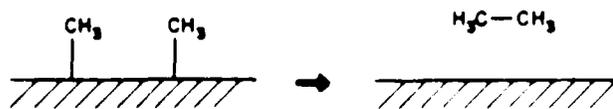
	Electron Densities in Fragment Orbitals					
	Ti(0001)	Cr(110)	Fe(110)	Co(0001)	Ni(100)	Ni(111)
5 $\sigma$	1.73	1.67	1.62	1.60	1.60	1.59
2 $\pi^*$	1.61	0.74	0.54	0.43	0.39	0.40



38

At the right it interacts, that is required for chemisorption. But  $2\pi^*$  lies above the d band. In the middle and left of the transition series, the Fermi level rises above  $2\pi^*$ .  $2\pi^*$  interacts more, is occupied to a greater extent. This is the initial indicator of CO disruption.<sup>9</sup>

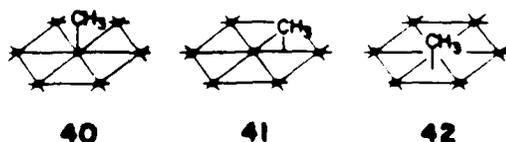
The second case we studied is one specific reaction likely to be important in the reductive oligomerization of carbon monoxide over a heterogeneous catalyst, the Fischer-Tropsch synthesis. The reaction is complicated and many mechanisms have been suggested. In the one I think likely, the "carbide/methylene" mechanism<sup>35</sup>, one follows a sequence of breaking up CO and H<sub>2</sub>, hydrogenating the carbon to produce methyl, methylene, methyne on the surface, followed by various chain-forming associations of these and terminating reductive eliminations. It is one of those terminal steps I want to discuss here, a prototype dissociation of two adsorbed methyls to give ethane, 39.<sup>31</sup>



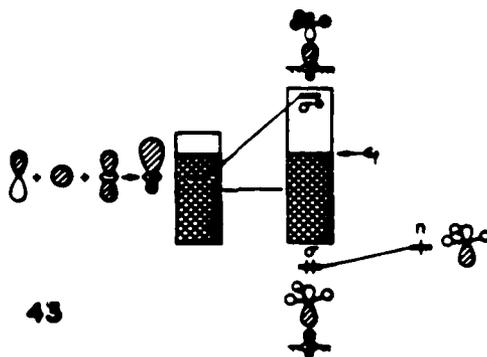
39

It's simple to write down 39, but it hides a wonderful variety of processes. First, given a surface and a coverage, there is a preferred site which methyls occupy, perhaps an equilibrium between several sites. Second, these methyls must migrate over the surface so as to come near each other. A barrier, call it the "migration energy", may intervene. Third, one methyl coming into the neighborhood of another may not be enough. It may have to come really close, for instance, on-top of a neighboring metal atom. That may cost energy, for one is creating locally a high-coverage situation, one so high that it might normally be inaccessible. One could call this a steric effect, but let's call it a "proximity energy". Fourth, there is the activation energy to the actual C-C bond formation, once the components are in place. Let's call this the "coupling barrier". Fifth, there might be an energy binding the product molecule to the surface. It is unlikely to be important for ethane, but might be substantial for other molecules. It is artificial to dissect the reaction in this way, nature does it all at once. But in our poor approach to reality (and here we are thinking in terms of static energy surfaces; we haven't even begun to do dynamics, to allow molecules to move on these surfaces), we can think of the components of the barrier impeding coupling: binding + migration + proximity + coupling + desorption energies.

To be specific, let's choose three dense surfaces: Ti(0001), Cr(110) and Co(0001). The calculations we carried out were for a 3-layer slab, and initially a coverage = 1/3. Three binding sites that were considered were on-top or one-fold, 40, bridging or two-fold, 41, capping or three-fold, 42. The preferred site for each metal is the on-top site, 40.<sup>31</sup>

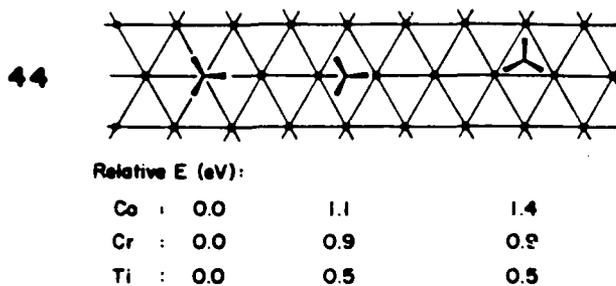


The total binding energy is greater for Ti than Cr than Co. 43 is an interaction diagram for  $\text{CH}_3$  chemisorption. The  $\text{CH}_3$  frontier orbital, a carbon-based directed radical lobe, interacts with metal  $s$  and  $z^2$ , much like the  $\text{CO } 5\sigma$ . Some  $z^2$  states are pushed up above the Fermi level, and this is one component of the bonding. The other is an electron transfer factor. We started with a neutral surface and a neutral methyl.



lobe has room for 2 electrons. Metal electrons readily occupy it. This provides an additional binding energy. And because the Fermi levels increase to the left in the transition series, this ionic component contributes more for Ti than for Co.<sup>31</sup>

In a sense, these binding energies of a single ligand are not relevant to the estimation of relative coupling rates of two ligands on different surfaces. But even they show the effect of the Fermi level. A first step in coupling methyls is to consider the migration barriers of isolated groups. This is done in 44. The relative energy zero in each case is the most stable on-top geometry.



The implication of 44 is that for Co the preferred migration itineraries are via bridged transition states, 45, but for Ti and Cr surfaces, 45 and 46 are competitive. For the reasons behind the magnitudes of the computed barriers, the reader is referred to our full paper.<sup>31</sup> Could one design an



45

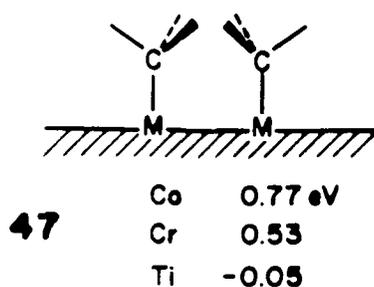


46

experiment to probe these migration alternatives?  $\text{CH}_3$  is still an uncommon surface fragment.<sup>25</sup>

If we bring two methyl groups to on-top sites on adjacent metals, we see a splitting in the occupied  $\text{CH}_3$  states. This is a typical two-orbital four-electron interaction, the way steric effects manifest themselves in one-electron calculations. If we compare the binding energy per methyl group in these proximate structures to the same energy for low coverage isolated methyls,

we get the calculated proximity energies of 47. The destabilization increases



with d electron count because some of the d levels occupied carry CH<sub>3</sub> lone pair contributions.

What happens when two CH<sub>3</sub> groups actually couple? The reaction begins with both CH<sub>3</sub> lone pairs nearly filled, i.e. a representation near CH<sub>3</sub><sup>-</sup>. A new C-Cσ bond forms, and, as usual, we must consider σ and σ\* combinations, n<sub>1</sub>±n<sub>2</sub>. Both are filled initially, but as the C-C bond forms, the σ\* combination will be pushed up. Eventually, it will dump its electrons into the metal d-band.

The actual evolution of the DOS and COOP curves allows one to follow this process in detail. For instance, Fig. 13 shows the contribution of the methyl n orbital, the radical lobe, to the total DOS along a hypothetical coupling reaction coordinate. Note the gradual formation of a two-peaked structure.

Figure 13

COOP curves show the lower peak is C-C bonding, the upper one C-C antibonding. These are the σ and σ\* bonds of the ethane that is being formed.

The total energy of the system increases along the reaction path, as n<sub>1</sub>-n<sub>2</sub> becomes more antibonding. At the Fermi Level, there is a turning point in the total energy. σ\* = n<sub>1</sub>-n<sub>2</sub> is vacated. The energy decreases, following τ = n<sub>1</sub>+n<sub>2</sub>. The position of the Fermi level determines the turning point. So the coupling activation energy is greater for Ti than for Cr than for Co.

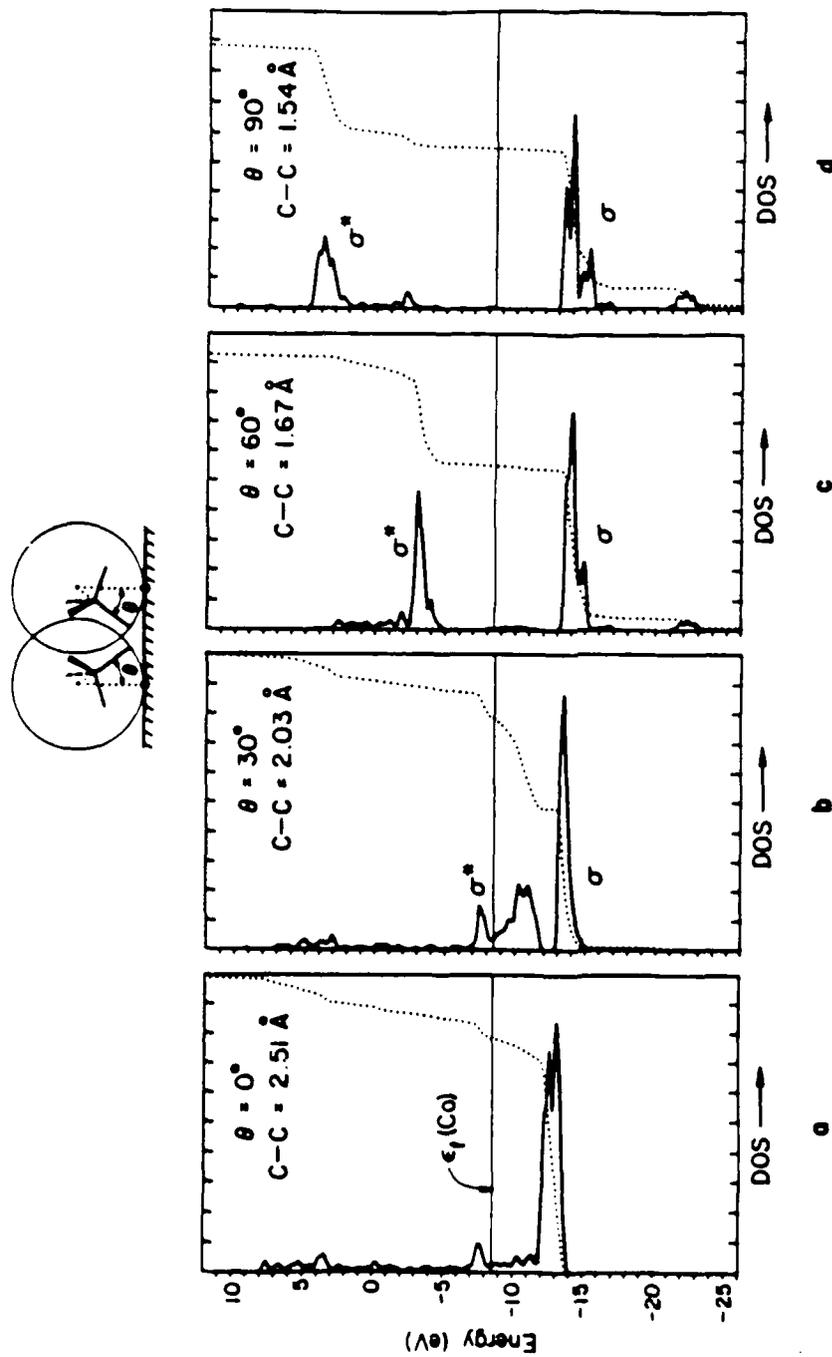


Figure 13. The evolution of the contribution of methyl lone pairs to the DOS of a chemisorption system (CH<sub>3</sub> on Co(0001)) as the two methyls couple to give ethane.  $\sigma$  is defined at top. Note the development of two peaks corresponding to  $\sigma$  and  $\sigma^*$  of the CC bond in ethane.

The reader familiar with reductive eliminations in organometallic chemistry will note essential similarities.<sup>29</sup> We also mention here again the relationship of our argument to the qualitative notions of Mango and Schachtschneider on how coordinated metal atoms affect organic reactions.<sup>28</sup>

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

Remarks

What I have tried to do in this work is to move simultaneously in two directions - to form a link between chemistry and physics by introducing simple band structure perspectives into chemical thinking about surfaces. And I have tried to interpret these delocalized band structures from a very chemical point of view - frontier orbital considerations based on interaction diagrams.

The elements of solid state physics, the ideas of Bloch functions, band structures, and densities of states need more exposure among chemists. And, incidentally, physicists might benefit from learning to explain these ideas, with which they are so familiar, with words and pictures rather than equations. I suspect that they would find that in the process they would understand their own physics better.

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

With these tools in hand, one can construct interaction diagrams for surface reactions, as one does for discrete molecules. The warning is that these diagrams are qualitative constructs, within the framework of a one-electron theory. This is not to downgrade them - witness how much they've contributed to our understanding of molecular chemistry.

In general, the interactions on a surface resemble those in molecules. The interesting and important differences are two: 1) There are essential consequences of strong four- and zero-electron two-orbital interactions turning into two-electron ones. 2) As a corollary, there are shifts of

electron density around the Fermi level which have bonding consequences.

In addition to providing a general picture of bonding of molecules to surfaces, the orbital interaction model, buttressed by detailed DOS and COOP tracing of consequences, provides us with many concepts. We see how effective chemisorption is one point, a compromise, in a continuum which embraces dissociative chemisorption and surface reconstruction. We see how barriers to chemisorption can arise. We see how in detail the Fermi level can influence reactivity. And, not the least, we can see the essential electronic similarities, and the important differences between bonding in discrete molecules and on surfaces.

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

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