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Molecular orbital studies of dissociative chemisorption of first period diatomic molecules and ethylene on (100) W and Ni surfaces

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The extended Hückel molecular orbital method is used to examine interactions of Li₂, B₂, C₂, N₂, O₂, F₂, CO, NO, O₂, and F₂ with nine atom clusters representing W(100) and Ni(100) crystal surfaces. The following predictions are made and are corroborated by experimental facts when available: (1) A strong tendency for charge transfer between the substrate and adsorbate exists as would be expected from electronegativity differences. (2) The adsorbed molecules display a tendency to dissociate because of Coulombic repulsions and frequently because of the filling of antibonding levels as well. At the same time Li₂ and F₂ form ionic bonds with the surface and covalent character is also evident for the others. (3) Strong bonding interactions form between the adsorbates and surfaces for any adsorbate orientation or position. Thus a connection is made with physical theories which exclude atomic detail. Such surface homogeneity can be resolved into detail with molecular orbital methods, but the emphasis in this paper is on examining orbital interactions between adsorbates and substrates with small regard to energy changes. (4) Active sites, which are atoms on a surface which have stronger chemisorptive capability, are found on steps and corners of metal clusters. These atoms, which stick out from the bulk, gain extra electronic charge as a result of orbital orthogonality and they form stronger bonds with electrophilic adsorbates, sometimes also strengthening the diatomic bond a little. This suggests rough surface areas might initially attract electrophilic adsorbates, but that dissociation could happen in a nearby region. (5) Photoemission spectra for CO on W(100) and Ni(100) and ethylene on Ni(111) are considered in some detail. The calculations corroborate the spectra. Comments are made on spectra of N₂, N₂O, NO, and O₂ on W(100), CO on W(110), and ethylene on W(100) and Ni(100). Bandwidths and positions are discussed. In general the extended Hückel molecular orbital method appears to be a valuable tool in surface chemisorption and catalysis studies.

I. INTRODUCTION

In this paper the nature of dissociative chemisorption of Li₂, B₂, C₂, N₂, O₂, F₂, CO, NO, and ethylene on tungsten and nickel (100) surfaces is explored. The extended Hückel molecular orbital method is employed. Previous work using this method has dealt with the properties of small clusters of metal atoms, with establishing the preferred sites for chemisorption of first period atoms and molecules on a graphite layer, with the orientation of CO on Ni(100), with the energetics of hydrogen atom adsorption on Ni(100), and with the energetics of hydrogen and nitrogen atom adsorption on W(100).

A systematic study using model structures for first period diatomic molecules is made here. It is probable that this type of study will provide a useful basis of understanding on a qualitative level because of the spectrum of calculated chemisorption characteristics existing from Li₂ to F₂ in the first period. The nature of the adsorbate bond weakening discussed so far in terms of molecular orbitals only for CO and adsorbate–substrate bond formation can be elucidated semiquantitatively in terms of well-known concepts without considering energy surfaces which as yet have no experimental check.

Because of economy, semiempirical molecular orbital methods are well-suited for calculating surface properties. Many molecular orbitals containing many electrons may be used. This allows one to consider a cluster of ten or twenty transition metal atoms for representing a surface. The calculated molecular orbitals of such a cluster will contain the short wavelength Bloch waves of the dimension of such absorbates as period one diatomic molecules. If one is interested in bonding to an infinite crystal, the finite surface effects present in the calculation using the small metal cluster may shift the magnitude of the bonding effects accompanying adsorption, but in most cases the conclusions drawn in this work should be unaffected. Moreover, the catalytic properties of small metal clusters and of rough infinite surfaces make a study of these surface effects interesting in itself. Bloch waves longer than the dimensions of the model cluster cannot be considered here, but the theme of this study should be unaffected. Such long wavelength low energy states buried deep in the s and d bands may turn out to be of interest in the future, but at present there is probably little motivation to involve such states in the understanding of dissociative chemisorption of first period diatomic molecules. The existing rules for predicting the structures of adsorbed monolayers of gases on crystal surfaces are formulated to depend on physical shapes and adsorbate–adsorbate and adsorbate–substrate interactions without recourse to many body or through-bond-coupling effects which might involve longer wavelength substrate states. One might imagine the dehydrocyclization of n-heptane on stepped Pt surfaces to involve several consequential local interactions rather than a single interaction or series of interactions with long wavelength Bloch states. Even if it is later necessary to consider larger clusters, semiempirical molecular orbital methods may be most suitable.

The extended Hückel molecular orbital method has as its forte the prediction of energy changes attending rotations of rigid groups in molecules about connecting
bonds, angular distortions in general, and the prediction of modifications in bond strengths during rotation or with substitution of atoms or groups with other atoms or groups. It was noted at the outset that the method gave poor potential energy functions for bond stretches and that such applications of the method are dangerous. Moreover, since the simplest versions of the extended Hückel method, as used here, employ charge-independent atomic ionization potentials, charge buildups on atoms are overestimated. The sign and relative magnitudes of the charges are nevertheless useful for qualitative discussions. The molecular orbitals and their energy levels are of established usefulness as well, and it is expected that minor changes in atomic valence state ionization energies will not change qualitatively the trends observed in these calculations of first period diatomic molecules on metal surfaces. The CNDO semi-empirical molecular orbital method, in its various materializations as CNDO/2, INDO, and MINDO, gives more satisfactory bond lengths and has been used to study small metal clusters and the adsorption of hydrogen atoms on Ni clusters, but the method has not enjoyed the popularity of the extended Hückel theory in this type of work because of its cost.

Recently a theory was developed for the chemical bond which identifies two energy components, a repulsive two-body electrostatic one and an attractive two or more body one. The repulsive one may be easily calculated using simple algebraic formulas stemming from atomic electronic charge densities and the attractive component may be well approximated by the extended Hückel molecular orbital state energy such that a simple summation yields potential functions with good equilibrium force constants and equilibrium internuclear distances. It is expected that this procedure will yield good surfaces in future chemisorption studies while at the same time retaining the interpretative value of the extended Hückel method. It is anticipated that the results of this paper will withstand the test of more quantitative molecular orbital theories of the future.

Some comments will be made in a later section about other current theoretical methods for studying chemisorption and catalysis on metal surfaces. Among these are the bond-energy-bond-order studies recently applied to ethylene adsorbed on Pt(111), the induced covalent bonding overlap population analysis and ionic interaction arguments. It is found that Li₂ loses its two bonding electrons to the surface, completely breaking the σ bond and leaving two repelling Li⁺ ions. These bond ionically to the negative surface atoms. At the other extreme F₂ accepts two electrons from the surface and forms an ionic bond with the surface. The F₂⁻ species dissociates not only because of the ionic repulsion, but also because the two electrons enter a σ antibonding level. In other cases ionic charge transfer is found with concomitant filling of diatomic bonding and antibonding states. In these calculations only the B₂ bond order becomes stronger in the presence of the metal surfaces. Some bonding overlap occurs with the surfaces in these latter cases but, since model geometries are employed, the value of the numbers is more instructive than quantitative. Because the Fermi levels lie at about the same energy and because the filled d bands of states are about the same width in these calculations for W and Ni, the chemisorption behaviors are similar for the two metals, as is known on a gross experimental scale.

In the third section the orientations of the diatomic molecules above the surfaces are considered. It is found that the surface molecular orbitals, which are linear combinations strong in d orbital character are quite flexible and can find ways to interact with the adsorbing molecules no matter what their orientations are. This result has obvious connections to the perturbation and charge density theories which do not contain detailed atomic orbital structure in their approximations of metal surfaces.

The fourth part of this study has to do with active sites for chemisorption. It is found in extended Hückel molecular orbital cluster calculations that charge buildup is likely to occur on corner and other metal atoms which "stick out." Electrophilic adsorbates favor the negatively charged sites. This explains the special reactivity and holding power of stepped Pt surfaces and small metal clusters.

The fifth and final feature of this work is a concern with the parameters used in the calculations. The possibility of calibrating the extended Hückel molecular orbital method against photoemission spectra for chemisorbed O and CO on W(100) and O and CO on Ni(100) is entertained. Photoemission spectra of ethylene on W and Ni are discussed. The effects of the parameters on the Fermi levels and the d band widths are considered.

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II. CHARGE TRANSFER BETWEEN THE ADSORBATE AND SURFACE

For the bulk bcc W(100) surface a 9 atom cluster with 5 atoms on top and 4 underneath, as shown in Fig. 1, is employed in the extended Hückel molecular orbital calculations. A similar model for fcc Ni(100) is shown in Fig. 2. These models present symmetric one-coordinate positions on top and symmetric four-coordinate positions underneath and have been used previously in studying the stretching energy for He and Ne on W(100). In this section free diatomic molecules are placed perpendicular to the surfaces in the one-coordinate positions with the distance between the nearer diatomic nucleus and the plane of surface nuclei being 2.0 Å in every case, this being a reasonable average number for this study. For remaining details incidental to the calculations the reader is referred to the Appendix.

When the extended Hückel molecular orbital method is employed for disparate interacting species, the charge transfers may be predicted from the filled and unfilled molecular orbital energy levels. These levels are shown in Fig. 3 for a single tungsten atom with a $5p^65d^46s^2$ configuration and for the free diatomic molecules Li$_2$, B$_2$, C$_2$, N$_2$, O$_2$, and F$_2$. The figure implies that if molecular wavefunction overlaps between the metal atom and the diatomic molecules are ignored Li$_2$ will donate 2 electrons to W, B$_2$, C$_2$, N$_2$, and F$_2$, and B$_2$ will accept 2 and N$_2$ 4 electrons. Actual calculations yield charge densities, according to the Mulliken definition, as given in Table I. Since, in the linear arrangements used, the distance from the W nucleus to the nearer diatomic nucleus is 2.0 Å and not infinite, orbital interaction usually decreases the charge transfer, but it is in the direction implied by Fig. 3.

In the 9 atom W and Ni clusters the metal $s$ and $d$ levels interact to form bands. The Fermi level for W lies at ~8.9 eV and for Ni at ~9.1 eV, reflecting the fact that work functions for transition metals are quite similar. The average W atom structure goes from $5p^65d^46s^2$ for the atom to $5p^55d^66s^2$. Similarly the Ni atom goes from $3p^63d^44s^2$ to $3p^53d^64s^2$ in the cluster compared to $3p^63d^44s^2$ from experimental considerations. The W filled $d$ band width for this cluster is 2.7 eV, compared to about 5.0 eV from photoemission experiments, although a less symmetric 11 atom cluster gives a width of about 3.7 eV. The Ni band width for the 9 atom cluster is calculated to be 1.8 eV, compared to about 3 eV from photoemission experiments. The conclusion is that the 9 atom W and Ni metal clusters represent bulk surface properties consistently and encouragingly well in the extended Hückel calculations. Moreover, the Fermi levels lie near enough to the atomic d state energies so that charge transfers involving the clusters will be qualitatively similar to those found in Table I for the lone W atom. This is because the W d band is about half-full.

Figures 4–6 show energy levels before and after interaction with the metal clusters for Li$_2$, C$_2$, and F$_2$. The atomic charges for the diatomic molecules are tabulated in Table II. The atomic charges for the diatomic molecules resulting from interaction with the 9 atom W cluster are indeed similar to those from interacting with a single atom, and they are quite close to the charges resulting from interaction with the Ni cluster. Thus a qualitative discussion of charge transfer for one system holds for the other transition metals.

The filled $d_0$ energy level in Li$_2$ lies 3 eV above the Fermi levels of W and Ni so that an essentially complete transfer of 2 electrons takes place to the clusters. In B$_2$ one of the degenerate $\pi_x$ and $\pi_y$, taking the $z$ direction to pass through the nuclei, is empty, so that about 1.6 electrons are taken from the W atom and cluster. When on the Ni cluster B$_2$ gains an additional 0.9 electrons because the $d_{xz}$ orbital mixes well with a $d_{dz}$ atomic orbital centered on the central Ni atom and contained in a cluster orbital near the top of the $d$ band. The interaction is depicted in Fig. 7. Due to orbital interaction C$_2$ gains over 2 electrons from the W atom and cluster, but not from Ni. This is caused by mixing of the $C_2\pi^*$ and $\pi^*$ with metal $d_{yz}$ and $d_{xz}$ orbitals in the W atom and in molecular orbitals near the top of the $d$ band as shown in Fig. 8.

In N$_2$ the two $\pi^*$ levels which lie below the Fermi levels are more than half filled, but, due to orbital interactions, not completely filled. Charge enters the $\sigma^*$ levels of CO and NO. The $\pi^*$ level of O$_2$ lies beneath the bands and is almost completely filled. The $\sigma^*$ level of F$_2$ lies at the bottom of the $d$ bands and is nearly filled. As may be expected, the W atom nearest the diatomic molecule in the cluster calculations possesses the most positive charge; its nearest neighbor underneath has a little positive charge and its next nearest neighbor on the surface generally has some negative charge. The same results hold for the free cluster and they may all be seen in Fig. 9.
In summary it is noted that gross charge transfer resulting in extended Hückel molecular orbital calculations on these systems fulfill expectations based on electronegativity differences. Orbital interactions mollify the tendency toward complete ionic behavior, however.

III. MECHANISM FOR DISSOCIATIVE CHEMISORPTION: BOND BREAKAGE AND BOND FORMATION

It was seen in the last section that the extended Hückel molecular orbital method predicts substantial charge transfers between a W or Ni surface and a period one diatomic molecule, of the order of 1 electron for each of the two atoms. Whereas such large positive charges are reasonable and have been observed experimentally for alkali metals adsorbed to W$^{35}$ and Ni$^{33}$ surfaces, and such negative charges are reasonable for adsorbed halides, for the other molecules the truth may lie closer to $0$ than $\pm 1$, due to intraionic electron repulsions which are neglected in the extended Hückel procedure. This omission does not affect the sign of charges on the other adsorbed molecules, and does not negate the possibility of charge transfer in these cases. If, however, electron repulsions in negative ions raise the diagonal Hamiltonian matrix elements enough and, if diagonal matrix of positive ions are lowered enough, then a substantial decrease charge transfer to or from the absorbate would result. This possibility is not tested here.

The charges on the adsorbate atoms will help to affect their dissociation while at the same time they will serve to bind them to oppositely charged atoms in the surface. This is only part of the story of dissociative chemisorption, for along with charging, there are important bonding changes in the diatomic molecular orbitals and there are important overlaps between these orbitals and the cluster molecular orbitals, primarily with the atomic orbitals of the nearest neighbor metal atom or atoms.

The changes in diatomic bond orders, which are defined as Mulliken overlap populations, are consistent with the emptying of bonding and filling of bonding and antibonding orbitals mentioned in the previous section. Results for interactions with a single W atom and the 9 atom W and Ni clusters are in Table III. Again, the changes on interacting with a single W atom typify those for interaction with the clusters. The $\sigma$ bonding orbital in Li$^2$ loses its two electrons to the metal and its bond is completely broken. Due to filling of the empty member of the degenerate pair of $\pi$ orbitals, B$^2$ has its bond strengthened. The strengthening of the $C_2$ bond due to filling of the empty $\sigma$ orbital is more than negated by

<table>
<thead>
<tr>
<th>Diatomic molecule</th>
<th>Li$^2$</th>
<th>B$^2$</th>
<th>C$^2$</th>
<th>N$^2$</th>
<th>O$^2$</th>
<th>F$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charges</td>
<td>+0.91</td>
<td>-0.70</td>
<td>-2.23</td>
<td>-1.47</td>
<td>-0.98</td>
<td>-0.97</td>
</tr>
<tr>
<td></td>
<td>+0.42</td>
<td>-0.90</td>
<td>-0.97</td>
<td>-0.67</td>
<td>-0.39</td>
<td>-0.84</td>
</tr>
</tbody>
</table>
mixing of the higher $\pi^*$ orbitals. Filling of the empty degenerate $\pi^*$ orbitals in $N_2$ and CO greatly weakens their bonds. The weakening of the CO bond was given a similar interpretation earlier, and formulas exist which connect shifts in vibrational frequencies to internuclear distances. Quantitative tests are not considered here, although vibrational analysis may become a useful tool in understanding surface structures. Similarly NO, which already has 1 electron in the $\pi^*$ system, and $O_2$, which has 2, both have weakened bonds. Finally, $F_2$...
assumes a negative bond order due to the nearly complete filling of the last orbital in the series, which is \( \sigma^* \). Thus, according to these calculations for all molecules except \( \text{B}_2 \), bond weakening in terms of overlap populations parallels the effects of repulsion due to charge buildup. With the exception of \( \text{Li}_2 \) and \( \text{F}_2 \), which have pertinent orbitals above and below the \( d \) bands such that orbital mixing is small and charge transfer nearly complete, the same orbitals which accept charge from the metal clusters also overlap with molecular orbitals in the clusters. The bond orders for interaction between the diatomic molecules and a single \( W \) atom and the 9 atom \( W \) and \( \text{Ni} \) clusters are shown in Table IV. All of the diatomic molecules form strong bonds with a single \( W \) atom, but they are much smaller for \( \text{Li}_2 \) and \( \text{F}_2 \) interacting with the clusters and they are about half as much for the other molecules in these circumstances. The weakenings are ascribed to the density of states in the \( d \) bands which allow charge transfers to involve other metal atoms.

The nature of the bonding interactions with the surface is easily predicted from the energy level diagrams in Fig. 3-6. In the case of \( \text{B}_2 \) the \( \pi \) orbitals of that molecule lie in the \( d \) band of the cluster. There is significant overlap of the \( \pi \) orbital of \( \text{B}_2 \) with metal atom \( d_\text{a} \) and \( d_\text{g} \) orbitals, as shown in Fig. 10, as well as some mixing of the empty \( \sigma \) orbital of the diatomic, as shown in Fig. 7. Both interactions lead to metal–diatomic bonding. In \( \text{C}_2 \), shown in Fig. 5, the diatomic \( \sigma \) orbital lies at the bottom of the cluster \( d \) band. It mixes well with the metal \( d_\text{g} \) orbital, as shown in Fig. 7, as well as with the symmetric metal \( s \) states, which, for both \( W \) and \( \text{Ni} \), lie below the \( d \) band. The interaction is illustrated in Fig. 11. In addition there is a lesser degree of mixing of diatomic \( \pi^* \) orbitals with the cluster. For \( \text{N}_2 \), \( \text{CO} \), and \( \text{NO} \) the \( \pi^* \) orbitals interact, but for \( \text{O}_2 \) the mixing of \( \pi^* \) and cluster orbitals is relatively weak since, as may be seen in Fig. 3, the \( \pi^* \) levels are below the cluster \( d \) bands. Only a very small overlap exists between \( \text{F}_2 \) and the clusters. Figure 6 shows this for the small perturbation of the bound diatomic levels relative to the free molecule.

It is concluded in this section that, for a first period diatomic molecule approaching a (100) surface metal...
atom in a colinear arrangement, dissociation with re-
bounding to the surface is the anticipated result. Furthermore, since the Fermi levels lie in nearly the same
place in other transition metals, similar results may be
expected to be obtained for calculations involving them.
This general result is dependent on the present use of
the extended Hückel molecular orbital method, to be
sure, but evidence for dissociative chemisorption is
widespread. In the next section some other geometries
of approach for diatomic molecules will be studied.

IV. DIATOMIC POSITION AND ORIENTATION;
SURFACE HOMOGENEITY; ETHYLENE

In Sec. III it was seen that a diatomic molecule which
is colinear with a surface atom and perpendicular to the
surface will mix its \( s \) and \( s^* \) orbitals with the metal’s
\( d_{xz} \) and \( d_{yz} \) orbitals, where \( z \) is the colinear direction,
and it will mix its \( \sigma_x \) and \( \sigma_y \) orbitals with the metal
\( d_{xy} \) orbitals and with the symmetric cluster \( s \) state be-
neath the \( d \) bands. Here other orientations are consid-
ered. The interesting finding is that the surfaces are so
tightly packed with available metal \( d \) orbitals, making
up the many band states, that interaction with the sur-
face is likely for any orientation of a diatomic molecule.

A glance at Table V quickly gives motivation for this
assertion, for the results for all orientations are gross-
ly the same. Calculated energies, diatomic bond orders,
and diatomic charges are tabulated for the old perpen-
dicular configuration and three new ones. All have 2.0
\( \text{Å} \) as the characteristic distance between the nearer
diatomic nucleus and the plane of surface nuclei. The
last three columns of the table specify what happens to
the energy, overlap population, and charge on a diatom-
ic molecule in different orientations relative to the sur-
face. The first of these columns describes the orienta-
tion of a diatomic parallel to the one-coordinate site
above the cluster of Fig. 1. The other columns describe
placement of the molecule perpendicularly or parallel to
a four-coordinate surface site underneath the cluster in
Fig. 1. It may be premature to assign diatomic orien-
tations on the basis of these energies, which do not ex-
licitly contain ionic contributions. Strong orbital inter-
actions between the diatomic and substrate can exist for
all these orientations, as well as additional ones in Ta-
gle VI. This suggests the surface presents aspects of
homogeneity.

Surface homogeneity is a result of the compact packing
of the surface with atomic \( d \) orbitals. A diatomic mole-
cule can have orbital interactions with a single colinear
metal atom as in Figs. 7, 8, and 10 or, when lying flat
on the surface, with the same metal atom as in Fig. 12.
When parallel to the surface in a two-coordinate position,
diatomic–metal interactions as in Fig. 13 take place,
and so on for the perpendicular orientation and the four-
coordinate positions. A glance at Figs. 3–6 tells for
which types of interactions to look for these orientations
over \( W \) and \( Ni \) surfaces and the implication exists for
similar behavior over other transition metal surfaces.

Surface homogeneity is an expected result within the
perspective of temperature dependent thermal mobili-
ty, \( 21,23,24 \) and it has been the basis for theoretical treat-
ments of hydrogen atom chemisorption to metal surfaces.
Binding energies for \( H \) have been accurately calculated
by means of self-consistently determining electronic
charge densities in the jellium model metal potential
with the proton potential. \( 23 \) This procedure omits atomic
surface structure entirely. Similarly the induced valence
bond perturbation theory omits surface atomic orbital
structure. \( 23 \) The validity of these theories depends on
the concept of an atom with bulk metal interaction. For
the greatest part of chemisorption energies this concept
is valid, \( 23 \) and the results of this paper are in support.
Furthermore, these results imply that it should be pos-
sible to develop a theory for dissociation by extending
the bulk theories, without introducing surface atoms, by
recognizing the existence of surface states which can
overlap with and populate antibonding adsorbate states.
The lattice constant would be a parameter in such theo-
ries. The dissociating influence of ionic charge transfer

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\[ \text{Fig. 7. Interaction between a diatomic } \sigma_x \text{ orbital and a metal } d_{xy} \text{ orbital.} \]

\[ \begin{align*}
\text{Fig. 8. Interaction between a diatomic } s^* \text{ orbital and a metal } \sigma_y \text{ or } d_{xy} \text{ orbital.}
\end{align*} \]
would be a more trivial result which would be obtained automatically in the absence of surface detail.

The bond weakenings in adsorbed diatomic molecules seen in Tables III and V have not yet been explicitly connected with dissociation into atoms, Table VII shows the weakening of the N₂ bond, the decrease in system energy and the increase in N-cluster bond order for N₂ dissociating parallel to the surface on a one-coordinate W atom in a cluster. The effects are pronounced and strongly argue for dissociation. Clearly similar results would be calculated for other diatomic species and chemisorption geometries, and as yet nothing about the actual experimental structures is implied. Experimental studies of dissociative chemisorption of H₂ on W27,36-38 show dissociation and a number of atomic states, and a theoretical treatment of dissociative chemisorption of H₂ on Ni has been proposed.39

The dissociative chemisorption of ethylene on Pt(111) has been treated in detail with the empirical bond-energy bond order method.21 In this method the formation and breakage of chemical bonds are handled with diatomic molecules perpendicular to metal cluster centers, or colinear with a 1 W atom, and 2,0 Å from the nearest metal nucleus. The metal overlap with the nearer atom is listed in Table IV. Bond orders, defined as Mulliken overlap populations, between atoms in diatomic molecules perpendicular to metal cluster centers, or colinear with 1 W atom, and the 9 W and 9 Ni clusters of Figs. 1 and 2. The geometry is colinear in triatomic cases and perpendicular to the central atom in cluster cases, the distance from the nearer nucleus to the metal nucleus being 2,0 Å in all cases. In CO and NO, C and N are nearer the surfaces.

The nature of the bonding to the surface may be quickly deduced by examination of the C₂ energy level diagram in Fig. 5 while realizing the the π₂ and σ₂ orbitals are substantially lowered by mixing with the hydrogen atomic orbitals to form CH bonds, while the π₂ and σ₂ orbitals are nearly unchanged. Therefore the lowest unoccupied orbital in ethylene is the σ₂ located at -8.64 eV, just below the Fermi level. This orbital mixes with tungsten d orbitals in a bonding way, gaining electron population with a concomitant weakening of the ethylenic C-C bond. The energy levels for ethylene and a 13 W atom cluster, with a row of 5 atoms on top and 8 nearest neighbors below are drawn in Fig. 14. Mixing of the ethylene π₂ level with the cluster symmetric s state at the bottom of the d band is evident, but ethylene C-C and C-H σ bonding orbitals are unaffected for this orientation. Additional comments concerning ethylene on W(100) from the point of view of photoelectron spectroscopy will be made in Sec. VI.

V. ACTIVE SITES

In the model studies of this paper there is a characteristic charge transfer from the metal clusters to diatomic state levels beneath the Fermi level. Only for Li₂ is the direction reversed. For this reason it is expected that any metal atoms which have excess charge compared with others in a cluster should facilitate a transfer of charge and form a stronger bond with electronegative adsorbates.
The interaction of the electronegative N₂ molecule with a line of 5 W atoms yields the charge dependent relationships shown in Fig. 16. The attractive interaction energy reflects the charges of the free line of metal atoms. The N-N and N₂-W bond orders reflect the energies. The fact that the N-N bond order goes up when the N₂-W bond order goes up suggests the more negative atoms are preferred sites for chemisorption, but not necessarily for dissociation.

A question of importance to this type of study is: What is the reason for the buildup of electronic charge on the ends of lines of W atoms. Clearly it is a structure effect depending on the orthogonality of the molecular orbitals obtained in the diagonalization of the Hamiltonian matrix over the atomic orbital basis. Charge on the atoms in a 6 W line due to all possible atomic populations are shown in Table IX. When the s + d valence band is completely empty or full, there is no charging of the atoms. As electrons are added one at a time to each atom, that is six at a time to the cluster, electron density builds up in the center of the line until the sixth electron is added; from then on charge builds up on the end atoms. Adding the first five electrons to each atom corresponds to filling the bottom half of the d band, since there is only a little atomic s character in these states. These states are bonding. The sixth to twelfth electrons go into generally antibonding states and electron density builds up on the end atoms. The nearest neighbor Mulliken overlap populations in parentheses in the table reflect the bonding and antibonding behavior. Consistent with Table IV is the finding that the end atom of a row of 6 Ni atoms has a charge of -1.50, as the clusters are neutral.

Some amusement is to be had on observing Fig. 17 where several flat clusters and calculated atomic charges are shown. Abrupt charge rearrangements are seen as clusters are expanded. There is nevertheless a trend toward negative charges on corner atoms and on the step atom as the clusters fill in. This charge buildup at the corner atom in the step may be the key to the enhanced reactivity of stepped surfaces which has been observed for Pt.\(^{12,13}\) Calculations of N₂ situated around the 13 W atom cluster approximating a cut of a stepped surface, as shown in Fig. 18, show the preferred site is around the corner atom, as seen in Table X, here the extended Hückel energies are the lowest, the N₂-W bond is the strongest, and the N₂ oxidation potential is 0.64 eV. Hence, if ionic contributions are ignored, the prediction is that the corner atom is most attractive to N₂ and can facilitate chemisorption. Because the N₂ bond is greatly weakened, dissociation, as demonstrated in Table VII, may be expected for adsorbed N₂. Simple structural and

![FIG. 10. Interaction between diatomic \(\pi\) orbital and a metal \(d_x\) or \(d_y\) orbital.](image)

![FIG. 11. Interaction between diatomic \(\sigma\) orbital and symmetric \(s\) cluster orbital.](image)

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**TABLE V.** Extended Hückel molecular orbital binding energies and diatomic overlaps and atomic charges for diatomic molecules on a 9 atom W cluster. The characteristic distance to the surface is 2.0 Å. Energies are in eV.

<table>
<thead>
<tr>
<th>Diatomic molecule</th>
<th>One coordinate position</th>
<th></th>
<th>Two coordinate position</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Perpendicular</td>
<td>Parallel</td>
<td>Perpendicular</td>
<td>Parallel</td>
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<tr>
<td>Li₂ Energy</td>
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<td>-5.04</td>
<td>-4.77</td>
<td>-5.44</td>
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<td>Atomic charges</td>
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<td>1.05</td>
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<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B₂ Energy</td>
<td>-0.14</td>
<td>-0.82</td>
<td>-0.49</td>
<td>-0.09</td>
</tr>
<tr>
<td>Mulliken overlap</td>
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<td>1.46</td>
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</tr>
<tr>
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<tr>
<td></td>
<td>-0.55</td>
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<tr>
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<td>0.68</td>
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<td>-0.14</td>
</tr>
<tr>
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<td>1.33</td>
<td>1.54</td>
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</tr>
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<td>-1.35</td>
<td>-1.59</td>
<td>-1.50</td>
</tr>
<tr>
<td></td>
<td>-0.92</td>
<td>-0.91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂ Energy</td>
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</tr>
<tr>
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<td>0.40</td>
<td>0.82</td>
</tr>
<tr>
<td>Atomic charges</td>
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<td>-1.53</td>
<td>-1.82</td>
<td>-1.23</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₂ Energy</td>
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<td></td>
<td>-1.58</td>
<td></td>
</tr>
<tr>
<td>Mulliken overlap</td>
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<td>1.38</td>
<td>0.95</td>
<td>1.72</td>
</tr>
<tr>
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<td>-0.38</td>
<td>-1.00</td>
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</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>F₂ Energy</td>
<td>-0.76</td>
<td></td>
<td>-0.93</td>
<td></td>
</tr>
<tr>
<td>Mulliken overlap</td>
<td>1.57</td>
<td>1.63</td>
<td>1.15</td>
<td>2.49</td>
</tr>
<tr>
<td>Atomic charges</td>
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<td>-0.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-0.94</td>
<td>-0.88</td>
<td>-1.00</td>
<td>-0.95</td>
</tr>
<tr>
<td></td>
<td>-0.99</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TABLE VI.** Extended Hückel molecular orbital binding energies and diatomic overlaps and atomic charges for diatomic molecules at the center of a 13 W atom cluster. Energies are in eV.

<table>
<thead>
<tr>
<th>Diatomic molecule</th>
<th>One coordinate position</th>
<th></th>
<th>Two coordinate position</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Perpendicular</td>
<td>Parallel</td>
<td>Perpendicular</td>
<td>Parallel</td>
</tr>
<tr>
<td>C₂ Energy</td>
<td>-1.47</td>
<td>-0.67</td>
<td>-0.92</td>
<td>-0.80</td>
</tr>
<tr>
<td>Mulliken overlap</td>
<td>1.19</td>
<td>1.21</td>
<td>1.18</td>
<td>1.21</td>
</tr>
<tr>
<td>Atomic charges</td>
<td>-2.10</td>
<td>-1.43</td>
<td>-1.79</td>
<td>-1.52</td>
</tr>
<tr>
<td></td>
<td>-1.13</td>
<td></td>
<td>-1.28</td>
<td></td>
</tr>
<tr>
<td>N₂ Energy</td>
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<td>-0.63</td>
<td>-0.25</td>
<td>-0.01</td>
</tr>
<tr>
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<td>0.31</td>
<td>0.34</td>
<td>0.50</td>
</tr>
<tr>
<td>Atomic charges</td>
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<td>-1.60</td>
<td>-1.36</td>
<td>-1.61</td>
</tr>
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<td></td>
<td>-1.27</td>
<td></td>
<td>-1.59</td>
<td></td>
</tr>
<tr>
<td>O₂ Energy</td>
<td>0.93</td>
<td>1.20</td>
<td>0.56</td>
<td>0.92</td>
</tr>
<tr>
<td>Mulliken overlap</td>
<td>0.45</td>
<td>0.49</td>
<td>0.44</td>
<td>0.47</td>
</tr>
<tr>
<td>Atomic charges</td>
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<td>-0.86</td>
<td>-1.03</td>
<td>-0.86</td>
</tr>
<tr>
<td></td>
<td>-0.74</td>
<td></td>
<td>-0.86</td>
<td></td>
</tr>
<tr>
<td>F₂ Energy</td>
<td>1.40</td>
<td>1.59</td>
<td>0.95</td>
<td>1.70</td>
</tr>
<tr>
<td>Mulliken overlap</td>
<td>-0.63</td>
<td>-0.63</td>
<td>-0.63</td>
<td>-0.58</td>
</tr>
<tr>
<td>Atomic charges</td>
<td>-0.99</td>
<td>-0.89</td>
<td>-0.93</td>
<td>-0.91</td>
</tr>
<tr>
<td></td>
<td>-0.99</td>
<td></td>
<td>-0.94</td>
<td></td>
</tr>
</tbody>
</table>
A. B. Anderson and R. Hoffmann: Dissociative chemisorption on W and Ni

FIG. 12. Interactions between orbitals in a diatomic molecule lying flat on the metal surface and the atom beneath.

statistical considerations may also play a role in increasing the reactivity at stepped surfaces.

Calculations of atomic charges in normally populated flat multiatom arrays show, for W and H, that a single atom, that is another W or H, sitting on top of an atom in the array gains one or two units of electronic charge. End and corner atoms in clusters of W and Ni atoms used for calculations in earlier sections of this paper also gain charge. It is at first sight surprising that such charges will build up on atoms of the same species in a neutral cluster. Of course actual charge buildups will be much smaller because charge transfer is a more complicated affair than assumed in an extended Hückel calculation. This simple method lets atomic states mix, but does not adjust the atomic state wavefunctions or ionization energies to agree with the effects of charge transfer. A self-consistent molecular orbital calculation will give smaller charge transfers primarily because it will include the repulsive interaction energy between the newly arriving electronic charge and the electronic charge present in the neutral atom. Moreover, an atom will lose charge less readily.

Despite the overestimations of atomic charge present

FIG. 13. Interactions between diatomic orbitals and surface when lying flat in a two-coordinate position.

TABLE VII. \( \text{N}_2 \) dissociating parallel to the surface on a one-coordinate W atom in a 9-atom cluster.

<table>
<thead>
<tr>
<th>N–N Distance (Å)</th>
<th>1.094</th>
<th>1.4</th>
<th>1.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{N}_2 ) Mulliken overlap</td>
<td>0.56</td>
<td>0.55</td>
<td>-0.09</td>
</tr>
<tr>
<td>( \text{N} ) charge</td>
<td>-1.53</td>
<td>-1.71</td>
<td>-2.31</td>
</tr>
<tr>
<td>N-cluster bond order</td>
<td>0.15</td>
<td>0.16</td>
<td>0.22</td>
</tr>
<tr>
<td>Extended Hückel energy (eV)</td>
<td>0.00</td>
<td>-4.45</td>
<td>-7.25</td>
</tr>
</tbody>
</table>

Therefore, a \( \text{N}_2 \) molecule, when parallel to the surface of a W atom in a 9-atom cluster, will have the following energies:

- Mulliken overlap: 0.56, 0.55, -0.09
- \( \text{N} \) charge: -1.53, -1.71, -2.31
- N-cluster bond order: 0.15, 0.16, 0.22
- Extended Hückel energy: 0.00, -4.45, -7.25

FIG. 14. Interaction diagram for ethylene and a 13 atom W cluster. On top are 5 W atoms, with 8 nearest neighbors below; the ethylene plane is parallel to the surface, 2 Å from it and symmetrically situated above the central of the line of 5 surface atoms.
in extended Hückel calculations the orbital orthogonality constraints are real in a single determinant electronic wavefunction approximation and experience indicates that they frequently allow for prediction of experimental facts; indeed, this has been the success of the application of the method to problems in organic chemistry. Because of this past experience, and because of the increased catalytic activity of small clusters of transition metal atoms,\textsuperscript{11} which seems at least partially understandable in terms of surface charge buildups, it is likely that the calculations discussed here reflect in an exaggerated way charge buildups which take place on actual clusters.

VI. PHOTOEMISSION SPECTRA: BAND WIDTHS AND FERMI LEVELS; CHEMISORBED MOLECULES

Photoemission studies give a direct picture of electron state energy levels and their distributions for surfaces with and without adsorbates. They provide an ideal means for calibrating molecular orbital methods. Ultimately it will be important to discuss surface structures of the various species present during chemisorption and catalysis by surfaces, but it is difficult to say when sensitive methods of doing this will be found, or indeed if they will involve laboratory experiments or theoretical calculations. For the present photoemission experiments give very helpful information about the electronic states of adsorbates during their interactions with surfaces, sometimes even implying the nature of their surface structures. This information is much in tune with the theoretical study presented in this paper. In the following comparisons will be made between calculations and some recent experimental findings. No attempts will be made here to match the experimental spectra as exactly as possible since this will be done in later work.

Recently determined photoemission spectra for CO on W(100)\textsuperscript{28} show two different states of adsorption. The $\beta$ states have a binding energy of about 3 eV and fill first, with the concomitant formation of a peak in the electronic energy distribution curve at 6 eV below the Fermi levels and a second increase, within the $d$ band, at 3.5 eV below. A possible interpretation that was put forth was that the lower peak is due to chemisorbed O, which has little orbital interaction with the metal, and the upper one to C, which interacts strongly with the $d$ band. This explanation is prima facie satisfactory because the extended Hückel calculations imply dissociation of CO, as discussed in Sec. II, and because experimental spectra for O on W(110) also show a peak at 6 eV below the Fermi level. The energy difference between the two states, which is about 2.5 eV, compares well with the 2.36–3.4 eV difference\textsuperscript{41} in O and C $p$ state valence state ionization energies. The latter value of 3.4 comes from the tabulation in the Appendix of parameters used in the extended Hückel calculations. The 2.36 eV value from Ref. 41 seems favored, ignoring C–W interactions, although no calculations for dissociatively adsorbed CO have been performed.

![FIG. 15. Atomic charges calculated for lines of W atoms spaced 3.165 Å from nearest neighbors.](image)

![FIG. 16. Calculated charges for atoms in a line of 5 W atoms spaced 3.165 Å from nearest neighbors. Also energies and N–W and N–N Mulliken overlaps for N2 perpendicular to the line and 2.0 Å from and collinear with the metal nuclei.](image)
TABLE IX. Charges, from left to right, on W atoms in a 6 atom row. Nearest neighbor Mulliken overlaps are in parentheses. The latter 3 atoms are a mirror image.

<table>
<thead>
<tr>
<th>Atom</th>
<th>No. of S+D electrons</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.60 (0.001)</td>
<td>0.60 (0.001)</td>
<td>0.60 (0.001)</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.37 (0.39)</td>
<td>-0.21 (0.44)</td>
<td>-0.16 (0.34)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.85 (0.61)</td>
<td>-0.43 (0.67)</td>
<td>-0.35 (0.50)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.55 (0.63)</td>
<td>-0.69 (0.71)</td>
<td>-0.08 (0.26)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.30 (0.63)</td>
<td>-0.29 (0.64)</td>
<td>-0.16 (0.75)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.35 (0.69)</td>
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<td>0.08 (0.74)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>-0.09 (1.00)</td>
<td>0.04 (0.67)</td>
<td>0.04 (0.75)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>-0.32 (0.96)</td>
<td>-0.17 (0.66)</td>
<td>0.47 (0.74)</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>-0.66 (0.59)</td>
<td>0.04 (0.67)</td>
<td>0.04 (0.82)</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>-0.72 (0.50)</td>
<td>0.74 (0.63)</td>
<td>-0.02 (0.73)</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>-0.52 (0.60)</td>
<td>0.31 (0.60)</td>
<td>0.22 (0.64)</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>-0.09 (0.36)</td>
<td>0.06 (0.38)</td>
<td>0.00 (0.30)</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.00 (-2.17)</td>
<td>0.00 (-2.47)</td>
<td>0.00 (-3.02)</td>
<td></td>
</tr>
</tbody>
</table>

The α state of CO is more weakly bound at about 1.0 eV. It was pointed out that the α-state peak is at -14.0 eV with respect to the vacuum level, which is the same energy as the σg energy level in CO, but this similarity may be accidental because of counterposed bonding and relaxation shifts. However, the suggestion that this state bonds though the carbon end of the molecule is reasonable, and the calculated energy levels for this state show the σg level to be at -14.2 eV, in rough agreement with this proposed level assignment.

Relative positions in the photoemission spectra of the CO adsorbate on W(100) are well accounted for in the extended Hückel calculations. The metal is less well represented because the calculated work function is 8.9 eV versus 5.6 eV from experiment and the d band width is 2.7 eV versus 4 eV obtained from photoemission experiments. One problem in the calculations is the cluster size: A larger cluster would widen the d band and raise the Fermi level thereby lowering the work function. Such widening would probably not be enough, for calculations on many clusters yield a maximum filled band width of 3.75 eV with a work function of 7.96 eV. A shifting upward by about 2 eV of the W 5d valence state ionization energies, presently at -10 eV, is unadvisable, and would distort the relationship between the d band and atomic C and O levels. Relaxation effects are expected to be largely responsible for raising the Fermi level. Finally, it is noted that CO on W(110) gives similar results.

The story for CO adsorbed on Ni(100) is similar to that for α-state CO on W(100). Here the CO molecule may bind to the surface through the C end. The energy level at 12.5 eV below the vacuum level, assigned to the σg orbital, corresponds to the calculated level at -14.1 eV. The π level is measured at 3.2 eV below the σg, whereas the calculated difference is 1.5 eV. The extended Hückel σg level for the free CO molecule is at -13.5 eV and the π level is 2.1 eV below, compared with -14.0 and 2.9 eV from experiment. The experimentally observed upward shifts of 1.5 and 1.2 eV for CO on the Ni surface will not be reproduced when the free CO levels in the extended Hückel calculation are adjusted to fit experiment. However, intramolecular

FIG. 17. Structures and charges of some flat W clusters.

FIG. 18. Orientations of N2 on 13 W cluster representing a stepped surface for use in Table X. Characteristic distance to a W atom is 2.0 Å.
TABLE X. Characteristics of N₂ oriented about the 13 atom model of a stepped W surface as shown in Fig. 18. In the perpendicular orientations the first atom is further from the surface.

<table>
<thead>
<tr>
<th>Position</th>
<th>Energy (eV)</th>
<th>N-N Mulliken overlap</th>
<th>N-W Mulliken overlap</th>
<th>N charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-2.31</td>
<td>0.83</td>
<td>-0.13</td>
<td>-1.52</td>
</tr>
<tr>
<td>B</td>
<td>-0.97</td>
<td>0.62</td>
<td>0.20</td>
<td>-1.43</td>
</tr>
<tr>
<td>C</td>
<td>-3.02</td>
<td>0.86</td>
<td>-0.13</td>
<td>-1.48</td>
</tr>
<tr>
<td>D</td>
<td>-2.29</td>
<td>0.82</td>
<td>0.23</td>
<td>-1.20</td>
</tr>
<tr>
<td>E</td>
<td>-3.145</td>
<td>0.85</td>
<td>-0.13</td>
<td>-1.49</td>
</tr>
<tr>
<td>F</td>
<td>-2.095</td>
<td>0.80</td>
<td>0.24</td>
<td>-1.24</td>
</tr>
<tr>
<td>G</td>
<td>-2.89</td>
<td>0.87</td>
<td>-0.13</td>
<td>-1.45</td>
</tr>
<tr>
<td>H</td>
<td>-1.80</td>
<td>0.84</td>
<td>0.26</td>
<td>-1.12</td>
</tr>
<tr>
<td>I</td>
<td>-1.49</td>
<td>0.83</td>
<td>-0.12</td>
<td>-1.49</td>
</tr>
<tr>
<td>J</td>
<td>-0.64</td>
<td>0.70</td>
<td>0.19</td>
<td>-1.27</td>
</tr>
</tbody>
</table>

Electronic repulsions due to partial filling of the π* levels will raise the σ and π levels. The conclusion, as for CO on W(100), is that these calculations already represent without any parameter selection the levels of CO on Ni(100), and parameter adjustments could tune the calculated results to even better agreement, except for level raising due to intramolecular electron repulsions. Even these repulsion energies could be added in, but further work is necessary along this line.

Recent photoemission studies of N₂, N₂O, NO, and O₂ on W(100)²⁹ point to dissociation into atoms. The N spectra shift with coverage, and are indicative of strong N–W bonding with N–N interaction. A study of which is beyond the scope of this work, but it was shown in Sec. IV that N₂ should easily dissociate on W(100). The spectra suggest N₂O and NO dissociate, with the appearance of the O level as for CO discussed above.

Photoemission spectra of ethylene on Ni(111) have been observed recently.⁴³ Comparison to the calculated spectrum is in Fig. 19. In order to approximately match the filled π state of ethylene to experiment the carbon 2p levels are raised 2.0 eV. Otherwise the spectra would be calculated to look essentially like those in Fig. 19 for ethylene on W(100) which in itself for this reason may display too weak an interaction. Because the ethylene π level is raised to about its proper position, it interacts strongly with the completely symmetric metal s state beneath the d band and shifts down 0.7 eV toward the σ levels. This shift compares nicely with the 0.9 eV experimental shift, remembering the model geometry and approximate band structures in these calculations. A similar shift has been obtained by an SCF-Xα scattered-wave calculation on a model Ni₂-ethylene system.⁴⁶ The π state also mixes to a lesser extent...
with some states at the bottom of the d band. As discussed above, the extended Hückel method does not show relaxation shifts corresponding to the lowering of the vacuum level for the covered surface, but the shift of the v bond seems to be accounted for in this model. The calculated levels for ethylene on Ni(111) differ from those for the 9 atom Ni(100) by only a few hundredths of an eV at most. The model Ni(111) surface consisted of Ni atom surrounded by 6 nearest neighbors in the surface plane and 3 in the plane below.

VII. CONCLUDING COMMENTS

The theme of this work has been the presentation of a way of looking at the phenomenon of transition metal surface chemisorption and catalysis. Although the calculations employed parameters and geometries which may require adjustment to fit some precise criteria, in the absence of such criteria the explanation of what are relatively sparse and crude experimental data has been handled with a numerically sparse and crude model. The success at this level appears to put molecular orbital studies in a favorable light. As more information concerning adsorbate charges, geometries, orbital energy levels, and catalyzed reactions leading to new products becomes available for more and more types of surfaces, the parameters in the method may be adjusted to provide an understanding of the information by using molecular orbitals. Even in the absence of such data some systems may present sufficient interest to stimulate extended Hückel studies. It is to be cautioned that these studies can frequently yield important facts about bonding behavior, but the energy surfaces cannot be trusted without careful justification in each instance. There are many degrees of freedom in a surface reaction about which nothing is known at this time. The extended Hückel method gives energy changes for rotational degrees of freedom between rigid and nonbonding groups, but surface reactions must have many changes in degrees of freedom involving bond length changes, and here the energy changes must be viewed with critical suspicion. The full extent of the applicability of the extended Hückel molecular orbital method to surface studies will not be known until many studies are made using the method, and the results are compared to experiment. There is a good chance that a more quantitative molecular orbital method can be developed which is as economical to use as the extended Hückel one. Such a method will allow for both calculating and understanding surface phenomena. Until that time qualitative studies similar to those reported here can be used to interpret, and to some extent predict, what the spectroscopists see.

ACKNOWLEDGMENTS

Informative discussions were had with T. N. Rhodin, R. R. Rye, R. H. Paulson, G. A. Somorjai, and other participants in the surface science seminars at Cornell. Our work was generously supported by the Advanced Research Projects Agency through the Materials Science Center at Cornell University, and by the National Science Foundation.

APPENDIX

The extended Hückel molecular orbital procedure uses molecular orbital wavefunctions \( \psi \) taken as linear combination of Slater-type atomic orbitals \( \varphi \):

\[
\psi = \sum_p c_p \varphi_p.
\]  

(A1)

The coefficients \( c_p \) are chosen to diagonalize the Hamiltonian matrix. The diagonal elements of this matrix are numbers which are approximately equal to the atomic

<table>
<thead>
<tr>
<th>Atom</th>
<th>Principal quantum No.</th>
<th>Slater exponent</th>
<th>Ionization energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>1,300</td>
<td>-13.60</td>
</tr>
<tr>
<td>Li</td>
<td>2</td>
<td>0,650</td>
<td>-5.40</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>1,300</td>
<td>-15.20</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>1,625</td>
<td>-21.40</td>
</tr>
<tr>
<td>N</td>
<td>2</td>
<td>1,950</td>
<td>-26.00</td>
</tr>
<tr>
<td>O</td>
<td>2</td>
<td>2,450</td>
<td>-33.00</td>
</tr>
<tr>
<td>F</td>
<td>2</td>
<td>2,655</td>
<td>-40.00</td>
</tr>
<tr>
<td>W</td>
<td>6</td>
<td>1,400</td>
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</tr>
<tr>
<td>Ni</td>
<td>4</td>
<td>1,500</td>
<td>-7.635</td>
</tr>
</tbody>
</table>

Diatomic molecule

<table>
<thead>
<tr>
<th>Li2</th>
<th>B2</th>
<th>C2</th>
<th>N2</th>
<th>CO</th>
<th>NO</th>
<th>O2</th>
<th>F2</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,6725</td>
<td>1,589</td>
<td>1,3117</td>
<td>1,094</td>
<td>1,1282</td>
<td>1,1508</td>
<td>1,207</td>
<td>1,412</td>
</tr>
</tbody>
</table>

*Reference 6 of text.

**Reference 7 of text.

valence state ionization energies. The off-diagonal Hamiltonian matrix elements are evaluated according to the Wolfsberg–Helmholtz formula

\[ H_{\sigma\sigma'} = \langle k/2 \rangle (H_{\sigma\sigma} - H_{\sigma\sigma'}) S_{\sigma\sigma'}, \]

where \( K \) is a constant, 1.75 in this paper, the \( H \)'s are valence state ionization energies for atomic orbitals on atoms, and \( S_{\sigma\sigma'} \) is the overlap integral for \( \varphi_\sigma \) and \( \varphi_{\sigma'} \). Because of angular orthogonality, there are no off-diagonal matrix elements between states on the same atom. The parameters used in calculations for this paper are listed in Table XI.

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