Alfred B. Anderson and Roald Hoffmann

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

Alfred B. Anderson* and Roald Hoffmann

Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14850
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The extended Hückel molecular orbital method is used to examine interactions of Li_2, B_2, C_2, N_2, CO, NO, O_2, and F_2 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 Li_2 and F_2 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 N_2, N_2O, NO, and O_2 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 Li_2, B_2, C_2, N_2, O_2, F_2, CO, NO, and ethylene on tungsten and nickel (100) surfaces is explored. The extended Hückel[1] molecular orbital method is employed. Previous work using this method has dealt with the properties of small clusters of metal atoms,[2] with establishing the preferred sites for chemisorption of first period atoms and molecules on a graphite layer,[3] with the orientation of CO on Ni(100),[4] with the energetics of hydrogen atom adsorption on Ni(100),[5] and with the energetics of hydrogen[6] and nitrogen[7] 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 Li_2 to F_2 in the first period. The nature of adsorbate bond weakening discussed so far in terms of molecular orbitals only for CO[8] and adsorbate–substrate bond formation can be elucidated semiquantitatively in terms of well-known concepts[9] 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[10] 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[11] and of rough infinite surfaces[12,13] 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[14] are formulated to depend on physical shapes and adsorbate–adsorbate and adsorbate–substrate interactions without recourse to many body or through-bond-coupling effects[15] which might involve longer wavelength substrate states. One might imagine the dehydrocyclization of n-heptane on stepped Pt surfaces[16] 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[1] 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 is 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 semiempirical molecular orbital method, in its various materializations as CNDO/2, INDO, and MINDO, gives more satisfactory bond lengths[17] and has been used to study small metal clusters[2] and the adsorption of hydrogen atoms on Ni clusters,[18] 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.[19] 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.[20] It is expected that this procedure will yield good energy 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),[21] the induced covalent bond[22] from perturbation theory for hydrogen on metal surfaces, and the statistical charge density method for hydrogen atom chemisorption where the surface is represented by the jellium model.[23] Other theoretical methods which give a description of metal surfaces in the absence of adsorbates[24] will not be discussed.

There are five separate features to be considered in detail in this description of dissociative chemisorption on (100) W and Ni surfaces. The first feature is charge transfer between adsorbate and substrate. Charge transfer is a result of the relative positions of empty and filled molecular orbital energy levels for the separated diatomic adsorbates and metal atom clusters. Generally, if the highest occupied molecular orbital in the molecule lies at a higher energy than the cluster's

Fermi level energy, then electrons are transferred to the cluster. This happens in the case of Li_2. The converse is true in these calculations for the other molecules, all of which gain electronic charge, for their lowest unoccupied levels lie below the Fermi level. Such behavior is naturally in accord with charge transfer predictions based on electronegativity differences[25] between the metals and adsorbates.

Secondly, this study examines bond weakening and strengthening in the diatomic adsorbates and bond formation with metal atoms by using the Mulliken atomic overlap population analysis[26] and ionic interaction arguments. It is found that Li_2 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 F_2 accepts two electrons from the surface and forms an ionic bond with the surface. The F_2^{2-} 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 B_2 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.[27]

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[22] and charge density[23] 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[12,13] and small metal clusters.[11]

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[28] and N_2, NO, and O_2[29] on W(100), and O and CO[30] 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.

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 H[6] and N[7] 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[25] 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 $5p^6 5d^4 6s^2$ 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, O_2, and F_2 will accept 2 and N_2 4 electrons. Actual calculations yield charge densities, according to the Mulliken definition,[26] 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.[27] The average W atom structure goes from $5p^6 5d^4 6s^2$ for the atom to $5p^6 5d^{5.37} 6s^{0.63}$. Similarly the Ni atom goes from $3p^6 3d^8 4s^2$ to $3p^6 3d^{9.63} 4s^{0.37}$ in the cluster compared to $3p^6 3d^{9.46} 4s^{0.54}$ from experimental considerations.[31] The W filled d band width for this cluster is 2.7 eV, compared to about 5.0 eV from photoemission
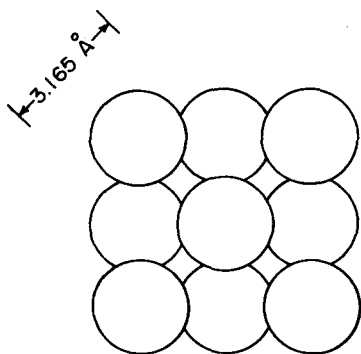

FIG. 1. Model of bcc W(100) surface. The characteristic distance 3.165 Å is from the *American Institute of Physics Handbook* (McGraw-Hill, New York, 1957).
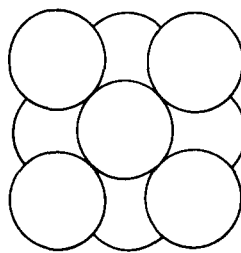

FIG. 2. Model of fcc Ni(100) surface. The characteristic distance 2.5 Å is from the reference in the caption to Fig. 1.

experiments,[28] 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.[30] 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 in 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 σ_s 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 π_x and π_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 σ_{p_z} orbital mixes well with a d_{z^2} 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 $C_2 \pi_x^*$ and π_y^* with metal d_{xz} and d_{yz} 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 π^* levels which lie below the Fermi levels are more than half filled, but, due to orbital interactions, not completely filled. Charge enters the π^* levels of CO and NO. The π^* level of O_2 lies beneath the bands and is almost completely filled. The σ^* 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.
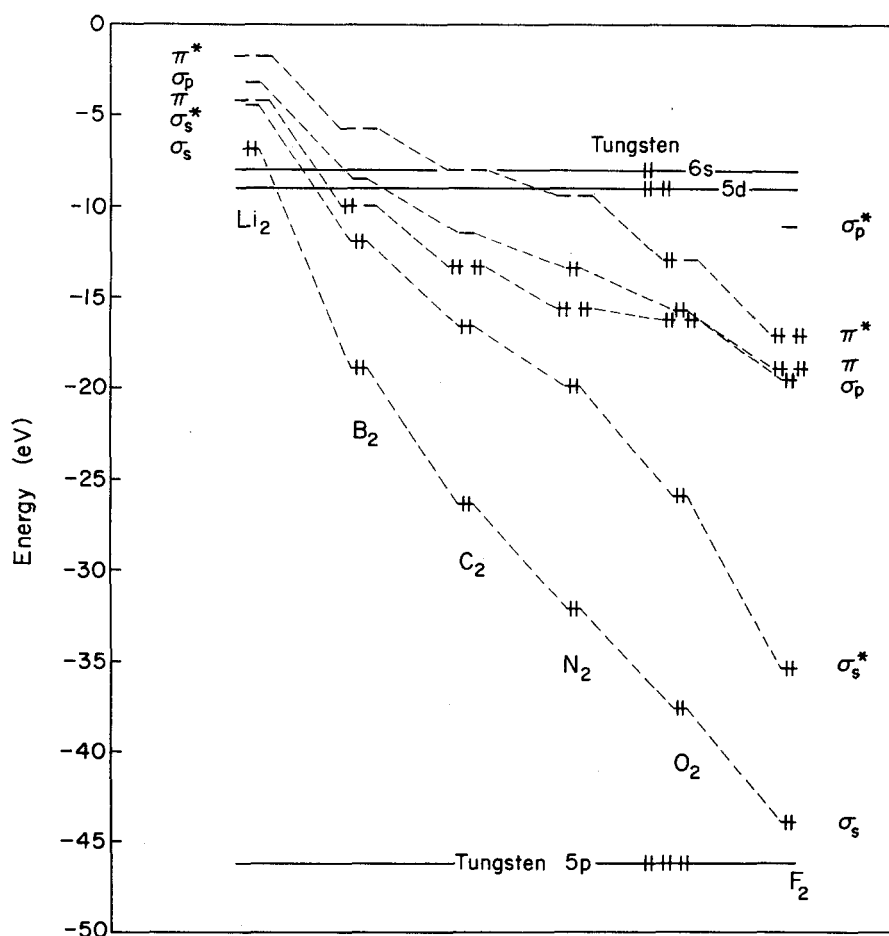
FIG. 3. Energy levels of a single tungsten atom and the homonuclear first row diatomic molecules.

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. Wheras such large positive charges are reasonable and have been observed experimentally for alkali metals adsorbed to W[32] 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 ±1, due to intraionic electron repulsions which are neglected in the extended Hückel procedure. This

TABLE I. Atomic charges calculated for homonuclear diatomic molecules with colinear geometry and 2.0 Å separation from a single W atom. The top number is for the further atom.

| | Diatomic molecule | | | | | |
	Li_2	B_2	C_2	N_2	O_2	F_2
Charges	+0.91	−0.70	−2.23	−1.47	−0.98	−0.97
	+0.42	−0.90	−0.97	−0.67	−0.59	−0.84

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 is 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 σ 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 π orbitals, B_2 has its bond strengthened. The strengthening of the C_2 bond due to filling of the empty σ orbital is more than negated by
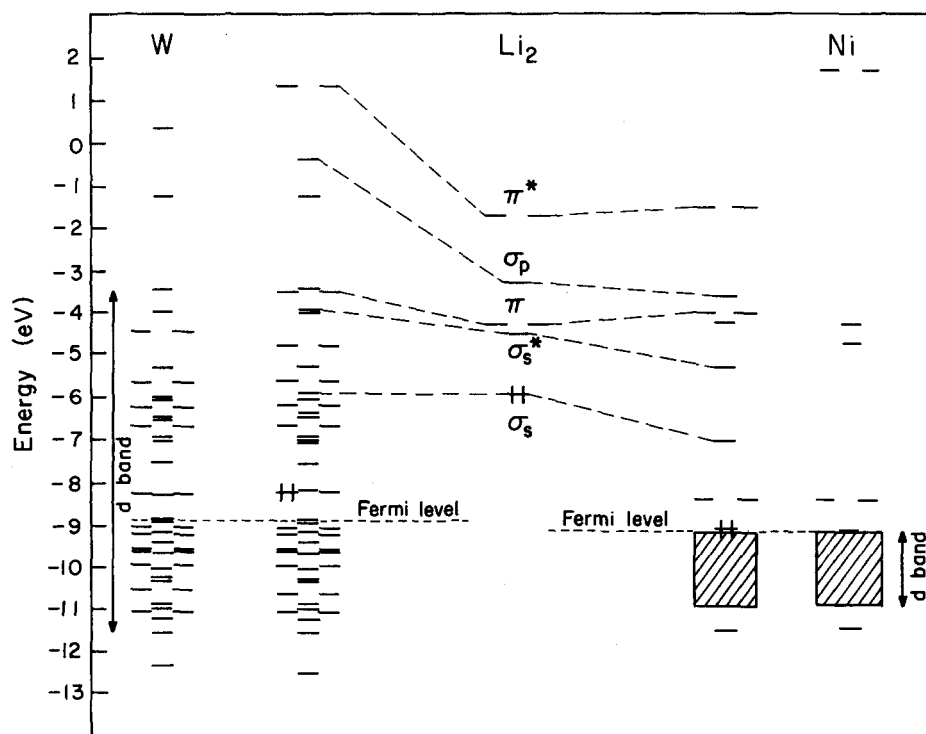
FIG. 4. Energy levels for 9 atom W and Ni clusters as in Figs. 1 and 2 and Li_2 before and after interaction. When interacting, the diatomic molecule is perpendicular to the surface above the central metal atom, the nearer nucleus being 2.0 Å from the plane of surface nuclei. Small changes of the metal or adsorbate atomic valence state ionization energies will not have a pronounced effect on the level orderings and charge transfers in this and other figures. On the far left are the W cluster levels approximating the d band. On the far right is the calculated Ni d band with some states in the s band. The d band levels are not drawn individually. In the center are the Li_2 levels, and to the near left and right are the levels after interacting with W and Ni. When identification is clear, correlation lines are drawn, but, when strong mixing occurs, it is impossible to indicate all orbitals that mix in.

mixing of the higher π^* orbitals. Filling of the empty degenerate π^* orbitals in N_2 and CO greatly weakens their bonds. The weakening of the CO bond was given a similar interpretation earlier,[8] and formulas exist which connect shifts in vibrational frequencies to internuclear

distances.[34] Quantitative tests are not considered here, although vibrational analysis may become a useful tool in understanding surface structures.[35] Similarly NO, which already has 1 electron in the π^* system, and O_2 which has 2, both have weakened bonds. Finally, F_2
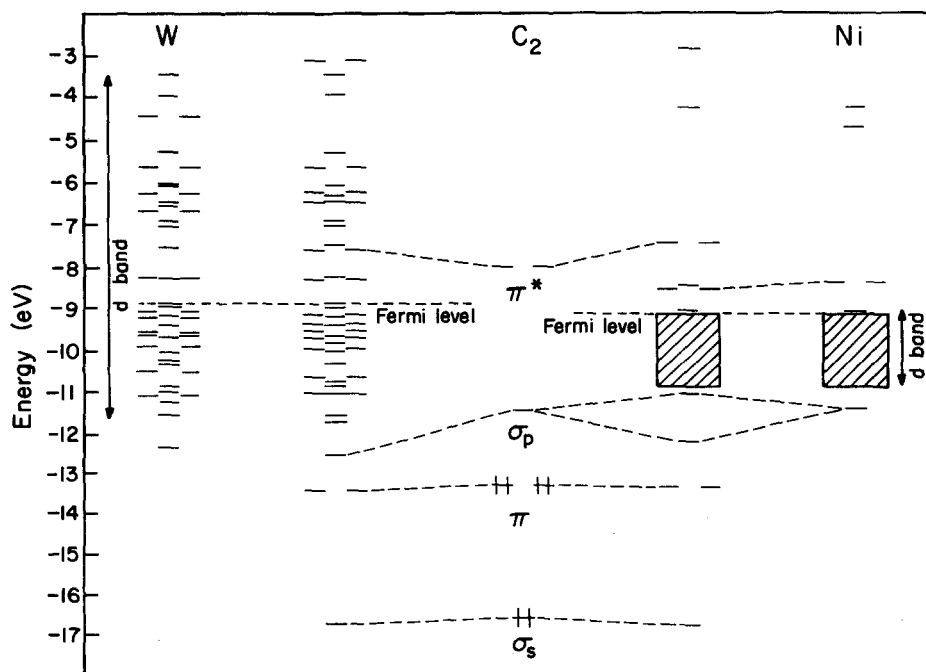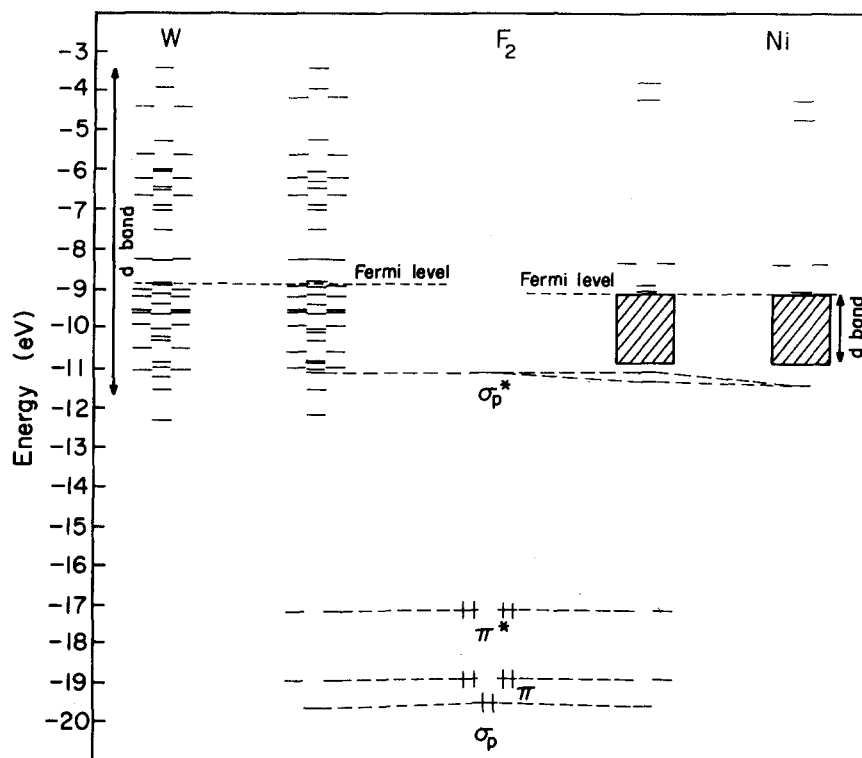

FIG. 5. C_2. See caption to Fig. 4.

FIG. 6. F_2. See caption to Fig. 4.

assumes a negative bond order due to the nearly complete filling of the last orbital in the series, which is σ^*. Thus, according to these calculations for all molecules except B_2, bond weakening in terms of overlap populations parallels the effects of repulsion due to charge buildup. With the exception of Li_2 and 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 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 Li_2 and 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 B_2 the π orbitals of that molecule lie in the d bond of the cluster. There is significant overlap of the π orbital of B_2 with metal atom d_{xz} and d_{yz} orbitals, as shown in Fig. 10, as well as some mixing of the empty σ_p orbital of the diatomic, as shown in Fig. 7. Both interactions lead to metal–diatomic bonding. In C_2, shown in Fig. 5, the diatomic σ_p orbital lies at the bottom of the cluster d band. It mixes well with the metal d_{z^2} orbital, as shown in Fig. 7, as well as with the symmetric metal s states, which, for both W and Ni, lie below the d band. The interaction is illustrated in Fig. 11. In addition there is a lesser degree of mixing of diatomic π^* orbitals with the cluster. For N_2, CO, and NO the π^* orbitals interact, but for O_2 the mixing of π^* and cluster orbitals is relatively weak since, as may be seen in Fig. 3, the π^* levels are below the cluster d bands. Only a very small overlap exists between 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

TABLE II. Atomic charges calculated for diatomic molecules perpendicular to the surfaces of Figs. 1 and 2, the nearer atom being 2.0 Å from the plane of surface nuclei, and in the 1 coordinate position. In CO and NO, C and N are nearer the surfaces. Closer atoms' charges are underneath.

Atomic charges	Diatomic molecule							
	Li_2	B_2	C_2	N_2	CO	NO	O_2	F_2
On W	+1.00	−1.08	−1.98	−1.47	−1.10	−1.14	−1.01	−0.99
	+1.03	−0.55	−0.92	−0.78	−0.66	−1.14	−0.76	−0.90
On Ni	+1.02	−1.61	−1.32	−1.26	−0.94	−1.19	−1.00	−0.99
	+1.06	−0.88	−0.73	−0.88	−0.48	−1.57	−0.90	−0.94
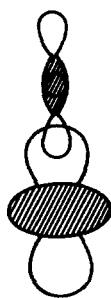
FIG. 7. Interaction between a diatomic σ_{p_z} orbital and a metal d_{z^2} orbital.

FIG. 9. Charges on W atoms in a 9-atom cluster as a function of diatomic adsorbate charges. O: central W atom; □: nearest neighbor underneath; △: neighbor in surface plane. See Fig. 1.

atom in a colinear arrangement, dissociation with re-bonding to the surface is the anticipated result. Further-more, 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 π and π^* orbitals with the metal's d_{xz} and d_{yz} orbitals, where z is the colinear direction, and it will mix its σ_{p_z} and $\sigma_{p_z}^*$ orbitals with the metal d_{z^2} orbitals and with the symmetric cluster s state beneath the d bands. Here other orientations are considered. 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 surface 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 grossly the same. Calculated energies, diatomic bond orders, and diatomic charges are tabulated for the old perpendicular configuration and three new ones. All have 2.0 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 diatomic molecule in different orientations relative to the surface. The first of these columns describes the orientation of a diatomic parallel to the one-coordinate site above the cluster of Fig. 1. The other columns describe placement of the molecule perpendicular or parallel to a four-coordinate surface site underneath the cluster in Fig. 1. It may be premature to assign diatomic orien-
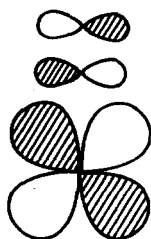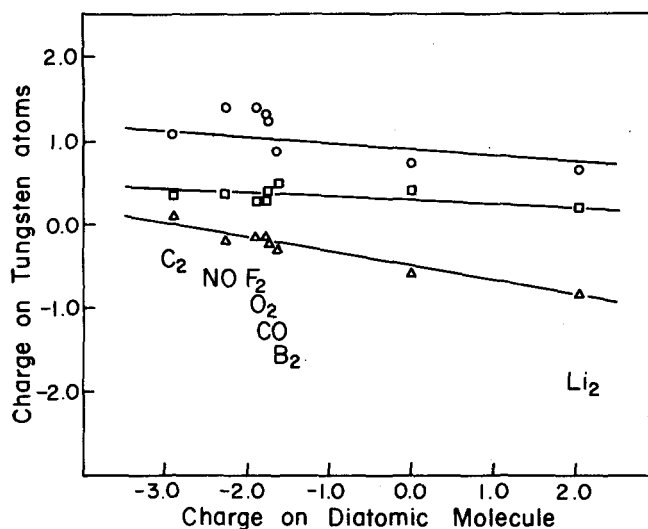

FIG. 8. Interaction between a diatomic π^* orbital and a metal d_{xz} or d_{yz} orbital.

tations on the basis of these energies, which do not explicitly contain ionic contributions. Strong orbital interactions between the diatomic and substrate can exist for all these orientations, as well as additional ones in Table 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 molecule 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 mobility,[27,28,36] and it has been the basis for theoretical treatments 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.[22] 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,[36] and the results of this paper are in support. Furthermore, these results imply that it should be possible 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 theories. The dissociating influence of ionic charge transfer

TABLE III. Diatomic bond orders, defined as Mulliken overlap populations, for diatomic molecules before and after interaction 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.

| | Diatomic bond order | | | | | | | |
	Li_2	B_2	C_2	N_2	CO	NO	O_2	F_2
Free	0.30	1.41	1.73	1.63	1.34	1.12	1.26	0.82
On 1 W	0.06	1.37	1.22	0.89	0.76	0.59	0.48	−0.62
On 9 W	−0.01	1.47	1.33	0.85	0.76	0.51	0.45	−0.63
On 9 Ni	−0.02	1.68	1.59	0.86	0.84	0.39	0.43	−0.64

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 N_2 bond, the decrease in system energy and the increase in N-cluster bond order for N_2 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[37] is implied. Experimental studies of dissociative chemisorption of H_2 on $W^{27,36,38}$ show dissociation and a number of atomic states, and a theoretical treatment of dissociative chemisorption of H_2 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 bond order–energy relationships guided by knowledge of the molecular orbitals. Here the molecular orbital interactions between ethylene and the W(100) surface are considered. Ethylene is known to chemisorb on several W crystal faces and to thermally decompose to a small amount of ethane with the major products being H_2 and carbon residue.[40] The nature of the bonding to the surface may be quickly deduced by examination of

the C_2 energy level diagram in Fig. 5 while realizing the the π_y and π_y^* and σ_{px} orbitals are substantially lowered by mixing with the hydrogen atomic orbitals to form CH bonds, while the π_z and π_z^* orbitals are nearly unchanged. Therefore the lowest unoccupied orbital in ethylene is the π_z^* 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 π_z 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 Li_2 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.

Figure 15 shows calculated charges on rows of W

TABLE IV. Bond orders, defined as Mulliken overlap populations between atoms in diatomic molecules perpendicular to metal cluster centers, or colinear with 1 W atoms, and 2.0 Å from the nearest metal nucleus. The metal overlap with the nearer atom is listed second. In CO and NO, C and N are nearer the surfaces.

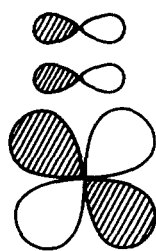| | Atomic bond order to metal | | | | | | | |
	Li_2	B_2	C_2	N_2	CO	NO	O_2	F_2
On 1 W	0.06	−0.05	−0.15	−0.13	−0.09	−0.07	−0.05	−0.05
	0.69	1.23	1.05	0.84	1.16	0.75	0.40	0.23
On 9 W	−0.02	−0.03	−0.05	−0.04	−0.08	−0.06	−0.04	−0.01
	−0.04	0.42	0.44	0.35	0.88	0.48	0.17	0.03
On 9 Ni	−0.03	−0.01	−0.11	−0.11	−0.03	−0.02	−0.02	−0.04
	−0.00	0.67	0.76	0.61	0.54	0.15	0.08	0.07

FIG. 10. Interaction between diatomic π orbital and a metal d_{xz} or d_{yz} orbital.

atoms of various lengths. The end atoms tend to accumulate charges of about -0.1, which are compensated by the middle atoms, as the clusters are neutral.

The interaction of the electronegative N_2 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 N_2–W bond orders reflect the energies. The fact that the N–N bond order goes up when the N_2–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. Charges 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 binding. 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 -0.011, its neighbor -0.005 and the center atoms $+0.016$, for Ni has 10 $s+d$ electrons.

Some amusement is to be had on observing Fig. 17 where several flat clusters and calculated atomic charges are shown. Abrupt charge rearrangements are
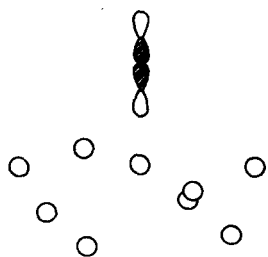

FIG. 11. Interaction between diatomic σ_p orbital and symmetric s cluster orbital.

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.

Diatomic molecule	One coordinate position		Four coordinate position	
	Perpendicular	Parallel	Perpendicular	Parallel
Li₂ Energy	−4.50	−5.01	−4.44	−4.73
Mulliken overlap	−0.01	0.01	−0.02	−0.00
Atomic charges	1.03	0.94	1.04	1.02
	1.00		1.10	
B₂ Energy	−0.14	−0.92	0.29	−0.09
Mulliken overlap	1.47	1.35	1.65	1.46
Atomic charges	−1.08	−0.76	−1.30	−0.77
	−0.55		−0.72	
C₂ Energy	−1.34	0.68	0.26	−0.14
Mulliken overlap	1.32	1.33	1.54	1.54
Atomic charges	−1.98	−1.35	−1.50	−1.50
	−0.92		−0.91	
N₂ Energy	−1.65	−0.25	0.98	0.12
Mulliken overlap	0.85	0.56	0.40	0.82
Atomic charges	−1.47	−1.53	−1.82	−1.22
	−0.78		−1.58	
O₂ Energy	1.00	1.38	0.95	1.72
Mulliken overlap	0.45	0.50	0.44	0.47
Atomic charges	−1.01	−0.58	−1.00	−0.91
	−0.76		−0.93	
F₂ Energy	1.57	1.63	1.15	2.40
Mulliken overlap	−0.63	−0.51	−0.64	−0.61
Atomic charges	−0.94	−0.88	−1.00	−0.95
	−0.90		−0.98	

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 N_2 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 N_2–W bond is the strongest, and the N_2 bond is the strongest. Hence, if ionic contributions are ignored, the prediction is that the corner atom is most attractive to N_2 and can facilitate chemisorption. Because the N_2 bond is greatly weakened, dissociation, as demonstrated in Table VII, may be expected for adsorbed N_2. Simple structural and

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. On top are 5 atoms in a row representing the surface, and below are 8 nearest neighbors. Energies are in eV.

| Diatomic molecule	One coordinate position		Two coordinate position	
	Perpendicular	Parallel	Perpendicular	Parallel
C₂ Energy	−1.47	−0.67	−0.92	−0.80
Mulliken overlap	1.19	1.31	1.18	1.21
Atomic charges	−2.10	−1.43	−1.79	−1.52
	−1.13		−1.28	
N₂ Energy	−0.60	−0.03	−0.25	−0.01
Mulliken overlap	0.50	0.51	0.34	0.50
Atomic charges	−1.83	−1.60	−1.92	1.61
	−1.27		−1.59	
O₂ Energy	0.93	1.20	0.56	0.92
Mulliken overlap	0.45	0.49	0.44	0.47
Atomic charges	−1.01	−0.86	−1.01	−0.86
	−0.74		−0.86	
F₂ Energy	1.40	1.59	0.95	1.70
Mulliken overlap	−0.63	−0.52	−0.63	−0.58
Atomic charges	−0.99	−0.89	−0.99	−0.91
	−0.89		−0.94	
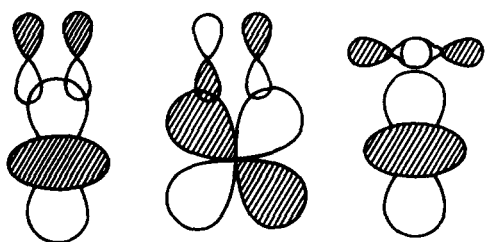
FIG. 12.   Interactions between orbitals in a diatomic molecule
lying flat on the metal surface and the atom beneath.

TABLE VII. N_2 dissociating parallel to the surface on a one-
coordinate W atom in a 9-atom cluster.

	N–N Distance (Å)		
	1.094	1.4	1.8
N_2 Mulliken overlap	0.56	0.55	−0.09
N charge	−1.53	−1.71	−2.31
N-cluster bond order	0.15	0.16	0.22
Extended Hückel energy (eV) (Relative)	0.00	−4.45	−7.25

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

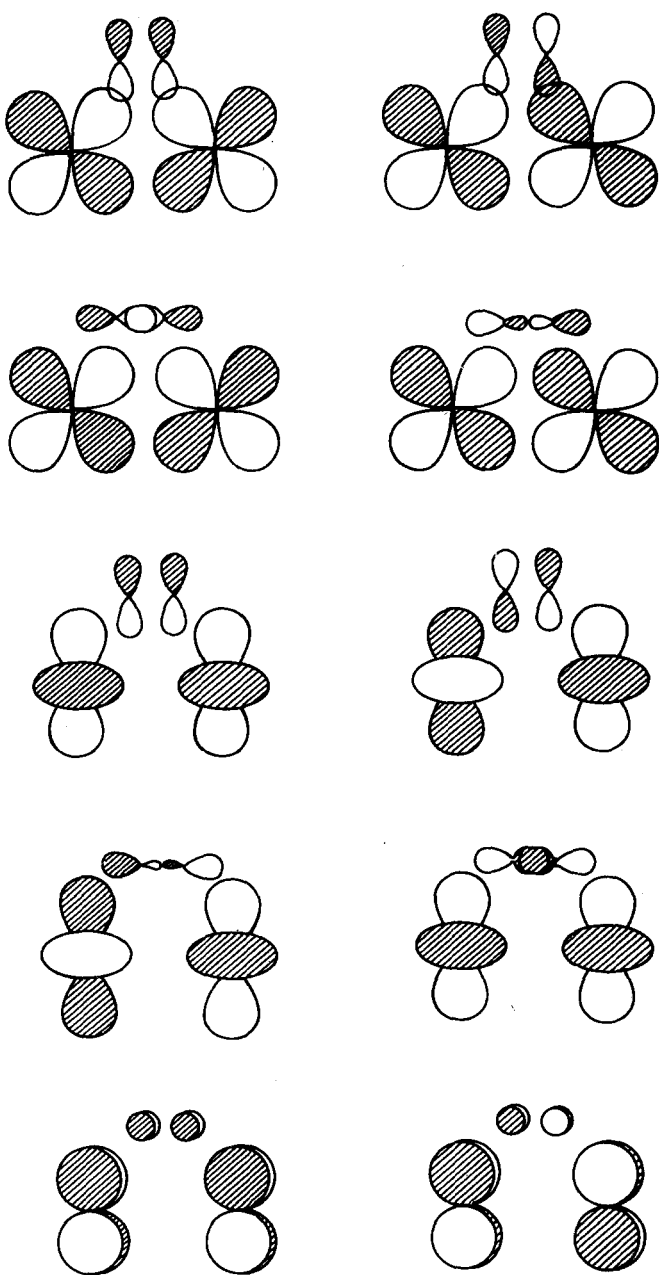Calculations of atomic charges in normally populated

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

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 calcula-
tion will give smaller charge transfers primarily be-
cause 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.

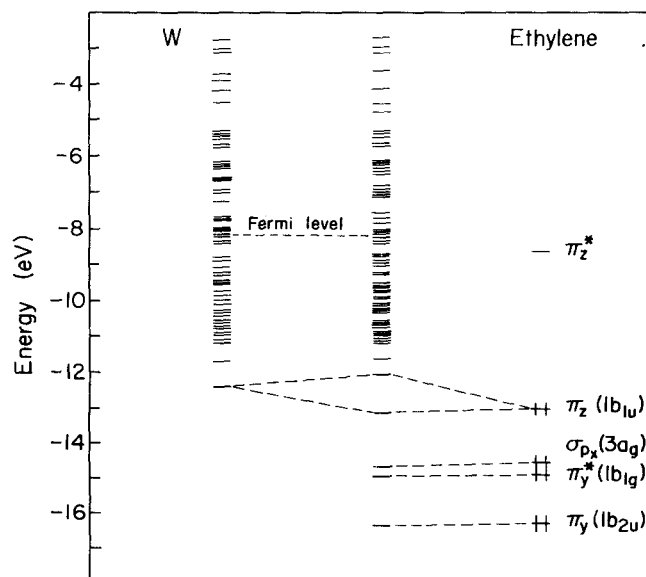Despite the overestimations of atomic charge present

FIG. 14.   Interaction diagram for ethylene and a 13 atom W
cluster.   On top are 5 W atoms, with 8 nearest neighbors be-
low; 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.

TABLE VIII. Bond orders, defined as Mulliken overlaps populations, and energies for ethylene on a 5 W atom row with 8 nearest neighbors below. The C–C bond parallels the row and the plane of the ethylene parallels the surface at a distance of 2.0 Å. The symmetric position puts ethylene above the central atom, the half bridging position puts one C atom above it, and the bridging position symmetrically bridges the central W and its nearest surface neighbor.

	Symmetric	Half-bridging	Bridging
C–C bond order	0.88	0.84	0.81
C–cluster bond order	0.15	0.13, 0.10	0.10
C atomic charge	–0.61	–0.62, –0.68	–0.70
Hückel energy (eV)	0.78	1.44	1.61

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 applications 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,[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
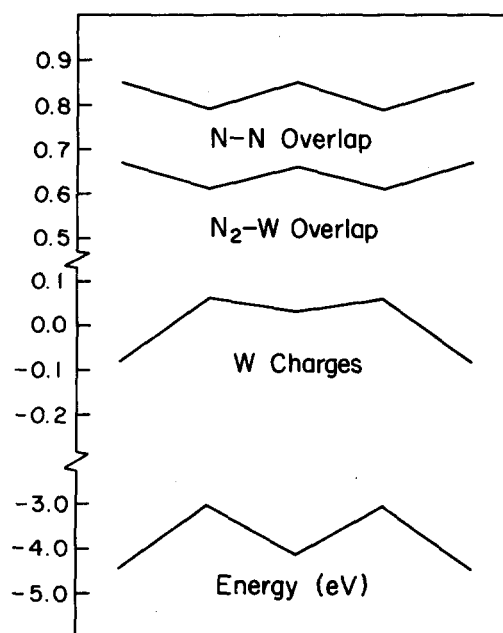

FIG. 16. Calculated charges for atoms in a line of 5 W atoms spaced 3.165 Å from nearest neighbors. Also energies and N_2–W and N–N Mulliken overlaps for N_2 perpendicular to the line and 2.0 Å from and colinear with the metal nuclei.

exactly as possible since this will be done in later work.

Recently determined photoemission spectra for CO on W(100)[28] show two different states of adsorption. The β 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[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.
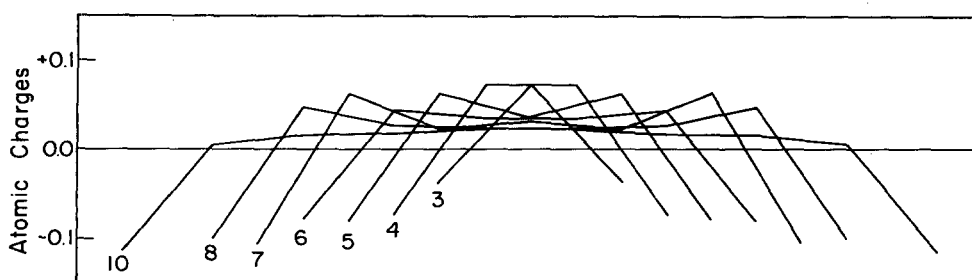

FIG. 15. Atomic charges calculated for lines of W atoms spaced 3.165 Å from nearest neighbors.

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.

No. of $S+D$ electrons	Atom 1	Atom 2	Atom 3
0	0.00 (0.001)	0.00 (0.001)	0.00 (0.001)
1	0.37 (0.39)	−0.21 (0.44)	−0.16 (0.34)
2	0.80 (0.61)	−0.45 (0.67)	−0.35 (0.50)
3	0.55 (0.85)	−0.63 (0.71)	0.08 (0.56)
4	0.36 (0.95)	−0.20 (0.64)	−0.16 (0.72)
5	0.55 (0.99)	−0.63 (0.67)	0.08 (0.74)
6	−0.08 (1.00)	0.04 (0.67)	0.04 (0.75)
7	−0.32 (0.96)	−0.15 (0.66)	0.47 (0.74)
8	−0.08 (0.89)	0.04 (0.67)	0.04 (0.62)
9	−0.72 (0.93)	0.74 (0.63)	−0.02 (0.73)
10	−0.52 (0.66)	0.31 (0.40)	0.22 (0.64)
11	−0.09 (0.36)	0.06 (0.00)	0.02 (0.30)
12	0.00 (−2.17)	0.00 (−2.87)	0.00 (−3.02)

FIG. 18. Orientations of N_2 on 13 W cluster representing a stepped surface for use in Table X. Characteristic distance to a W atom is 2.0 Å.

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 σ_p energy level in CO, [42] but this similarity may be accidental because of counterposed bonding and relaxation shifts. [43] However, the suggestion that this state bonds though the carbon end of the molecule[43] is reasonable, and the calculated energy levels for this state show the σ_p 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 vs 5.64 eV from experiment[28] and the d band width is 2.7 eV vs about 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
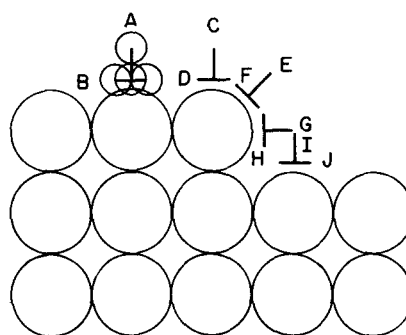
of 7.96 eV. A shifting upward by about 2 eV of the W $5d$ valence state ionization energies, presently at −10 eV, is unadvisable, [41] and would distort the relationship between the d band and atomic C and O levels. Relaxation effects[44] are expected to be largely responsible for raising the Fermi level. Finally, it is noted that CO on W(110) gives similar results. [45]

The story for CO adsorbed on Ni(100)[30] 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 σ_p orbital, corresponds to the calculated level at −14.1 eV. The π level is measured at 3.2 eV below the σ_p whereas the calculated difference is 1.5 eV. The extended Hückel σ_p 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. [42] 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
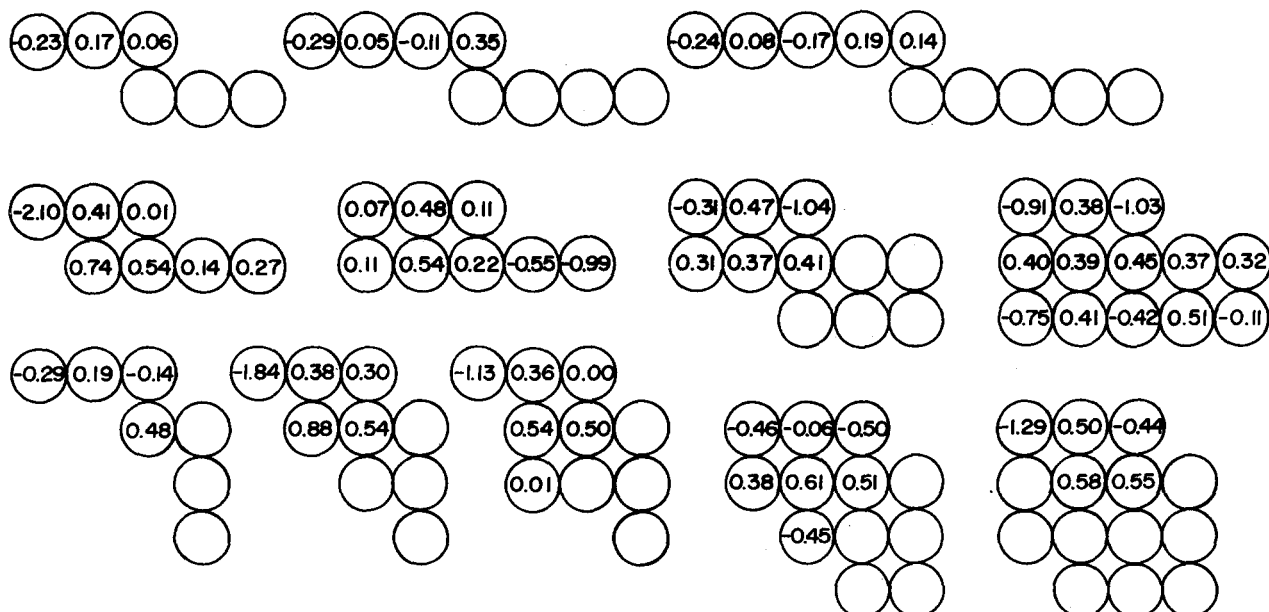

FIG. 17. Structures and charges of some flat W clusters.

TABLE X. Characteristics of N_2 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.

Position	Energy (eV)	N–N Mulliken overlap	N–W Mulliken overlap	N charge
A	−2.31	0.83	−0.13 0.74	−1.52 −0.76
B	−0.97	0.62	0.20 0.20	−1.43 −1.44
C	−3.02	0.86	−0.13 0.76	−1.48 −0.73
D	−2.29	0.82	0.23 0.26	−1.20 −1.20
E	−3.145	0.85	−0.13 0.76	−1.49 −0.75
F	−2.095	0.80	0.24 0.25	−1.24 −1.24
G	−2.89	0.87	−0.13 0.76	−1.45 −0.73
H	−1.80	0.84	0.26 0.23	−1.12 −1.20
I	−1.49	0.83	−0.12 0.70	−1.49 −0.80
J	−0.64	0.70	0.19 0.18	−1.27 −1.37

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 N_2, N_2O, NO, and O_2 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 N_2 should easily dissociate on W(100). The spectra suggest N_2O 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 cal-

culations. A similar shift has been obtained by an SCF-$X\alpha$ scattered-wave calculation on a model Ni_2-ethylene system.[46] The π state also mixes to a lesser extent
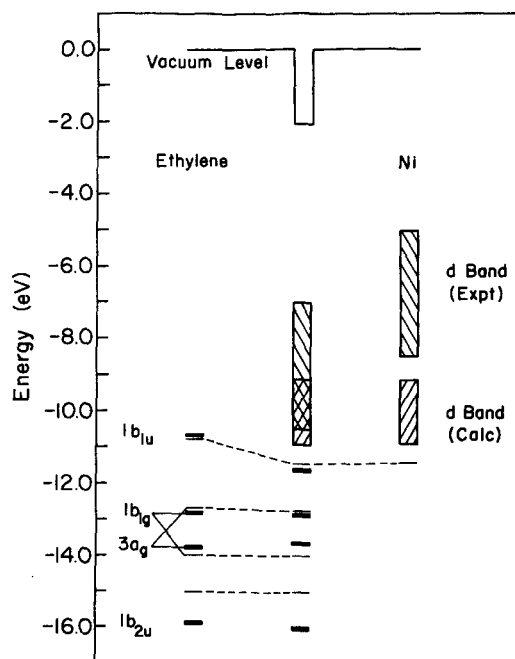

FIG. 19. Ethylene spectrum calculated (light) and experimental (heavy) before and after interaction with Ni(111). The plane of ethylene is 2.0 Å from the surface plane. The ethylene is symmetrically above a Ni atom which is at the center of a hexagon of nearest neighbors, and has three neighbors beneath. As drawn, the levels are invarient to ethylene rotation in this imperfect model.

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 π 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 orbitals 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 Hück-

el 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

APPENDIX

The extended Hückel molecular orbital procedure uses molecular orbital wavefunctions Ψ taken as linear combination of Slater-type atomic orbitals φ:

$$\Psi = \sum_\gamma c_\gamma \varphi_\gamma. \tag{A1}$$

The coefficients c_γ are chosen to diagonalize the Hamiltonian matrix. The diagonal elements of this matrix are numbers which are approximately equal to the atomic

TABLE XI. Parameters used in calculations in this paper.

Atom	Principal quantum No., Slater exponent and ionization energy (eV)								
	S			P			D		
H	1	1.300	−13.60	···	···	···	···	···	···
Li	2	0.650	−5.40	2	0.650	−3.50	···	···	···
B	2	1.300	−15.20	2	1.300	−8.50	···	···	···
C	2	1.625	−21.40	2	1.625	−11.40	···	···	···
N	2	1.950	−26.00	2	1.950	−13.40	···	···	···
O	2	2.275	−32.30	2	2.275	−14.80	···	···	···
F	2	2.425	−40.00	2	2.425	−18.10	···	···	···
W	6	1.400[a]	−8.00[a]	5	4.910[a]	−46.07[a]	5	2.200[a]	−9.00[a]
Ni	4	1.500[b]	−7.635[c]	3	4.600[b]	−78.31[d]	3[b]	5.750[b]	−10.00[c]

	Diatomic molecule							
	Li₂	B₂	C₂	N₂	CO	NO	O₂	F₂
Bond length (Å)[e]	2.6725	1.589	1.3117	1.094	1.1282	1.1508	1.207	1.412

[a]Reference 6 of text.
[b]J. W. Richardson *et al.*, J. Chem. Phys. **36**, 1057 (1962). The d orbital is a double zeta type: the coefficient of the Slater-type orbital in the table is 0.5683, the coefficient of the second one is 0.6292 and its exponent is 2.00.
[c]Reference 41 of text.
[d]F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Englewood Cliffs, NJ, 1960).
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valence state ionization energies. The off-diagonal Hamiltonian matrix elements are evaluated according to the Wolfsberg–Helmholtz formula

$$H_{\gamma\gamma'} = (K/2)(H_{\gamma\gamma} + H_{\gamma'\gamma'})S_{\gamma\gamma'}, \qquad (A2)$$

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

*Present address: Department of Chemistry, Yale University, New Haven, CN 06520.

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