

Chemisorption theory for metallic surfaces: Electron localization and the description of surface interactions

J. L. Whitten

Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794

Tapani A. Pakkanen

Department of Chemistry, University of Joensuu, 80101 Joensuu 10, Finland

(Received 13 September 1979)

A theory for describing molecule-solid surface interactions using correlated configuration-interaction (CI) wave functions for the surface region is described. Starting with a delocalized self-consistent-field wave function for the lattice, approximated as a cluster of atoms, a local surface region is defined by a unitary, localization transformation of the single-particle orbitals of the lattice wave function based on electron exchange maximization with the surface sites of interest. CI calculations on the resulting N -electron subspace plus adsorbate permit an accurate description of bonding at the surface. *Ab initio* computational techniques for treating the many-electron problem and large clusters of metal atoms are described.

I. INTRODUCTION

The chemisorption of molecules on solid surfaces has been a subject of long-standing interest due to its practical importance and the complexity of experimental and theoretical characterizations of the problem. The many contributing factors tend to obscure even an elementary understanding at the molecular level. Thus, there are questions of the composition of the solid, the surface geometry, the coverage of the surface by adsorbed species, the poisoning of active sites, adsorption and desorption processes, and the dynamics of reactions on the surface. Recently, however, a great deal of progress has been made in the development of experimental techniques for monitoring the rates of chemical reactions on single crystal surfaces of known structure.¹⁻⁶ Kinetic studies have been reported for a variety of reactions on transition metal surfaces of well-defined geometry with specific crystal faces, monolayer steps, and steps with monatomic kinks, and rates of reaction are found to depend significantly on surface structure.¹ Through such controlled experiments, the opportunity for a critical evaluation of theoretical models is greatly increased.

From the standpoint of theory the initial problem in chemisorption is electronic in origin: the electronic description of the adsorbate and clean surface, the treatment of bonding at the surface, and the inclusion of the response of the solid and adsorbate to bond formation.⁷⁻¹² For the metallic solid and clean surface certain qualitative features of the electronic structure can be deduced immediately from general principles: For an infinite lattice, there exists an energy band structure and delocalized single-particle states; in-

roducing a surface boundary can significantly modify these one-electron wave functions even though the position of the energy bands may not be greatly altered; in addition, new (surface) states can occur separated from the band structure continuum.⁸ By analyzing the local density of states,¹³ defined by projection of the orbitals of the solid onto atomic basis functions, the influence of the surface and the availability of orbitals on the surface can be ascertained.^{8, 10, 12} For such purposes a variety of theoretical techniques have been employed ranging from band theoretic methods for the semi-infinite lattice¹⁴⁻¹⁹ to linear combination of atomic orbitals (LCAO) expansions for finite clusters.²⁰⁻²⁵ In both cases density functional exchange approximations,^{26, 27} and in particular the Slater's statistical theory of exchange correlations, $X\alpha$ method, have greatly increased the tractability of the many-electron problem.^{20, 21}

Concerning the description of the adsorbate, powerful computational methods have likewise been developed for treating molecules, most notably configuration interaction theory which permits an accurate determination of molecular potential energy curves, equilibrium geometries, the energetics of bonding and electronic spectra.²⁸⁻³¹

However, on the question of treating adsorbate-solid surface interactions, differences inherent in the solid state and molecular theories make it difficult to couple the two approaches.^{32, 33} While this impasse may eventually be resolved, one direction that has been taken in recent years is to try to simulate solids by considering clusters of atoms,³³⁻⁴⁶ and thereby to make greater use of the techniques of molecular theory.³⁸⁻⁴¹ If one contemplates proceeding in this way to simulate

chemisorption on metallic surfaces, it is constructive to consider possible objections that could be raised at the outset to the following three possible alternatives.

(a) *Adsorption on a very small cluster of metal atoms (the equivalent of a supermolecule)*. The advantage here is that a sophisticated level of theory, significantly beyond Hartree-Fock theory, could be employed. For example, an *ab initio* configuration interaction treatment would be expected to describe accurately the bond breaking and formation processes that accompany adsorption. If the cluster is small, however, the criticism is that the model could miss important delocalization effects associated mainly with *s, p* bands.

(b) *The global treatment of adsorption on a large cluster*. Here the intent would be to treat the adsorbate and large cluster by one calculation. While the delocalization effects are now properly included, the quality of the treatment for practical purposes would necessarily be less than that in (a), and if sufficiently diminished, might be incapable of describing polarization effects or changes in electron correlation accompanying adsorption.

(c) *A global treatment of a large cluster, but improved in quality at the site of adsorption*. This approach meets the objections to both (a) and (b), however, the drawback is that an imbalance in the treatment in one region of space, especially that due to an improvement in the single-particle basis, can cause charge polarization errors which in turn can affect the bonding at the surface.

While the extent of the above problems is certainly not known in quantitative detail, it does appear possible to circumvent many of the formal difficulties by giving up the idea of treating the adsorbate and lattice (cluster) in a single calculational step, and the manner in which this might reasonably be accomplished is the main topic of the present paper. The following sections deal with the general theory, computational techniques, and an illustrative application to a close packed cluster of 54 titanium atoms. In subsequent studies, the electronic characteristics of adsorption sites will be examined as a function of lattice (cluster) size in 1, 2, and 3 layer structures and the adsorption of H₂ and CO at different sites on Ti surfaces will be reported.

II. THEORY

The main premise of the present approach is that a description of molecule-surface interactions and dissociative processes on surfaces will require a reasonably sophisticated wave function in

the surface region to account for changes in electron correlation accompanying the reactions. It thus appears advantageous to consider a multi-stage model to avoid treating the adsorbate and metal lattice as one system at the same, and consequently lower, level of accuracy. Proceeding in three main stages, we assume initially that an approximate description of the metal lattice can be found by treating the metal as a finite cluster of atoms, and assume further that an effective single-particle theory such as Hartree-Fock (HF) or Hartree-Fock plus density-functional correlation corrections is adequate for this purpose. A local (surface) region is then defined by a localization transformation of the single-particle orbitals of the lattice wave function. Finally, the adsorbate and local region are treated (by configuration interaction at an *ab initio* level) as embedded in the fixed field of the interior of the lattice.⁴²⁻⁴⁶

A. Treatment of the metal atom lattice (cluster)

Although there are encouraging developments which suggest that it may be possible to translate band calculations into a suitable starting point for the present analysis, this is not yet feasible. We proceed instead to utilize unrestricted Hartree-Fock theory to describe transition-metal atom clusters and to carry out the many-electron calculations using an error bound theory for treating the less significant electron-electron interactions.^{47,48} Atomic core electrons are assumed to be localized, but give rise to Coulomb and exchange potentials which are accurately evaluated along with contributions due to core-valence orbital overlap. Computational aspects of the problem are discussed in Sec. III. It should be emphasized that it is the overall simplification due to the approximation techniques that permits the treatment of large clusters without prohibitively long integral computations.⁴⁸

The result of the SCF treatment of the lattice (cluster) is a single determinant total wave function for the *N* valence electrons of the system

$$\Psi = \mathcal{A}(\varphi_1 \varphi_2 \varphi_3 \cdots \varphi_N),$$

where the φ_k are orthonormal spin orbitals. For example, for titanium the ground configuration is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$ and the valence basis for expansion of φ_k could be chosen as $4s_j, 3d_j$ plus additional functions $4s'_j, 3d'_j$ and $4p'_j$ on nucleus *j* to ensure orbital optimization in the lattice (molecular) field. Calculations on incompletely filled *d* shells must necessarily be performed at the unrestricted HF level to avoid unfavorable repulsion resulting from a double occupancy of spa-

tial d orbitals.⁴⁹ In practice, it may prove unnecessary to require this much flexibility in the basis to obtain a satisfactory initial description of the lattice. Furthermore, since the main purpose of the lattice description is to describe the major delocalization effects involving the s, p band, it may also be possible to localize the d electrons of the metal in the initial lattice calculations.^{49,50} Such simplifications, if made in the treatment of the lattice, would not be made in the subsequent treatment of the local region where the level of treatment is refined upward.

The cluster size required for a reliable treatment of surface energetics is of course of great concern since it is clear that if the lattice level spacing is much too large (small-cluster limit) serious errors will occur. Thus, before proceeding, it must be assumed that the initial cluster, treated approximately, has produced a sufficiently dense set of single-particle levels; what minimum cluster size is actually required to accomplish this is not yet known, however. It is in fact this conflict of large cluster size vs surface accuracy that suggests separating the theoretical treatment into the two distinct stages.

B. Localization at surface sites

Let us assume that molecular adsorption is to take place at a specific, but freely chosen, site on a solid surface of well-defined geometry. To discuss the energetics, assume the adsorbate is characterized by a set of orbitals $\{\varphi_k^A\}$ with energies $\{\epsilon_k^A\}$ and the lattice is characterized by a dense set of levels $\{\varphi_k\}$ with energies $\{\epsilon_k\}$. Bond formation associated primarily with an adsorbate orbital φ_k^A qualitatively involves the summation of interactions over those lattice and adsorbate levels in the neighborhood of ϵ_k^A . Since the lattice levels are dense, the summation necessarily involves many single-particle states. Instead of viewing the problem as the interaction of nearby levels, another alternative is to sum over contributions φ_k for which the interaction $|\langle \varphi_k^A | H_{\text{ext}} | \varphi_k \rangle|$ is large. Again, since the lattice orbitals are delocalized, this leads to a sum over many states. On the other hand, it is clear that a unitary transformation $\vec{\varphi}' = \vec{A} \vec{\varphi}$, $\vec{A}^\dagger = \vec{A}^{-1}$, exists in principle such that $|\langle \varphi_k^A | H_{\text{ext}} | \varphi_k' \rangle|$ is maximized. If found, the problem of summing over contributions from N functions $\varphi_1 \varphi_2 \cdots \varphi_N$ could be reduced to the inclusion of contributions from the first p important members of the transformed set $\varphi_1' \varphi_2' \cdots \varphi_p' \varphi_{p+1}' \cdots \varphi_N'$. While the transformed functions φ_k' are no longer eigenfunctions of the Fock operator of the lattice, the total wave function of the lattice remains invariant under the unitary transformation,

$$\Psi = \mathcal{G}(\varphi_1 \varphi_2 \varphi_3 \cdots \varphi_N) = \mathcal{G}(\varphi_1' \varphi_2' \varphi_3' \cdots \varphi_N').$$

It is clear that spatial considerations plus the orthogonality constraints largely determine the transformation; thus, the problem can be restated as one of finding those functions $\varphi_{p+1}' \cdots \varphi_N'$ with small amplitudes in the region near the site of adsorption. The functions $\varphi_1' \varphi_2' \cdots \varphi_p'$ in order to be orthogonal to the other members must be largely, but not completely, localized in the surface region.

It is not particularly useful to have the transformation scheme depend on specific adsorbate orbitals or on the precise location of the adsorbate, and in practice we propose to define the localization transformation based on the maximization of exchange interactions with all atoms on the surface in the vicinity of the adsorption site. Thus, given a specific adsorption site, atoms within a radius R would be selected to represent the *general vicinity* of the adsorption site, e.g., for a small molecule on a transition metal surface 3–7 lattice atoms would likely suffice for most crystal faces. Let the set of functions $\{\chi_k\}$ represent the valence orbitals of the designated atoms, where the precise functional form of χ_k is not crucial to the argument, the only requirement being that the χ_k represent the spatial size of the valence shell. Now, consider the lattice system described by a single determinant wave function

$$\Psi = \mathcal{G}(\varphi_1 \varphi_2 \cdots \varphi_N),$$

where there are N_α and N_β spin orbitals $\{\varphi_k\}$. We wish to transform the $\{\varphi_i\}$ set to determine a set of linearly independent orbitals $\{\varphi_i'\}$ containing individual members which interact strongly with the designated surface atoms. To accomplish this, the following exchange integral sum is maximized:

$$\gamma = \sum_{k=1}^M \left(\chi_k(1) \varphi'(1) \left| \frac{1}{r_{12}} \right| \chi_k(2) \varphi'(2) \right) \geq 0,$$

where $\varphi' = \sum c_i \varphi_i$ (normalized) and the α and β spin orbitals are considered separately. This leads to an eigenvalue problem with solutions, ordered in eigenvalues $\gamma_1 \geq \gamma_2 \geq \cdots \geq \gamma_N$,

$$\gamma_1: \varphi_1' = \sum_i c_{i1} \varphi_i,$$

$$\gamma_2: \varphi_2'$$

...

$$\gamma_p: \varphi_p'$$

$$\gamma_{p+1}: \varphi_{p+1}'$$

...

$$\gamma_N: \varphi_N' = \sum_i c_{iN} \varphi_i.$$

Alternatively, since the extrema conditions are identical, the problem could be viewed as a minimization of γ to determine those orbitals φ'_i which have insignificant interaction with the $\{\chi_b\}$ set. The resulting total wave function

$$\Psi = \mathcal{A}(\varphi'_1 \varphi'_2 \cdots \varphi'_N)$$

is identical to the initial wave function, and we suppose that after some member γ_p in the eigenvalue spectrum, the orbitals $\varphi'_{p+1} \cdots \varphi'_N$ exhibit negligible exchange interaction with the representative orbitals, $\{\chi_b\}$. It is clear that the member p occurs early in the list since only a relatively small number of orthogonal functions derived from the $\{\varphi_b\}$ set can be packed into the local region. The functions $\varphi'_1 \varphi'_2 \cdots \varphi'_p$ physically represent, but not in a 1:1 correspondence, orbitals localized on the designated atoms, bonds between these atoms, and bonds linking the designated atoms with the remainder of the lattice. It does not follow that all orbitals $\{\varphi'_i\}$, $i \leq p$, will be localized only over one or two atoms, and tails into the lattice which are in part a consequence of orthogonality will occur.

Similarly, it is also of interest to carry out a localizing transformation within the virtual space since the resulting localized orbitals are those orbitals primarily needed for configuration interaction refinement of the local region.

It should be noted that it is the existence of a dual orbital space, one associated with the designated atoms, and one associated with the lattice wave function, that distinguishes the present localization scheme from the Ruedenberg exchange maximization method.⁵¹ Since the set $\{\chi_b\}$ is invariant, the present localization calculation is not iterative and corresponds in computational difficulty to a single SCF iteration.^{52,53}

For purposes of discussion the occupied transformed orbitals $\varphi'_{p+1} \varphi'_{p+2} \cdots \varphi'_N$ which have small amplitudes in the local region will be referred to as interior orbitals, while those defining the local region are the localized occupied orbitals $\varphi'_1 \varphi'_2 \cdots \varphi'_p$ and the localized virtual orbitals $\varphi''_1 \varphi''_2 \cdots \varphi''_a$. The local region is thus best defined as a p -electron subspace localized around a designated surface site; it cannot be equated to the set of atoms used to generate the localization, nor to any particular set of atoms near the site of interest. In summary, the objective of the localization scheme is to define an interior part of the lattice electron distribution which can be taken as invariant during the course of interaction with the adsorbate, and to introduce the important (delocalization) characteristics of an extended lattice into the concept of a local region near the surface.

C. Refinement of the electronic basis of the surface region and the inclusion of adsorbate orbitals

An orbital basis that gives an elementary account of the delocalized orbitals of the atom cluster is not necessarily adequate to describe the interaction of the adsorbate with the surface. Likewise, a configuration interaction treatment of the adsorbate-surface system will require orbitals that are outside the space spanned by the localized orbitals obtained from the transformation of the lattice wave function. The inclusion of such orbitals will be crucial to the description of changes or orbital occupancy of the surface atoms on interaction with the adsorbate. Thus, in addition to the localized orbitals obtained previously, additional basis functions are to be introduced on designated surface atoms to allow flexibility of the valence shell basis allowing for polarization and radial changes in shape of the atomic orbitals. It is also at this stage that the adsorbate basis functions are to be introduced. One might consider introducing all of the additional basis functions in the initial calculations; however, as noted earlier it is desirable to avoid the possibility of artificial polarization effects in the initial lattice description which can occur if different atoms are imbalanced in their orbital description.

D. Configuration-interaction treatment of adsorbate-surface interactions

If we consider an adsorbate molecule interacting with the surface of a solid, it is evident that a proper account of electron correlation is required to achieve an accurate description of the following phenomena: the energetics of interaction, the vibrational frequency of the incoming molecule, bond breaking and formation processes, and the electronic response of the lattice to the incoming adsorbate. The potential complexity of these interactions is the main factor that dictates the present stepwise analysis. The calculation is organized so that in the final stage it will be possible to carry out a sophisticated configuration-interaction treatment of the adsorbate-surface interactions.

In intramolecular bonding, and in the formation of bonds with the surface atoms, the most elementary purpose of configuration interaction is to allow variable ionic and covalent character, and thereby to ensure proper dissociation limits and the description of weak bonds. In the case of the solid lattice itself, in particular the surface region, there are additional important considerations. The existence of closely spaced single-particle states in clusters of metal atoms neces-

sarily leads to a large number of electronic states near the ground state. Thus, in a computational sense, the ground state can be effectively highly degenerate, and the only satisfactory way to proceed is to allow nearly degenerate electronic configurations to enter on equal footing by allowing a direct mixing of configurations.

Configuration-interaction wave functions are formulated²⁹ as

$$\Psi = \sum_k c_k \Psi_k,$$

where

$$\Psi_K = \mathcal{Q}(\Phi_1 \Phi_2 \cdots \Phi_M \varphi'_{M+1} \cdots \varphi'_N).$$

Here it is supposed that there are M electrons in the adsorbate-surface system, where the number of electrons contributed by the cluster itself is p , defined by the localizing transformation. The orbitals $\varphi'_{M+1} \cdots \varphi'_N$ are associated with the interior of the lattice (cluster) and are the eigenfunctions corresponding to the smaller exchange eigenvalues of the localizing transformation; they are taken as an invariant core in each configuration. Thus, the interior orbitals contribute a fixed Coulombic and exchange field acting on the M electrons included explicitly in the remainder of the system.

The molecular orbitals, $\{\Phi_i\}$, for the M -electron system are expanded in terms of the subset of localized orbitals in the designated surface region, $\{\varphi_i\}$, $i=1, 2, \dots, M$, plus the additional basis functions introduced on the surface atoms, and the basis functions of the adsorbate. To facilitate the CI treatment, these orbitals are to be orthogonalized. However, since the interior orbitals are excluded from the surface region, the resulting orbital tails into the interior are not large and the resulting interactions should be amenable to simple approximation.⁴⁸

III. COMPUTATIONAL TECHNIQUES

Starting with the full electrostatic Hamiltonian of the adsorbate-lattice system, for N' electrons, Q nuclei

$$H = \sum_i^{N'} -\frac{1}{2} \nabla_i^2 - \sum_i^{N'} \sum_k^Q \frac{Z_k}{r_{ki}} + \sum_{i<j}^{N'} \frac{1}{r_{ij}};$$

localization of the core electrons into a set of atomic core orbitals $\{Q_M\}$ reduces the dimensionality of the problem to N valence electrons in the Coulomb and exchange field of the core. Gaussian basis functions are used to expand the single-particle orbitals from which SCF and CI functions are constructed. The core electron density matrix $\gamma_c(1, 2) = \sum_M Q_M(1) Q_M(2)$ and the core electron den-

sity $p_c(1) = \gamma_c(1, 1)$ are likewise expanded in terms of Gaussians. The Hamiltonian for the valence electrons then becomes

$$H = \sum_i h_i + \sum_{i<j} \frac{1}{r_{ij}},$$

where

$$\begin{aligned} \langle f_i | h_i | f_j \rangle = & \left\langle f_i \left| -\frac{1}{2} \nabla_1^2 - \sum_k \frac{Z_k}{r_{k1}} \right| f_j \right\rangle \\ & + \langle f_i(1) f_j(1) | \gamma_{12}^{-1} | p_c(2) \rangle \\ & - \langle f_i(1) f_j(2) | \gamma_{12}^{-1} | \gamma_c(1, 2) \rangle. \end{aligned}$$

Spin orbitals for the valence electrons f'_i are orthogonalized to the core orbitals, $f'_i = f_i - \sum_M \langle f_i | Q_M \rangle Q_M$.

A. Error bounds on electrostatic interactions

In computing electrostatic interactions over densities expressed in terms of basis functions, $(f_i f_j | \gamma_{12}^{-1} | f_k f_l)$, it is advantageous computationally to approximate the densities $f_i f_j$ and $f_k f_l$ by simpler expansions providing approximations of sufficient accuracy can be found. For this purpose, the error bound theory described in Ref. 47 is ideally suited. The general argument can be summarized briefly. If we are interested in the electrostatic interaction of two arbitrary charge distributions $A(1)$ and $B(2)$, for particles 1 and 2, respectively, and if A' and B' are proposed approximations, a simple upper and lower bound on the interaction can be written. Thus,

$$\begin{aligned} |(A(1) | \gamma_{12}^{-1} | B(2)) - (A'(1) | \gamma_{12}^{-1} | B'(2))| \\ \leq (\epsilon_A K_B)^{1/2} + (\epsilon_B K_A)^{1/2}, \end{aligned}$$

where $\epsilon_A = (A(1) - A'(1) | \gamma_{12}^{-1} | A(2) - A'(2))$, $K_A = (A(1) | \gamma_{12}^{-1} | A(2))$, and similarly for B . The approximating function $A' = \lambda A''$ is determined by minimizing ϵ_A with respect to λ and (optionally) with respect to other parameters in A'' . In practice, as shown in Refs. 47 and 48, it is often possible to evaluate many component Gaussian integrals using only a few Gaussians providing that approximating functions are determined by minimizing the error bound, and this is accomplished by minimizing ϵ_A and ϵ_B separately. The latter point is what makes the approach feasible in practice since the minimizations occur at the basis function pair, $M(M+1)/2$, stage of the calculation. For long-range interactions, it is even more advantageous to employ approximating functions A' and B' of a well-defined multipole structure to guarantee correct limiting behavior; see Ref. 49 for further details.

TABLE I. Atomic orbitals 4s and 4p for titanium. The expansions are orthogonalized to accurate 1s, 2s, 2p, 3s, 3p core orbitals of the ground state using an auxiliary basis of single Gaussians.

4s orbital		4p orbital	
exponent	Coefficient	exponent	Coefficient
129.0	-0.034 834 9	18.6	0.023 36
7.89	0.143 837 0	0.883	-0.122 50
0.716	-0.471 734 5	0.194	0.120 00
0.0774	0.589 136 3	0.0434	0.411 70
0.0328	0.531 334 4		

B. Core-valence overlap

Core-valence overlap considerations are usually handled by constructing a pseudopotential for the valence electrons. In the present work, we proceed along somewhat different lines. First, the valence basis functions of a given atom are rigorously orthogonalized to the core orbitals of that atom using a simple auxiliary basis (Gram-Schmidt orthogonalization would of course introduce the core orbitals into the valence space which is precisely the difficulty to be circumvented). For example, let u be a 4s basis function not orthogonal to the core of s orbitals. Gram-Schmidt orthogonalization gives

$$|u'\rangle = |u\rangle - \sum_{k=1}^3 \langle u|k_s\rangle |k_s\rangle.$$

Alternatively, let functions s_1, s_2, s_3 be approximations to the 1s, 2s, and 3s core orbitals; it is possible to define

$$|u'\rangle = |u\rangle - \sum_{k=1}^3 \lambda_k |s_k\rangle,$$

with linear coefficients chosen such that $\langle k_s|u'\rangle = 0$ for all k . The significant point from atomic calculations⁴⁹ is that an accurate representation of valence orbitals of transition metals can be found using simple Gaussian expansions for the auxiliary basis $\{s_k\}$. Table I shows such results for titanium using one-term Gaussians for the s_k , to give a 5-component 4s and 4-component 4p atomic orbitals. Each of these functions is rigorously orthogonal to the core orbitals. It might be argued that the increase in size of the 4s and 4p expansion should be avoided; however, in practice there is

TABLE II. Overlap of 4s and 3d atomic orbitals on one nucleus with the core orbitals on a second nucleus at an internuclear distance equal to the nearest-neighbor distance in titanium metal, 5.5769 a.u.^a

	4s	3d
1s	0.002 3	0.0001
2s	0.017 50	0.0009
3s	0.088 4	0.0084
2p	0.002 3	0.0007
3p	0.045 7	0.0135
3d	0.035 7	0.0385

^a Tabulated values are for a $d_{x^2-y^2}$ orbital with an internuclear axis x . For comparison the 4s-4s overlap is 0.466. The 4s and 3d orbitals are rigorously orthogonal to core atomic orbitals on the same nucleus.

no real disadvantage to this increase since the core contributions to multicenter integrals diminish rapidly with increasing distance between basis functions.

The effect of orthogonalizing valence basis functions to their respective core orbitals is to eliminate all one-center overlaps. For nearest-neighbor Ti atoms at an internuclear distance corresponding to the bulk value the largest core-valence overlap is 0.09 for $\langle 4s_A|3s_B\rangle$; other values are given in Table II. These nonzero overlaps are not negligible, but their smallness permits certain approximations of the energy expression as described below.

Consider the determinantal wave function

$$\psi = (\text{norm}) \mathcal{G}(Q_1 Q_2 \cdots Q_c \chi_1 \chi_2 \cdots \chi_N),$$

where Q_k and χ_k are spin orbitals for the core and valence electrons respectively, after an orthogonalizing linear transformation,

$$\psi = (\text{norm})' \mathcal{G}(Q_1 Q_2 \cdots Q_c \chi'_1 \chi'_2 \cdots \chi'_N),$$

where $\chi'_i = \chi_i - \sum_M \langle \chi_i | Q_M \rangle Q_M$, $\langle Q_i | Q_j \rangle = \delta_{ij}$ (by assumption), and $\langle \chi'_i | \chi'_j \rangle = \delta_{ij}$, $\langle \chi'_i | Q_j \rangle = 0$ (by construction). Defining

$$\gamma'(1, 2) = \sum_j \chi'_j(1) \chi'_j(2), \quad \rho'(1) = \gamma'(1, 1),$$

$$\gamma_c(1, 2) = \sum_j Q_j(1) Q_j(2), \quad \rho_c(1) = \gamma_c(1, 2)$$

permits expression of the total energy as

$$E = \langle \psi | H | \psi \rangle = E_{\text{core}} + \sum_i \langle \chi'_i | h | \chi'_i \rangle + (\rho'(1) | r_{12}^{-1} | \frac{1}{2} \rho'(2) + \rho_c(2)) - \langle \gamma'(1, 2) | r_{12}^{-1} | \frac{1}{2} \gamma'(1, 2) + \gamma_c(1, 2) \rangle.$$

Defining $\gamma(1, 2) = \sum_j \chi_j(1) \chi_j(2)$, $\rho(1) = \gamma(1, 1)$ gives

$$E = E_{\text{core}} + \sum_i \langle \chi_i | \hat{h} | \chi_i \rangle + (\rho | r_{12}^{-1} | \frac{1}{2} \rho + \rho_c) - \langle \gamma | r_{12}^{-1} | \frac{1}{2} \gamma + \gamma_c \rangle$$

$$+ \sum_i (\langle \chi_i' | \hat{h} | \chi_i' \rangle - \langle \chi_i | \hat{h} | \chi_i \rangle) + (\rho' - \rho | r_{12}^{-1} | \frac{1}{2} \rho + \frac{1}{2} \rho' + \rho_c) - \langle \gamma' - \gamma | r_{12}^{-1} | \frac{1}{2} \gamma + \frac{1}{2} \gamma' + \gamma_c \rangle.$$

Writing $\rho' - \rho = \sum_M (\rho' - \rho)_M$ and $\gamma' - \gamma = \sum_M (\gamma' - \gamma)_M$ to show the contributions from individual core orbitals and introducing atom densities $\bar{\rho}_M, \bar{\gamma}_M$,

$$E - E_{\text{core}} = \sum_i \langle \chi_i | \hat{h} | \chi_i \rangle + (\rho | r_{12}^{-1} | \frac{1}{2} \rho + \rho_c) - \langle \gamma | r_{12}^{-1} | \frac{1}{2} \gamma + \gamma_c \rangle \quad \text{A}$$

$$+ \sum_i [\langle \chi_i' | -\frac{1}{2} \nabla^2 | \chi_i' \rangle - \langle \chi_i | -\frac{1}{2} \nabla^2 | \chi_i \rangle] + \sum_M \left((\rho' - \rho)_M \left| \frac{-z_M}{r_M} \right. \right) + \sum_M \left((\rho' - \rho)_M | r_{12}^{-1} | \bar{\rho}_M \right) - \sum_M \left((\gamma' - \gamma)_M | r_{12}^{-1} | \bar{\gamma}_M \right) \quad \text{B}$$

$$+ \sum_M \left[\left((\rho' - \rho)_M | r_{12}^{-1} | \frac{1}{2} \rho' + \frac{1}{2} \rho + \rho_c - \bar{\rho}_M \right) + \left((\rho' - \rho)_M \left[\sum_N^{\neq M} - \frac{z_N}{r_N} \right] \right) \right] \quad \text{C}$$

$$- \sum_M \left((\gamma' - \gamma)_M | r_{12}^{-1} | \frac{1}{2} \gamma' + \frac{1}{2} \gamma + \gamma_c - \bar{\gamma}_M \right). \quad \text{D}$$

The above energy expression is still exact. Term A requires only interactions of the valence orbital basis for its evaluation. Term B, by construction, is rigorously $\sum_i \sum_M \langle \chi_i | Q_M \rangle^2 (-\epsilon_M)$, assuming the core orbitals Q_M are eigenfunctions with eigenvalues ϵ_M of the atomic operator defined by $-\frac{1}{2} \nabla^2 - z_M/r_M$ and the atomic densities $\bar{\rho}_M$ and $\bar{\gamma}_M$. In practice, the Q_M could be chosen as atomic Hartree-Fock orbitals and the only requirement on an approximate representation of Q_M is an accurate reproduction of the valence-core overlap $\langle \chi_i | Q_M \rangle$.

Terms C and D require approximation, but neither term is large in magnitude. In term C, the density $(\rho' - \rho)_M$ localized near nucleus M interacts with a distribution of nuclear and electronic charge of nearly zero net charge distributed outside the core region. Term D involves nonlocal core-valence exchange since the atomic contribution $\bar{\gamma}_M$ has been subtracted out. In the present work, the C and D terms are reduced further in magnitude since orthogonalization of the valence basis to core orbitals on the same nucleus greatly diminishes overlap effects and hence the differences $(\rho' - \rho)$ and $(\gamma' - \gamma)$. Approximations of these terms are made, however, using the integral approximation expansions described previously.

Table III shows the result of test calculations on Ti_2 comparing approximate energy calculations with exact (constrained core) results. Good agreement is found for transition energies to all five low-lying excited states calculated.

IV. CALCULATIONS ON $\text{Ti}_{5,4}$

In this section calculations on the s band of a 54-atom cluster of titanium atoms are reported.

The structure, shown in Fig. 1, consists of a 24-atom closed packed surface layer plus two additional layers of atoms in an hcp structure; inter-nuclear distances are the same as in bulk Ti metal. The purpose of the present study is only to illustrate localization in the surface region and we report later on comparisons with experimental measurements on the s, p band and with the results of recent theoretical calculations on thin films, particularly local density-of-states results.¹⁹ The convergence of the localized orbital description as a function of cluster size and structure must also be examined since this question is central to the validity of the subsequent adsorbate-surface calculations. Preliminary results on other clusters are available, and detailed comparisons with

TABLE III. Comparison of approximate and exact CI calculations on Ti_2 . Exact calculations refer to the explicit inclusion of the $1s, 2s, 3s, 2p, 3p$ core orbitals in calculations on the $4s, 3d$ valence system, but otherwise constraining the core orbitals to give a fixed Coulomb and exchange field. Approximate calculations are performed using approximate core potentials and the approximate inclusion of core-valence overlap as described in Sec. III, terms C and D of the energy expression are omitted. Transition energies (a.u.) relative to the lowest state are reported.

State	Exact	Approximate
1	0.0	0.0
2	0.0463	0.0460
3	0.1059	0.1060
4	0.1587	0.1587
5	0.1599	0.1588
6	0.1882	0.1814

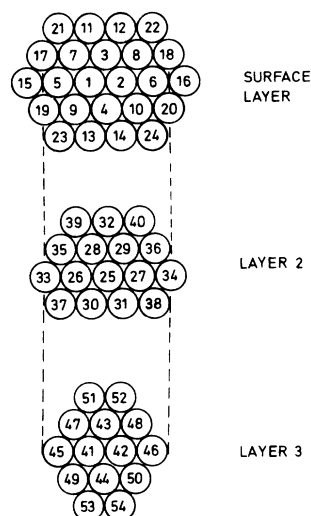


FIG. 1. Titanium hcp cluster containing 54 atoms. The localization site in the surface layer is labeled by atoms 1-4.

experiment and theory plus the convergence studies will be reported in the second paper of this series.

Since the main purpose of the lattice calculations, prior to adsorption, is to describe the major delocalization involving the 4s band, we assume that the 3d electrons are localized in atomic orbitals to give a $(3d)^3$ core configuration. As discussed earlier, such simplifications made in the initial, approximate lattice calculations would not be made in the subsequent treatment of the adsorption site where 3d and 4p orbitals are to be introduced in the basis.

A second point concerns the 4s basis used to describe the s band of Ti. In large clusters it would be difficult to employ many basis functions per

atom for two reasons: computational expense and the tendency toward linear dependency of the basis. Even for a double-zeta 4s basis the more diffuse 4s component on a central atom can be expanded to an overlap of 0.994 using an atomic 4s orbital on that atom plus the double zeta basis functions from surrounding atoms. Similarly, it is also possible to obtain an approximate representation of 4p atomic orbitals in the bulk in terms of 4s orbitals from neighboring sites. To investigate the 4s basis question, calculations were performed on a Ti_{10} planar sheet using a double zeta basis consisting of optimized 4s orbitals for the $(3d)^2(4s)^2$ ground state and the $(3d)^3(4s)^1$ excited state. These results are compared in Table IV with those from a minimal 4s basis treatment (a single 4s atomic orbital per atom) in which the 4s orbital was optimized. Since in the double zeta treatment the effective atomic orbital can change on different atoms and in different cluster orbitals, the two approaches are fundamentally different. The optimized minimal basis results are found, however, to agree very well with the results of the more flexible basis, both in total energy and in the eigenvalue spectrum. The optimum 4s orbital does not correspond to the atomic orbital of either atomic state, $(3d)^2(4s)^2$ or $(3d)^3(4s)^1$, but instead is approximately an equal mixture of the two. If the 3d configuration of the cluster atoms is changed, the optimized 4s orbital is found to change. This suggests that near the adsorption site the double zeta 4s basis flexibility should be retained.

Also shown in Table IV are results from a calculation employing a single-Gaussian (monopole) representation of overlap densities for electron repulsion-repulsion integrals $\langle ij | r_{12}^{-1} | kl \rangle$ with centroids of charge separated by distances greater

TABLE IV. Optimization of the 4s basis orbital in a ten-atom Ti cluster. Calculations are for the 4s band of Ti_{10} in a close-packed monolayer structure with three localized atomic 3d electrons per atom. Total valence electron energies E_T and SCF eigenvalues are shown for three choices of atomic orbitals: 4s [optimum Ti orbital for the atomic ground state $(3d)^2(4s)^2$], 4s' [optimum orbital for the atomic state $(3d)^3(4s)^1$]; 4s'' (optimum 4s orbital in Ti_{10}). The 4s'' gives the minimum valence energy and is closely approximated by an equal mixture, $(4s + 4s'')/2$. The double zeta calculation employs a 4s plus 4s' basis. For comparison, the results of a monopole calculation (see text) are shown using the 4s'' basis.

Double zeta 4s, 4s'	Atomic 4s	Optimum 4s''	Atomic 4s'	Monopole approximation 4s''
$E_T - 7.015$ a.u.	-6.967	-6.995	-6.962	-6.994
ϵ -0.26	-0.23	-0.25	-0.27	-0.25
-0.20	-0.17	-0.18	-0.20	-0.18
-0.17	-0.14	-0.16	-0.17	-0.16
-0.11	-0.08	-0.10	-0.12	-0.10
-0.10	-0.06	-0.09	-0.11	-0.09

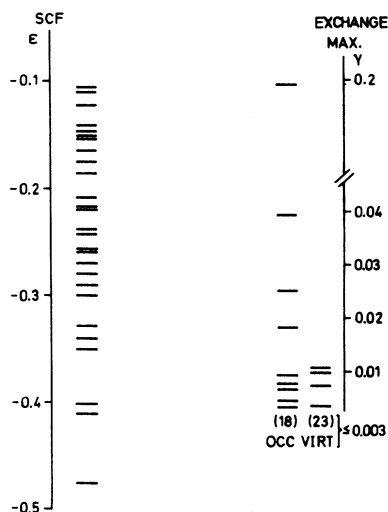


FIG. 2. Eigenvalue spectrum of Ti_{54} showing SCF orbital energies and exchange-energy eigenvalues obtained by localization at a four-atom surface site.

than the nearest-neighbor distance. A general discussion of this type of approximation is contained in Ref. 49. In the present application the corresponding results are in excellent agreement.

Self-consistent-field calculations on the Ti_{54} cluster were performed to determine delocalized cluster (molecular) orbitals, and the resulting eigenvalue spectrum is shown in Fig. 2. Since the $3d$ distribution was spherically averaged spatially and averaged over α and β spin components, restricted SCF theory was used to describe the s band. Eigenvalues of the occupied orbitals range from -12.5 to -2.5 eV and all single-particle states, cluster orbitals, $\{\varphi_k\}$, are delocalized. We consider now localization about a designated site in the first layer, choosing the site as atoms 1, 2, 3, and 4 as labeled in Fig. 1. Following the procedure outlined in Sec. II, we define a function to represent the

four atom site

$$u(1,2) = \sum_{k=1}^4 \chi_k(1)\chi_k(2),$$

where χ_k is a $4s$ atomic orbital on nucleus k . Defining $\varphi' = \sum_k c_k \varphi_k$ where the sum is over the 27 doubly occupied orbitals, followed by maximization of the exchange integral

$$\gamma = \langle \varphi'(1)\varphi'(2) | r_{12}^{-1} | u(1,2) \rangle,$$

gives the exchange eigenvalue spectrum shown in Fig. 2.

The first observation is that the large gap in the exchange eigenvalue spectrum predicted in Sec. II, occurs after the first, most localized, orbital and a secondary gap occurs after the fourth orbital. As would be expected, the main contributions to these orbitals occur from atoms 1–4 and the neighboring atoms in the second layer. A representation of the orbitals showing their nodal properties and atomic populations is given in Table V. Similarly, localized orbitals are projected out of the virtual space $\{\varphi_k\}$, $k = 28 \dots 54$; exchange eigenvalues and atomic populations are shown in Fig. 2 and Table V.

As discussed earlier, an alternative viewpoint is to regard the transformation as an exchange minimization to determine those interior orbitals of the lattice that are excluded from the surface region. Examination of the eigenvalue spectrum shows that there are 18 occupied and 23 virtual orbitals with exchange interactions with the four-atom site less than 3×10^{-3} a.u. These are the so-called interior orbitals of the lattice that would be excluded from the adsorption calculations except for the contribution of a fixed Coulombic and exchange field of the occupied set. It is noteworthy that none of these orbitals has a population exceeding 0.01 on any of the four atoms in the localization site.

TABLE V. Population analysis of the localized occupied and virtual orbitals of Ti_{54} . The localization site is defined by atoms 1–4 in Fig. 1, atoms 25–31 are in the second layer immediately below the localization site. Populations ≤ 0.04 are not shown.

	Atoms																
	1	2	3	4	5	6	7	8	9	10	25	26	27	28	29	30	31
Occupied																	
1	0.28	0.28	0.17	0.22							0.11						
2			0.31	0.26			0.10	0.10	0.07	0.07				0.07	0.07		
3	0.12	0.12			0.11	0.11	0.11	0.11	0.07	0.07		0.11	0.11	0.06	0.06		
4											0.37	0.11	0.11	0.22	0.22	0.06	0.06
Virtual																	
1	0.14	0.14		0.37			0.08	0.08									
2	0.34	0.34			0.08	0.08						0.04	0.04				
3	0.06	0.06	0.40						0.09	0.09							

In summary, the localization argument satisfies the qualitative objectives set forth earlier. Its computational usefulness at the chemisorption stage remains to be proved, however, and this and related questions will be considered in the second paper in this series.

ACKNOWLEDGMENTS

Computer services by the SUNY Computing at Stony Brook Center have been invaluable in this study. Support of this research by the U.S. De-

partment of Energy, Grant No. EG-77-SO24387, is gratefully acknowledged; support of the initial stage of this research by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is acknowledged. One of the authors (J.L.W.) expresses his appreciation to the Alexander von Humboldt Foundation for a Senior U.S. Scientist Award during the latter stages of the research; helpful discussions with Professor S. D. Peyerimhoff and Professor R. J. Buenker during his stay at the University of Bonn are also gratefully acknowledged.

- ¹G. A. Somorjai, *Adv. Catal.* **26**, 2 (1977); *J. Colloid Interfac. Sci.* **58**, 150 (1977); *Acc. Chem. Res.* **9**, 248 (1976).
- ²E. W. Plummer, J. W. Gadzuk, and D. R. Penn, *Phys. Today* **28**, 63 (1975).
- ³J. B. Pendry, *Low Energy Electron Diffraction* (Academic, New York, 1974).
- ⁴H. D. Shih, F. Jona, D. W. Jepsen and P. M. Marcus, *J. Vac. Sci. Technol.* **15**, 596 (1978).
- ⁵R. S. Williams, P. S. Wehner, S. D. Kevan, R. S. Davis, D. A. Shirley, *Phys. Rev. Lett.* **41**, 323 (1978).
- ⁶P. Mahaffy, P. B. Masterson, R. S. Hansen, *J. Chem. Phys.* **64**, 3911 (1976).
- ⁷J. Koutecký, *Adv. Chem. Phys.* **9**, 85 (1965).
- ⁸J. R. Schrieffer and P. Soven, *Phys. Today* **28**, 24 (1975).
- ⁹T. B. Grimley, in *Electronic Structure and Reactivity of Metal Surfaces*, edited by E. G. Derouane and A. A. Lucas (Plenum, New York, 1976).
- ¹⁰R. P. Messmer, in *The Nature of the Surface Chemical Bond*, edited by G. Ertl and T. N. Rhodin (North-Holland, Amsterdam, 1978).
- ¹¹J. A. Appelbaum and D. R. Hamann, *Rev. Mod. Phys.* **48**, 479 (1976).
- ¹²G. S. Painter, *Mater. Res. Bull.* **13**, 541 (1978).
- ¹³D. G. Dempsey and L. Kleinman, *Phys. Rev. B* **16**, 5356 (1977).
- ¹⁴G. S. Painter, *Phys. Rev. B* **7**, 3520 (1973); **17**, 3848 (1978).
- ¹⁵M. C. Desjonqueres and F. Cyrot-Lackmann, *J. Phys. F* **5**, 1368 (1975); *Surf. Sci.* **53**, 429 (1975).
- ¹⁶C. S. Wang and A. J. Freeman, *Phys. Rev. B* **19**, 793 (1979).
- ¹⁷J. G. Gay, J. R. Smith, and F. J. Arlinghaus, *Phys. Rev. Lett.* **38**, 561 (1977).
- ¹⁸H. Stoll and H. Preuss, *Int. J. Quantum Chem.* **IX**, 775 (1975).
- ¹⁹P. J. Feibelman, J. A. Appelbaum, and D. R. Hamann (unpublished).
- ²⁰R. P. Messmer, S. K. Knudson, K. H. Johnson, J. B. Diamond, and C. Y. Yang, *Phys. Rev. B* **13**, 1396 (1976).
- ²¹O. Gunnarsson, J. Harris, and R. O. Jones, *J. Phys. C* **9**, 2739 (1976).
- ²²C. F. Melius, T. H. Upton, and W. A. Goddard III (unpublished).
- ²³A. B. Anderson and R. Hoffman, *J. Chem. Phys.* **61**, 4545 (1974).
- ²⁴K. Mednick and C. C. Lin, *Surf. Sci.* **81**, 347 (1979).
- ²⁵J. Lauher, *J. Am. Chem. Soc.* **100**, 5305 (1978); **101**, 2604 (1979).
- ²⁶J. C. Slater, in *Advances in Quantum Chemistry*, edited by P. O. Löwdin (Academic, New York, 1972), Vol. 6.
- ²⁷W. Kohn and L. J. Sham, *Phys. Rev. A* **140**, 1135 (1965).
- ²⁸R. J. Buenker, S. D. Peyerimhoff, and W. Butscher, *Mol. Phys.* **35**, 771 (1978).
- ²⁹J. L. Whitten and M. Hackmeyer, *J. Chem. Phys.* **51**, 5584 (1969).
- ³⁰I. Shavitt, in *Modern Theoretical Chemistry, Methods of Electronic Structure Theory*, edited by H. F. Schaefer (Plenum, New York, 1977).
- ³¹G. H. F. Diercksen, W. P. Kraemer, and B. Roos, *Theoret. Chim. Acta.* **36**, 249 (1975).
- ³²N. D. Lang and A. R. Williams, *Phys. Rev. B* **18**, 616 (1978).
- ³³D. W. Bullett and M. L. Cohen, *J. Phys. C* **10**, 2083 (1977); **10**, 2101 (1977).
- ³⁴G. S. Painter, *Phys. Rev. B* **17**, 662 (1978).
- ³⁵R. P. Messmer, D. R. Salahub, K. H. Johnson, C. Y. Yang, *Chem. Phys. Lett.* **51**, 84 (1977).
- ³⁶R. P. Messmer and D. R. Salahub, *Phys. Rev. B* **16**, 3415 (1977).
- ³⁷S. G. Davison and Y. S. Huang, *Solid State Commun.* **15**, 863 (1974).
- ³⁸C. F. Melius, J. W. Moskowitz, A. P. Mortola, M. B. Baille, and M. A. Ratner, *Surf. Sci.* **59**, 279 (1976).
- ³⁹C. W. Bauschlicher, Jr., P. S. Bagus, and H. F. Schaefer III, *IBM J. Res. Develop.* **22**, 213 (1978).
- ⁴⁰S. P. Walch and W. A. Goddard, *Surf. Sci.* **75**, 609 (1978); **72**, 645 (1978).
- ⁴¹W. A. Goddard III, S. P. Walch, A. K. Rappé, T. H. Upton, and C. F. Melius, *J. Vac. Sci. Technol.* **14**, 416 (1977).
- ⁴²M. L. Cohen, M. Schlüter, J. R. Chelikowsky, and S. G. Louie, *Phys. Rev. B* **12**, 5575 (1975).
- ⁴³A. J. Martin, *Surf. Sci.* **74**, 479 (1978).
- ⁴⁴C. Pisani, *Phys. Rev. B* **17**, 3143 (1978).
- ⁴⁵A. Barry Kunz and D. L. Klein, *Phys. Rev. B* **17**, 4614 (1978).
- ⁴⁶A. van der Avoird, H. de Graaf, and R. Berns, *Chem. Phys. Lett.* **48**, 407 (1977).
- ⁴⁷J. A. Jafri and J. L. Whitten, *J. Chem. Phys.* **61**, 2116 (1974).
- ⁴⁸T. A. Pakkanen and J. L. Whitten, *J. Chem. Phys.* **69**, 2168 (1978).
- ⁴⁹T. A. Pakkanen, Ph. D. thesis, State University of

New York at Stony Brook, 1977 (unpublished).

Wave functions of the restricted Hartree-Fock type could become suitable, however, if the electrostatic potential is modified to include electron correlation effects, as for example in a local density-functional method.

⁵⁰C. F. Melius, *Chem. Phys. Lett.* 39, 287 (1976).

⁵¹C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.* 35, 457 (1963).

⁵²For the direct use of localized orbitals in the construction of wave functions for the lattice see H. Stoll and H. Preuss, *Theoret. Chim. Acta.* 46, 11 (1977).

⁵³Iteratively determined localized orbitals in molecular applications are discussed by D. L. Wilhite and J. L. Whitten, *J. Chem. Phys.* 58, 948 (1973); a similar scheme could be applied to the determination of orbitals for a surface region.