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THEORETICAL STUDIES OF CHEMISORPTION ON TRANSITION-METAL SURFACES:
INTERACTION OF HYDROGEN WITH TITANIUM*

FINAL REPORT
FOR PERIOD JUNE 1, 1977 TO AUGUST 31, 1982

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Theoretical Studies of Chemisorption on Transition Metal Surfaces:

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Contract No. DE-AC02-77ER04387

June 1, 1977 to August 31, 1982 Final Report

Summary

The research concerns the theory of chemisorption of molecules on solid surfaces: the development of a general formalism, and specific applications to the hydrogen-titanium system. The objective is to develop a suitable formalism for treating electronic interactions at an ab initio level when both localized and delocalized interactions occur, as in the case of molecular adsorption on a metallic surface. For H_2 and CO adsorption on titanium, the goal is a determination of the energetics of adsorption and molecular dissociation as a function of surface site.

The first phase of the research concerned primarily the formalism and the second the modeling of the titanium surface, preparatory to the chemisorption studies. The final phase of the research has dealt with applications of the chemisorption theory to several systems: H_2 on Ti(0001), CO on Ti(0001), interstitial H in titanium, H on Cu(100) and H_2 dissociation on Cu(100). Work on stepped copper surfaces and CO interactions with Ni(100) was also begun. With the exception of the latter two projects now underway, the results of all studies have been published. Brief summaries of the individual projects are included in this report.

Theoretical Studies of Chemisorption on Transition Metal Surfaces:
Interaction of Hydrogen with Titanium*

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Final Report**

Research Scope and Objectives

The research is concerned with the theory of chemisorption of molecules on solid surfaces: the development of a general formalism, and specific applications to the hydrogen-titanium system. The objective is to develop a suitable formalism for treating electronic interactions at an ab initio level when both localized and delocalized interactions occur, as in the case of molecular adsorption on a metallic surface. For H₂ on titanium, the goal is a determination of the energetics of adsorption and molecular dissociation as a function of surface site, and a general description of bonding in the surface region including the response of the lattice to the adsorbate.

Description of Research Effort

The premise of the present approach is that a description of molecule-surface interactions will require a reasonably sophisticated wavefunction in the surface region in order to account for changes in electron correlation accompanying 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, consequently lower, level of accuracy. Proceeding in three main stages, we consider initially an approximate description of the metal lattice (cluster), proceed to define a local (surface) region determined by a localization transformation of the single particle orbitals of the lattice

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wavefunction, and conclude with a refined treatment of the local region and adsorbate in the fixed field of the interior of the lattice. The key step of partitioning into surface and interior regions is accomplished by an electron exchange maximization with surface sites of interest where the associated eigenvalue spectrum permits identification of orbitals to be assigned to the local region. The other major aspect of the problem is a computational one. Here the central idea is to treat electron repulsion interactions over basis functions, and over iteratively determined density matrices in terms of a recently developed theory employing rigorous electrostatic error bounds.

The first phase of the research concerned primarily the formalism and the second the modeling of the titanium surface, preparatory to the chemisorption studies. The final phase of the research dealt with applications of the chemisorption theory to several systems: H_2 on Ti(0001), CO on Ti(0001) interstitial H in titanium, H on Cu(100) and H_2 dissociation on Cu(100). Work was also begun on H_2 dissociation on stepped Cu surfaces and on the interactions of CO with Ni(100).

The general theory is described in the next section with emphasis on new approaches developed as part of this research. The succeeding section contains abstracts of all published work during the contract period describing the chemisorption applications.

Theory

In this section the theoretical formulation is briefly reviewed; details of the theory are given in Refs. 3 and 7 and specific applications are described in Refs. 6 - 13. Alternative theoretical techniques for treating the semi-infinite lattice or finite clusters are reviewed in Reference 3. The main premise in the present approach is that a description of molecule-surface interactions and dissociative processes on surfaces may necessitate a reasonably sophisticated treatment of the surface region to account for changes in polarization and electron correlation accompanying reactions. For a metal this is not easily accomplished since electronic delocalization precludes a partitioning of the system into a small number of atoms proximate to the adsorbate independent of the remainder of the system. An alternative possibility adopted here is to define a local region not as a set of atoms but as an N-electron subspace extracted from the remainder of the system by a localization transformation. The adsorbate and local region are then treated at high accuracy (e.g. by configuration interaction at an ab initio level) as embedded in the fixed Coulomb and exchange field of the remainder of the electronic system. The more direct approach of modelling the metal as a large cluster of atoms and improving the electronic description of only the adsorption region can lead to artifacts of lattice polarization due to an imbalance in the electronic description.

The use of electron exchange as the basis of a localization transformation, with reference to designated atoms on the surface, is discussed in Ref. 3. To summarize the argument, suppose that several adsorption sites on the surface are of interest. Let $u(1,2)$ denote a density matrix constructed by summing over the valence orbitals of atoms belonging to or

bordering these sites. The single-particle states $\{\phi_n\}$ of the lattice are transformed, $\vec{\phi}' = C \cdot \vec{\phi}$, by maximization of the positive definite exchange integral,

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

with respect to coefficients $\vec{C}$. This leads to an eigenvalue problem with solutions ordered in eigenvalues $\gamma_1 \geq \gamma_2 \geq \dots \geq \gamma_N$, with corresponding eigenfunctions $\{\phi'_k\}$. Transformation of the unoccupied (virtual) orbitals is carried out separately, and thus the total wavefunction of the system,

$$\psi = \mathcal{A}(\phi'_1 \phi'_2 \dots \phi'_N)$$

is invariant to the localization transformation. Only a relatively small number of orthogonal functions derived from the $\{\phi_k\}$ set can be packed into the local region and these functions $\phi'_1 \phi'_2 \dots \phi'_N$ physically represent orbitals localized on the designated surface atoms, bonds between these atoms, bonds linking the surface atoms with the remainder of the lattice, and interior bonds of the lattice, with the overall order dictated by decreasing exchange eigenvalues.

Fig. 1 shows, as a typical example, the localization of 4s-band, single-particle states of titanium clusters carried out in connection with convergence studies.⁷ The density plots show the existence of localized orbital tails into the lattice which are a nonnegligible consequence of orthogonality requirements.

Following localization, the orbital basis is improved locally on the adsorbate and surface regions by adding atomic orbitals to provide radial and polarization flexibility. Also, in the case of transition metals any prior constraint used to determine s-band orbitals, such as the assignment of d electrons to an invariant atomic core, is removed on selected surface atoms. The final basis is fully orthonormal by construction.

Fig. 1. Localization of Ti 4s band orbitals, $\{\phi_k\}$, by exchange maximization with the four atom region (1-4) on Ti(0001), and a density representation of localized occupied and virtual orbitals, $\{\phi'_k\}$, of Ti_N , $N = 10/28$ (....), 54(----), and 84 (—). The three layer clusters show convergence of the local description with increasing size. In adsorption studies a subset of the localized orbital basis (occupied and virtual) is augmented by additional atomic functions on surface atoms and the adsorbate and the system treated by configuration interaction.

Configuration-interaction wave functions are then formulated as

$$\Psi = \sum_k C_k A(\phi_1^k \phi_2^k \cdots \phi_M^k \phi_{p+1}' \cdots \phi_N').$$

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 defined by the localizing transformation. The orbitals $\phi_{p+1}' \cdots \phi_N'$ are associated with the interior of the lattice and are the eigenfunctions corresponding to the smaller exchange eigenvalues of the localizing transformation; they are taken as an invariant core in each configuration.

In summary, the purpose of the localization transformation is twofold: (1) to introduce the delocalized character of the extended lattice into an electronic subspace involving the adsorption site, and in the case of a cluster (2) to insulate the physically incorrect boundary of the cluster and the roughly described interior region from orbital refinements in the local region. Overall, the transformation scheme can be viewed as an alternative way of enumerating the component orbitals to be included in the treatment of adsorption. Instead of basing the treatment on delocalized orbitals, the argument is that adsorption breaks the symmetry so strongly that an effective enumeration can be made by taking the adsorption region as an origin and counting outward over the set of localized orbitals.

Applications of the above procedure can be found in the following studies: hydrogen on copper where local improvement of the basis is important but 3d electrons can be assigned to an invariant core,^{8,10} the dissociation of H_2 on Ti(0001) where 3d interactions and configuration interaction significantly strengthen the bonding of hydrogen to the lattice and basis flexibility is necessary to describe the extensive electron transfer to the hydrogen;^{6,9} and CO on Ti(0001) where exothermic adsorption requires a proper treatment of the d level splitting on surface Ti atoms neighboring the adsorbate.¹¹ Fig. 2. shows a schematic representation of the theoretical model.

THEORETICAL MODEL

I. LATTICE (Clean surface)

- simple theory (SCF) to describe the s-band

$$\{\phi_k\}$$

II. LOCALIZATION OF S-BAND ORBITALS

- exchange maximization with surface sites-S

$$\{\phi'_k\}_I \quad \{\phi'_k\}_{II}$$

$$\phi' = \sum_k U_k \phi_k$$

$$\max \gamma = \langle S(1) \phi'(1) | r_{12}^{-1} | S(2) \phi'(2) \rangle$$

$$\begin{array}{l} \gamma \left\{ \begin{array}{l} - \phi'_1 \gamma_1 \\ - \phi'_2 \gamma_2 \\ \vdots \\ - \phi'_P \gamma_P \end{array} \right\} \quad \text{SURFACE REGION} \\ \left\{ \begin{array}{l} - \phi'_{P+1} \gamma_{P+1} \\ \vdots \\ - \phi'_\eta \gamma_\eta \end{array} \right\} \quad \text{INTERIOR REGION} \end{array}$$

III. CONFIGURATION INTERACTION (ADSORBATE & LOCAL REGION)

- variable d occupancy on surface sites
- local improvement of basis (radial/polarization/correlation)
- rigorous antisymmetry
- fixed coulomb and exchange field of the interior region

$$\Psi = \sum_k \lambda_k \mathcal{A} \left(\underbrace{\chi_1^{(k)} \chi_2^{(k)} \cdots \chi_N^{(k)}}_{\text{variable occupancy}} \underbrace{\phi'_{P+1} \cdots \phi'_\eta}_{\text{fixed field}} \right)$$

Fig. 2. Schematic representation of the embedding theory.

References and Abstracts of Published Work*
and Submitted Manuscripts

1. Electron Density and Density Matrix Approximations Using Potential Energy Error Bounds

T. A. Pakkanen and J. L. Whitten, J. Chem. Phys. 69, 2168 (1978).

The possibility of simplifying expansions of the total electron density, $\rho(1)$, and the first order density matrix, $\gamma(1,1')$, derived from a given total wavefunction is considered based on the minimization of positive definite error bound integrals, $\epsilon_\rho = \langle \rho(1) - \rho'(1) | v_{12} | \rho(2) - \rho'(2) \rangle$ and $\epsilon_\gamma = \langle \gamma(1,2) - \gamma'(1,2) | v_{12} | \gamma(1,2) - \gamma'(1,2) \rangle$. Expansions, ρ' and γ' , are in terms of a subset of the full basis and are designed for iterative use in energy variational calculations. In all of a variety of cases investigated, simple one-center expansions are found to be very accurate for the ρ expansion which determines the total coulombic energy of the system. However, correspondingly simple, one-center $\gamma(1,2)$ expansions produce significant errors in the exchange, self-energy when the electron distribution is highly delocalized requiring that important two-center distributions be included for accurate calculations. Applications to localized electron distributions and to problems in which a lower level of accuracy is acceptable are discussed.

2. Electronic Structure of TiH and Ti Chains

C. R. Fischer and J. L. Whitten, Phys. Rev. B20, 1353 (1979).

The SCF $X\alpha$ -SW method has been used to study the electronic structure of TiH, Ti_2 and Ti chains of five and ten atoms. Relative s, p and d orbital occupancies are considered, and charge densities and eigenvalue spectra are

* Work referenced in the text published during the contract period,

reported for several low lying states of each system. The possible validity of a localized 3d electron model is investigated by performing constrained SCF calculations; the results show no major discrepancies with the unconstrained calculations on Ti_{10} .

3. Chemisorption Theory for Metallic Surfaces: Electron Localization and the Description of Surface Interactions

J. L. Whitten and T. A. Pakkanen, Phys. Rev. B21, 4357 (1980).

A theory for describing molecule-solid surface interactions using correlated configuration-interaction (CI) wave functions for the surface region is considered. 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.

4. Electron Repulsion Interactions: Approximations with Error Bounds, Multipole Expansions and the Use of Local Symmetry

T. A. Pakkanen and J. L. Whitten (to be published). (From the Ph.D. thesis of T. A. Pakkanen, Stony Brook, 1977.)

Methods for treating electron repulsion interactions in large systems are considered. Rigorous electrostatic error bounds are used to derive and to justify an auxiliary basis for use in approximating intermediate range interactions. For long range interactions, approximating functions which reproduce the multipole moments of exact densities through quadrupole

terms are employed. The use of the local symmetry properties of a system are considered, and local translational symmetry in particular is discussed in detail for lattice systems.

5. Intermediate Molecular Species in the Oxidation of H_2S

S. Besnainou and J. L. Whitten, J. Am. Chem. Soc. 102, 7444 (1980).

An ab initio configuration interaction study of the intermediate products H_2SO , HSO and HSOH of the oxidation reaction of H_2S in an argon matrix has been carried out. The variation of energy with respect to SH asymmetric stretch is determined near the equilibrium geometry for H_2SO , and the SH bonding energy is estimated. HSOH is found to be more stable than H_2SO . A normal coordinate analysis of the former gives a frequency assignment in good agreement with matrix IR spectroscopy.

6. Chemisorption Theory: Dissociation of H_2 on Ti(0001)

P. Cremaschi and J. L. Whitten, Phys. Rev. Lett. 46, 1242 (1981).

The chemisorption of H_2 on Ti(0001) is treated using an ab initio configuration-interaction theory for the surface region. Dissociation of H_2 occurs above the surface but more stable threefold coordination sites lie closer to the surface at $\sim 1.3 \text{ \AA}$. Adsorption in adjacent threefold sites is less stable than in separated sites sharing only one surface atom. Bonding is predominantly with the 4s electrons of the metal leading to hydridic hydrogens and a polarized lattice electronic distribution.

7. Chemisorption Theory for Metallic Surfaces: Convergence of Surface Localized Orbitals for Ti(0001) Clusters

J. L. Whitten, Phys. Rev. B24, 1810 (1981).

A theory for treating chemisorption on metallic surfaces is proposed based on a large cluster model for the lattice, treated approximately from

which an N-electron subspace for a local region is defined by a unitary, localization transformation. The local N-electron subspace is then treated accurately by configuration interaction as embedded in the fixed field of the interior of the lattice. Exchange energy maximization with sites on the Ti(0001) surface is examined for clusters of titanium atoms Ti_M ($M = 1, 10, 28, 30, 54, 84$) to study the convergence of the localized-orbital description as a function of cluster size. Localized orbitals are obtained by transformation of the self-consistent-field solution and the energetics of these orbitals are examined by diagonalization of the Fock operator subject to the localization constraint. Results for one-, two-, and three-layer models show rapid convergence of the localized description with increasing cluster size in contrast to much slower convergence of the bulk description, which for clusters is strongly influenced by the ratio of boundary to interior atoms.

8. Hydrogen adsorption on Copper: Embedding theory based on Orbital Localization

P. Madhavan and J. L. Whitten, Surf. Sci. 112, 38 (1981).

The chemisorption of H on Cu(100) is treated (a) using small cluster models, and (b) using an embedding theory based on orbital localization (Phys. Rev. B21, 4357 (1980)). The small cluster calculations on Cu_9 and Cu_9H show adsorption in the 4-fold coordination site to be much more stable energetically than atop atom adsorption; binding energies are 3.7 and 1.1 ev., respectively. The entry of H into the eigenvalue spectra is below the d levels in the 4-fold site and above for atop atom adsorption. Cu remains d^{10} , with hydrogen bonding essentially with the 4s-band. Calculations on Cu_{25} and $Cu_{25}H$, carried out with an s-basis only, illustrate the effects of embedding. The binding energy is reduced to 1.9 ev. (SCF) and 2.6 ev. (CI) for the in-plane, 4-fold site, the latter being in good agreement with experiment.

9. Chemisorption of Hydrogen on Titanium: Embedding Theory and Comparisons with Small Clusters

P. Cremaschi and J. L. Whitten, Surf. Sci. 112, 343 (1981).

The chemisorption of H_2 on Ti(0001) is treated using an ab initio CI theory for the surface region. Dissociation of H_2 occurs above the surface but more stable 3-fold coordination sites lie closer to the surface at $\sim 1.3 \text{ \AA}$. Adsorption in adjacent 3-fold sites is less stable than in separated sites sharing only one surface atom. The calculated adsorption energy of 45 kcal/mol H_2 compares favorably with experiment. Bonding involves mainly the 4s electrons of the metal leading to hydridic hydrogens and a polarized lattice electron distribution, but d bonding and correlation effects significantly increase the binding energy. Calculations on small metal clusters also show dissociative adsorption but much larger hydrogen binding energies are obtained.

10. Theoretical Studies of the Chemisorption of Hydrogen on Copper

P. Madhavan and J. L. Whitten, J. Chem. Phys. 77, 2673 (1982).

The chemisorption of H_2 on Cu(100) is treated using a many-electron embedding theory in which the copper lattice is modelled as a 38 atom cluster. Ab initio CI calculations carried out on a local electronic subspace permit an accurate description of bonding at the surface. Dissociated hydrogen is found to bind exothermically to the (100) surface at several stable adsorption sites in four-fold, bridge and atop atom H positions. Calculated H_2 binding energies are in the range 13-22 Kcal/mole. However, high energy barriers to dissociation of 35-40 Kcal/mole exist due to the repulsion of molecular H_2 by the surface and the difficulty of stretching H_2 significantly above the surface. A characteristic of stretched or dissociated H_2 , is the occurrence of H levels well up into the Cu 4s-bond from 5.5 to 7.8 ev. below E_F .

11. Correlated Wave Function Calculation of the Chemisorption of CO on Ti(0001)

C. R. Fischer and J. L. Whitten, Phys. Rev. Lett. 49,344 (1982).

The chemisorption of CO on Ti(0001) is treated using a many-electron CI theory for adsorbate-surface interactions. Comparing perpendicular, parallel to the surface, atop atom and bridge adsorption sites, CO parallel with C and O stretched toward adjacent 3-fold sites is the most stable. An upward shift of CO core energy levels occurs for stretched-parallel CO adsorption due to increased electron transfer from the lattice. A splitting of d levels on the surface Ti atoms neighboring the adsorbate occurs and contributes significantly to the stabilization of adsorbed CO. The calculated binding energy of 35 Kcal/mole is in good agreement with experiment.

12. Interstitial Hydrogen in Titanium

P. Cremaschi and J. L. Whitten (to be submitted for publication).

Hydrogen atom absorption by hcp titanium is treated using an embedding theory (Phys. Rev. B21, 4357 (1980)) to describe the electronic bonding. The very low concentration limit is modelled by treating a single H atom in a 43 atom titanium cluster to compute binding energies of different interstitial sites. An energy barrier to H penetration of the surface layer of 25 Kcal/mole is found and this result is attributed simply to short TiH distances in the surface plane. Hydrogen in an octahedral hole below the close packed titanium surface layer is about 25 Kcal/mole more stable than H in either of the two types of tetrahedral holes for an unrelaxed lattice and this appears to be a consequence of the large negative charge developed on hydrogen. The migration of H between different interstitial sites is discussed.

13. Electronic Structure of the Silicon Monovacancy

J. Malvido and J. L. Whitten, Phys. Rev. B26, (1982).

Electronic structure calculations are carried out on the unrelaxed silicon monovacancy using an embedding theory based on orbital localization. Ab initio configuration interaction treatments are designed to give an accurate account of electron correlation in the vacancy multiplet states while permitting variability in the electronic structure over a 28 electron subspace surrounding the vacancy. Calculated multiplet states are in the order ${}^1E < {}^3T_1 < {}^5A_2 < {}^1T_2 < {}^1A_1$ with corresponding transition energies from the 1E ground state of 0.1, 0.7, 3.6 and 5.0 ev. respectively. Jahn-Teller relaxation of the vacancy geometry is discussed.