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

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Theoretical Studies of Chemisorption on Transition Metal Surfaces:

Interaction of Hydrogen with Titanium

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Summary

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 H_2 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. To investigate surface models, SCF calculations on Ti_{10} at Ti_{30} closed packed sheets and a Ti_{54} three layer model were carried out. A key element of the theory is the partitioning of the lattice wavefunction into localized surface components and an interior region and such localizations were examined for the Ti_{10} , Ti_{30} and Ti_{54} models.

In addition questions concerning the extent of d orbital localization were investigated by X_α calculations on linear chains of Ti atoms and results were compared with previous ab initio SCF calculations.

Preliminary calculations of H_2 on a 10-atom Ti monolayer are also reported.

Theoretical Studies of Chemisorption on Transition Metal Surfaces:

Interaction of Hydrogen with Titanium*

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Annual Progress 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 H_2 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 wavefunction, and conclude with a refined treatment of the local region and adsorbate in the fixed field of the interior of the lattice.

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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, recently completed, was concerned primarily with the development and implementation of the basic computational techniques. Accomplishments in the second phase of the research are outlined briefly below, and further details are included in attached preprints.

1. The theoretical formalism has now been fully worked out and a complete discussion of the general theory plus illustrative applications of the localization scheme is contained in the preprint I (attached).

2. Advances in computational methods have enabled larger Ti clusters than were originally proposed to be treated. Of these methods the use of densities which reproduce the lower multipole moments of exact densities has proved particularly advantageous in evaluating interactions between the interior of the lattice and the orbitals localized near the surface. Preprint II. (attached) summarizes the computational methods used in evaluating electrostatic interactions.

3. The possibility of using a localized 3d electron model for the initial (approximate) description of Ti atom clusters has been investigated by several different approaches. Unrestricted Hartree-Fock calculations on a Ti_{10} monolayer indicate closely spaced energy states corresponding

to different d occupancies. Spherically averaging each atomic d distribution in the Ti configuration $(3d)^3 (4s)^1$ is found to give a satisfactory representation of the d distribution insofar as reproducing its effect on the s band is concerned. The TiH, Ti₂, Ti₅, and Ti₁₀ linear systems were also treated using the X α -SW method. Charge densities and eigenvalue spectra for several low lying states are reported, and the possible validity of a localized 3d model is discussed in Preprint III (attached).

4. Calculations on Ti₁₀ and Ti₃₀ close-packed monolayers, a two layer Ti₅₄ cluster and a three layer Ti₅₄ hexagonal close packed structure have also been carried out in modeling studies to determine a suitable cluster for the chemisorption studies. For the initial, approximate description, SCF calculations were performed to describe the delocalized 4s band assuming localized atomic d electrons. Localized orbitals were then determined by exchange maximization with a four atom surface site. Typical results are shown in Attachment IV for the two-layer Ti₅₄ systems. These results are preliminary but the degree of localization and the degree of exclusion of the interior orbitals from the surface region are very encouraging. In studies in progress, the convergence of the localized orbitals as a function of cluster size is being examined.

5. Results for H₂ adsorbed on Ti₁₀ at a bridge site have been obtained by a very elementary treatment. Calculations are only at the SCF level which precludes significant stretch of the H-H band, and also the localized d model is used. The results must therefore be regarded as very preliminary, and subject to change on refinement. Attachment V shows the portion of the potential curve calculated. The most significant feature is its flatness for internuclear distance up to 0.1 Å, induced by the presence of the Ti surface. Refinements in the treatment of H₂ on Ti₁₀ at the CI level are in progress.

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