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Chemisorption theory for metallic surfaces: Convergence of surface localized orbitals for Ti(0001) clusters

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A theory for treating chemisorption on metallic surfaces has been 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.

I. INTRODUCTION

In treating the chemisorption of molecules on a metallic surface the existence of strong adsorbate-metal bonds may make it desirable to formulate the theory in terms of localized electronic interactions.[1,2] For the d electrons of a transition metal this is clearly an acceptable approach; however, the inherent delocalization of valence s,p electrons could be problematic. In Ref. 1 a localization transformation based on electron exchange maximization with atoms at the adsorption site was proposed, and in this paper its usefulness in the localization of the valence s,p band orbitals is demonstrated using the Ti(0001) surface as an example. The convergence of the localized orbital description is studied as a function of cluster size for one-, two-, and three-layer clusters, Ti_N, $N = 2$, 10, 28, 30, 54, and 84. Many-electron self-consistent-field (SCF) calculations on the atomic clusters are carried out at an *ab initio* level using an error-bound theory for treating the less-significant electron-electron interactions. Atomic-core electrons are assumed localized but give rise to Coulomb and exchange potentials which are accurately evaluated along with contributions due to core-valence orbital overlap. Computational techniques are discussed elsewhere.[1] Atomic clusters are not the only type of system in which to consider the possibility of a localization transformation. For the metal itself, the semi-infinite lattice would be a better starting point for the localization analysis, but the subsequent problem of treating the adsorbate-lattice interactions accurately is not yet solved. In the following sections we discuss briefly the localization transformation as the basis of an embedding scheme and the details of the transformation theory, and then analyze numerical calculations on the titanium clusters and the convergence of the localized orbital description.[3]

II. THEORY

A brief review of the proposed approach to the chemisorption problem is useful to define the objectives of the localization scheme; further details are given in Ref. 1. Alternative theoretical techniques[4–21] for treating the semi-infinite lattice or finite clusters are reviewed in Ref. 2. The central premise is that a description of molecule-surface interactions and dissociative processes on surfaces requires a reasonably sophisticated wave function in 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 partitioning of the system into a small number of atoms proximate to the adsorbate independent of the remainder of the system. An alternative possibility is to define the 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 plan would then be to treat the adsorbate and local region 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 use of electron exchange as the basis of a localization transformation, with reference to designated atoms on the surface, is discussed in Ref. 1. 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, $\vec{\phi}\,' = \vec{C} \cdot \vec{\phi}$, 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 $\gamma_1 \geq \gamma_2 \geq \cdots \geq \gamma_N$, with corresponding eigenfunctions $\{ \phi_k' \}$. Similarly, an independent localization within the virtual space is carried out to determine orbitals of primary importance for configuration-interaction refinement of the local region. The nature of this transformation is such that the first few members with large eigenvalues attempt to replicate orthogonalized combinations of valence orbitals on the designated surface atoms as completely as possible, subject to the constraint of mixing strictly within the occupied space or strictly within the virtual space. The next set of orbitals with smaller eigenvalues represent bonds between atoms in the designated region and the rest of the lattice. Remaining orbitals with extremely small exchange eigenvalues are effectively excluded from the local region, since otherwise the exchange would not be small, and thus represent bonds within the lattice itself.

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.[22]

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 labeling the 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.

III. LOCALIZATION CALCULATIONS

In this section calculations on the $4s$ band of titanium clusters containing from 2 to 84 atoms are reported in a study of surface site localization. One-, two-, and three-layer clusters are considered with all geometries derived from that of the hcp Ti_{84} structure[23] shown in Fig. 1 by deletion of atoms as specified in the figure caption. Since the objective is to describe the major delocalization of the lattice $4s$ band we assume that the $3d$ electrons are localized in atomic orbitals to give a $(3d)^3$ core configuration. The $3d$ distribution is spherically averaged spatially and averaged over α and β spin components. Self-consistent-field calculations employ a single $4s$ basis orbital per atom, expanded as a five-term linear combination of Gaussians where the $4s$ function was obtained by optimization for a Ti_{10} planar sheet. The optimized $4s$ basis reproduces very well the total energy and eigenvalue spectrum of a more flexible double-zeta basis calculation on Ti_{10}.[1]

Eigenvalue spectra showing the single-particle levels of Ti clusters are compared in Fig. 2 for monolayer, two-layer, and three-layer structures. Calculations are for the complete electrostatic Hamiltonian for the valence electrons

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

where h_i contains core-electron contributions to the Coulomb and exchange potential, and corresponding nonlocal, diagonalized Fock operator F,

$$\langle \Phi(1)|\mathrm{F}|\phi_k(1)\rangle = \langle\Phi(1)|h_1|\phi_k(1)\rangle + \sum_j \langle \Phi(1)\phi_j(2)|r_{12}^{-1}|2\phi_k(1)\phi_j(2)-\phi_k(2)\phi_j(1)\rangle = \epsilon_k\langle\Phi(1)|\phi_k(1)\rangle .$$

In the SCF results of Fig. 2 there is no indication of convergence with increasing cluster size except in the similarity in bandwidth of the multilayer structures. Nor is convergence clearly evident in the local density of states (LDOS) of the surface layer since the eigenvalue spectrum of Ti_{54} is too sparse compared with Ti_{84} to permit an unambiguous analysis. Comparing the surface and second layer of Ti_{84} shown in Fig. 3 there is a shift of the second layer toward greater stability. In these LDOS calculations only those atoms with a complete set of neighbors were included in the population analysis, i.e., 9 and 12 neighbors for the surface and second-layer atoms, respectively. If additional surface-layer atoms are included, thereby adding atoms on the boundary of the cluster, the density of states near the calculated Fermi level increases. For Ti_{84}, the higher four levels contain large contributions from boundary atoms and this along with the inflexibility of the basis precludes taking the highest orbital energy as a measure of the work function of the metal.[24] In the context of adsorption, one purpose of the localization argument is to insulate the adsorption site from physically incorrect boundary effects. Other alternatives, discussed elsewhere, are to complete the valence of boundary atoms by adding hydrogen atoms or to stabilize the boundary by an appropriate potential.

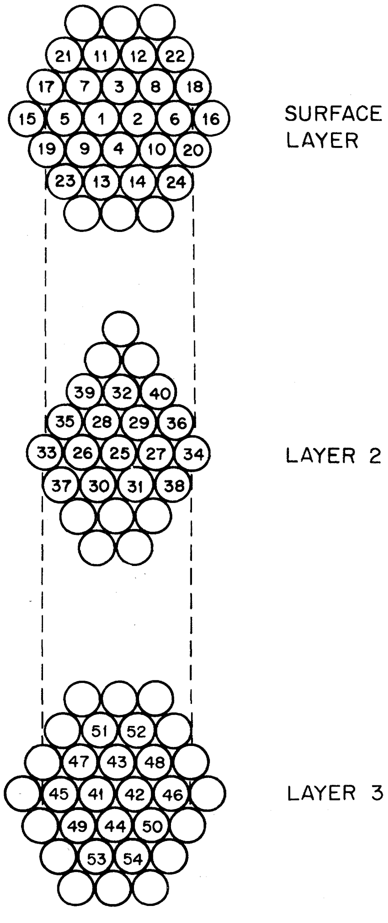

FIG. 1. Three-layer hcp cluster model of the Ti(0001) surface. The Ti_{54} (three-layer) model consists of the numbered atoms and additional atoms in Ti_{84} are shown as open circles. Other clusters considered are Ti_{28} (three-layer) defined by atoms 1 – 10, 25 – 32, and 41 – 50; a two-layer Ti_{54} consisting of a 30-atom surface layer and a second layer 1 – 24; Ti_{30} as a 30-atom surface layer; and Ti_{10} with atoms 1 – 10. The localization site in all cases is the set of atoms 1 – 4; atom 25 is below the 1-2-4 site. The Ti – Ti nearest-neighbor distance is 5.5769 a.u., the same as in the bulk metal.

The ultraviolet photoemission spectroscopy spectrum for a Ti film[25] is characterized by a sharp peak slightly below the Fermi level and another peak 5 eV lower that may be attributable to hydrogen contamination. Local density of states calculations by Feibelman *et al.*[21] employing a local exchange-correlation potential show a narrow surface-layer *d* density of states near E_F and a broad *s-p* density of states for the surface layer with a strong peak at E_F. However, as noted, the calculational method does not permit unambiguous assignment of the latter peak entirely to the *sp* band.

Although the Hartree-Fock and density functional exchange methods of calculations differ greatly so as to preclude a close correspondence of *d* levels, the *s*-band results should agree qualitatively. This appears to be the case, comparing layer 2 with layer 1, if we interpret part of the peak in the surface layer *s-p* density of states near E_F as indicating a shift toward higher energy. However, it must be emphasized that considerable uncertainty is associated with both density-of-states calculations in the partitioning of overlap charges. The difficulties become serious when contributing basis functions have greatly different spatial ranges (exponents) and point to the need for population assignments which take into account the location of the centroid of charge of overlap distributions.

Proceeding to the localization analysis, we consider surface sites in the vicinity of atoms 1, 2, 3, and 4

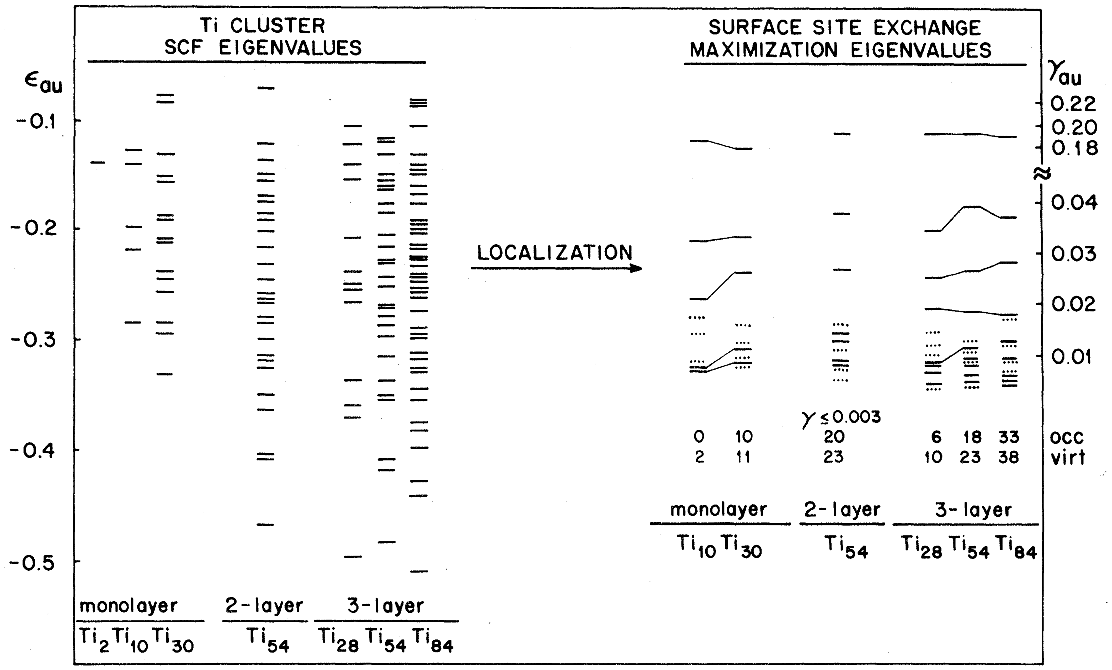

FIG. 2. Ti cluster SCF eigenvalues and surface site exchange maximization eigenvalues. Many-electron SCF calculations are followed by a unitary localization transformation of the 4*s*-band orbitals by electron exchange maximization with surface atoms 1—4 of Fig. 1. SCF orbitals for the different clusters are unrelated; however, the localized orbitals are very similar for both occupied (——) and virtual (· · ·) sets. The number of localized orbitals with very small exchange eigenvalues, less than 0.003 a.u., is indicated for each cluster, e.g., 33 occupied and 38 virtual orbitals for Ti_{84}.

of Fig. 1, and define a two-particle function $u(1,2)$ to represent the four-atom region,

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

where χ_k is a 4*s* atomic orbital on nucleus k. Defining $\phi' = \sum_k C_k \phi_k$, where the sum is over either occupied or virtual orbitals, considered separately, followed by maximization of the exchange integral

$$\gamma = \langle \phi'(1)\phi'(2) \,|\, r_{12}^{-1} \,|\, u(1,2) \rangle \geq 0$$

gives the exchange eigenvalue spectra of Fig. 2.

In contrast to the SCF results, the upper portion of the exchange eigenvalue spectrum shows convergence as do the corresponding localized orbitals discussed below. After the first three upper levels which correspond closely for all cases, except Ti_{10} where some discrepancy in the third level is indicated, the most prominent feature is the appearance of a new fourth level in the multilayer structures involving second-layer atoms. The steady diminution of exchange eigenvalues is due to two factors: the increasing distance of orbitals from the localization site and the orbital nodal structure. The latter is a consequence of both symmetry and the unitary localization transformation. Thus, because of the orthogonality requirement only a relatively small number of orbitals can be localized in the same spatial region. Identically zero eigenvalues due to cancellations are not possible since γ is positive definite.

In Fig. 2, for Ti_{84}, only nine localized orbitals out of a total of 42 doubly occupied orbitals have exchange eigenvalues exceeding 0.003 a.u. Similarly, in the virtual space there are four orbitals out of 42 with $\gamma > 0.003$ a.u. Smallness of γ implies small atomic populations in the localization region and this assertion is borne out for all clusters treated. After the first five localized orbitals no remaining orbital has a population exceeding 0.01 electron on any of the four atoms of the localization region. If a sixth localized orbital is considered, populations are also reduced on the second-layer atom (labeled 25 in Fig. 1) immediately below the four-atom site to values ≤ 0.02 for all remaining orbitals. The converse regarding populations of localized orbitals

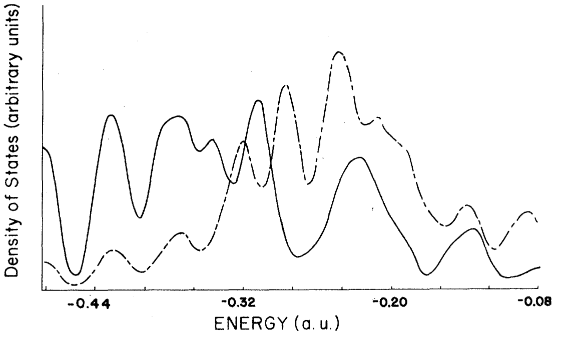

FIG. 3. Local density of 4*s* states for the surface layer (— — —) and second layer (———) of Ti$_{84}$. Only those atoms with a complete set of neighbors were included in the population analysis. Overlap charges were divided equally between contributing atoms. Final curves are expressed as a linear combination of Gaussians, $\sum_k p_k \exp(-0.1x_k^2)$, centered at each single-particle level where p_k is the surface or second-layer population, respectively. The exponent was arbitrarily chosen to show reinforcement of closely spaced levels.

outside the localization region does not hold since localized orbitals are found to exhibit significant tails extending into the lattice. Clearly this must be so since the atoms in the site are coupled electronically to the rest of the lattice.

Localized orbitals are depicted in Fig. 4 where atomic populations are shown for the first six occupied and first four virtuals of 10, 28, 54, and 84 atom clusters. The first two occupied orbitals are highly localized around the four-atom reference site and the three atoms immediately below in the second layer. The third is similarly localized but spread slightly outward in the surface layer. Orbital four is localized in the second layer immediately below the four-atom site. Orbitals five and six involve mainly first- and second-layer atoms neighboring the localization region at increasing distance from its center. Insets depict the nodal structure of the orbitals, which classified successively are a surface layer symmetric *s*, surface layer p_x and p_y (*z* is

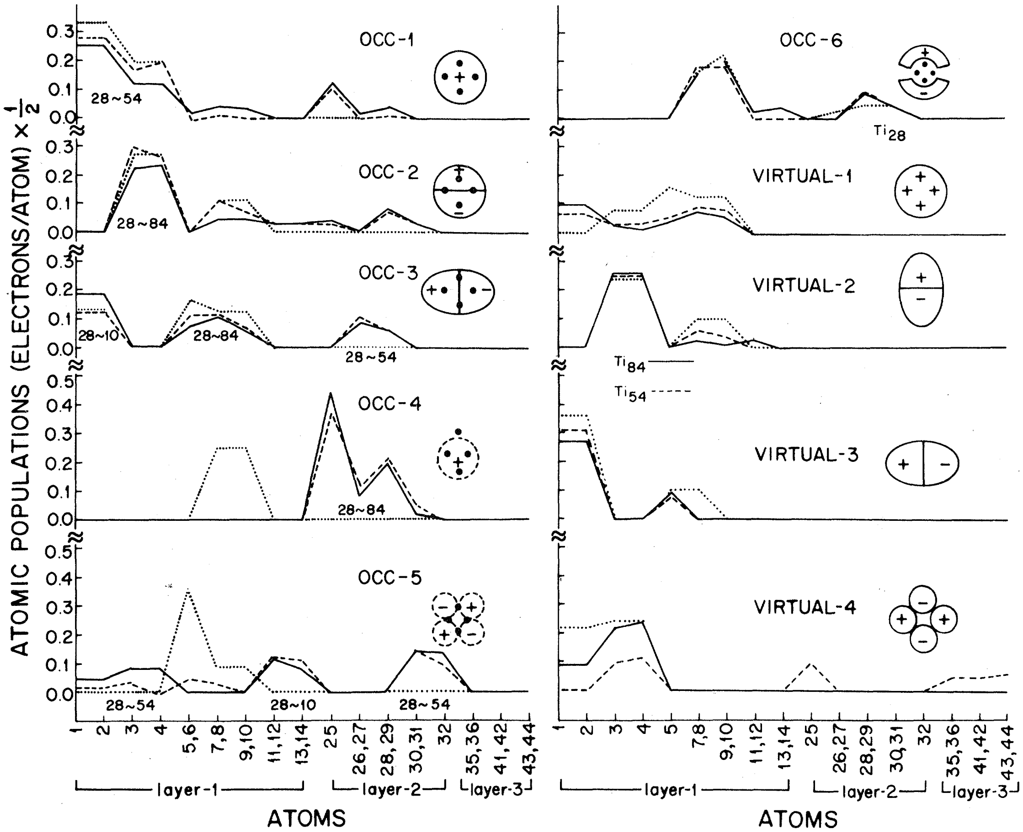

FIG. 4. Atomic populations of localized orbitals of Ti$_{10}$(· · ·), Ti$_{54}$(— — —), and Ti$_{84}$(———); Ti$_{28}$ is shown in the sixth occupied orbital instead of Ti$_{10}$, otherwise the orbital corresponding most closely to Ti$_{28}$ is indicated. Populations for the first six occupied and first four virtual orbitals are shown. Atoms are labeled as in Fig. 1 with the surface localization site defined by atoms 1—4. Insets depict the nodal structure and approximate concentration of orbitals. Atoms not included have populations ≤ 0.04.

normal to the surface), second-layer symmetric s, second layer d_{xy}, and a sixth p-type band around the localization region. None of the first six localized orbitals contains a significant contribution from the third layer.

Virtual localized orbitals are also generally localized in the four-atom region but the nodal structure is more complicated and populations are the result of the considerable cancellation. The first orbital extends over the entire localization region. Other orbitals two to four show strong antibonding contributions from $4s$ orbitals on adjacent atoms. In contrast are the slightly more spatially expanded orbitals of the same symmetry in the occupied space. Overall, the virtual orbitals can be viewed simply as complementing the electronic subspace defined by the occupied orbitals.

On the question of convergence with increasing cluster size, the three-layer 54- and 84-atom results are in good agreement for all six occupied orbitals. The monolayer Ti_{10} (and Ti_{30} not shown) results are qualitatively similar for the first three except for the second-layer contribution, but thereafter fail completely. Ti_{28} deteriorates slightly at the fifth occupied level compared to the other three-layer structures in failing to reproduce the second peak. The virtual orbitals, which are equally important as acceptor orbitals and in providing a response of the lattice to adsorption, are in similarly good agreement for Ti_{54} and Ti_{84} for the first three levels. The fourth levels differ in showing a larger contribution from the second and third layers in Ti_{54}. Ti_{28} results are similar for the first two levels but differ more significantly in the third where the density resembles Ti_{10}. Neither Ti_{10} nor Ti_{28} agrees with the larger cluster results for the fourth virtual level, the former showing a greater population in the local region and the latter a negligibly small population.

In summary, in terms of the electron density all of the multilayer structures, including the two-layer structure not shown, are capable of reproducing the first six occupied localized orbitals. Only in the fifth level of Ti_{28} is a partial breakdown observed. The same is true for the larger clusters through the third localized virtual orbital. Remaining orbitals, although possibly more closely related by a unitary transformation, are not in a close one-to-one correspondence with those of the Ti_{84} cluster.

Finally, it is of interest to investigate the field acting on the local region produced by electrons in occupied orbitals outside the localized subset. To explore this question we consider partitioning the total electronic distribution into an eight-electron local subspace and a complementary (external) subspace defined by the localization transformation. Thus for Ti_{84}

$$\Psi = \mathbf{A}((\phi'_1\overline{\phi}'_1 \cdots \phi'_4\overline{\phi}'_4), (\phi'_5\overline{\phi}'_5 \cdots \phi'_{42}\overline{\phi}'_{42})) ,$$

where the first parenthetical expression refers to the local subspace and the second parentheses to the external, and where this total wave function is identical to the SCF result since ϕ' is related by ϕ by a unitary transformation. The orbitals ϕ'_k, which are the localized orbitals of Fig. 4, no longer diagonalize the Fock operator, however. A partial diagonalization of the Fock operator is now carried out subject to the constraint that prevents mixing of the local orbitals ($\phi'_1 - \phi'_4$) with the external orbitals ($\phi'_5 - \phi'_{42}$). The four most localized virtual orbitals which do not mix with the occupied members are included as well in the local basis.

Eigenvalues from the local diagonalization of the Fock operator are shown in Fig. 5 for the different clusters. The calculation which could equally well be performed with a larger number of functions defining the local region provides a sensitive test of the Coulomb and exchange field due to the external subspace. The most notable difference in comparing the clusters is the decrease in localized orbital energies in going from the monolayer to multilayer structures. Also there is a significant drop in energy comparing Ti_{28} with Ti_{54}, but in general the occupied levels in the three-layer structures appear to be converging. In the virtual space energy variations are small for two of the levels, but in Ti_{84} a level is split off toward lower energy. This result can be traced to the mixing of the first and fourth localized orbitals and indicates that a virtual component capable of lowering the energy is missing in the first four members of Ti_{28} and Ti_{54}.

IV. CONCLUSION

The localization of $4s$-band SCF orbitals for Ti clusters by exchange maximization with a four-atom site on the Ti(0001) surface produces highly localized orbitals and a complementary set which has only small contributions from atoms in the localization region. For one-, two-, and three-layer clusters containing 10, 28, 30, 54, and 84 atoms the first three localized orbitals are always in fairly close agreement. Orbitals for the three-layer structures agree more closely and the agreement extends to six occupied and three virtual orbitals. In contrast, delocalized SCF solutions show greater sensitivity to boundary effects arising from the large ratio of surface to interior atoms in the atomic cluster models.

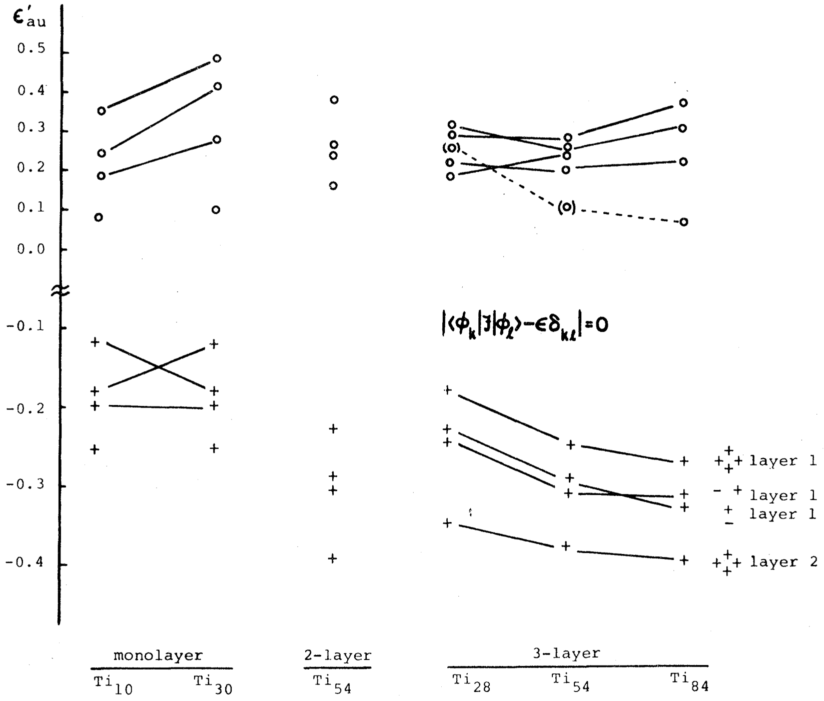

FIG. 5. Energetics of localized orbitals as a function of cluster size. The Fock operator of the SCF solution is diagonalized in the subspace defined by the four most localized occupied and virtual orbitals. The calculation provides a sensitive test of the field acting on the localized electron distribution. Corresponding orbitals of different clusters are connected. The lowest-energy virtual orbital of Ti_{84} has no precise counterpart in Ti_{54} and Ti_{28}.

In chemisorption the localized orbitals are proposed as a basis for defining a local region which is to be treated accurately by the addition of polarization functions and configuration interaction. The extension of adsorption effects into the lattice is then treated by enlarging the local set as needed rather than by treating the entire system in one computational step.

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