

# Localized nature of the chemisorption bond: Configuration-interaction calculations of the chemisorption energies for $\text{Li}_n\text{-H}$ systems employing various localization procedures

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The chemisorption phenomenon has been studied for different chemisorption sites ("cage," "bridge," and "on top") of  $\text{Li}_8(6,2)\text{-H}$ ,  $\text{Li}_{12}(6,6)\text{-H}$ ,  $\text{Li}_{14}(6,6,2)\text{-H}$ ,  $\text{Li}_{10}(5,4,1)\text{-H}$ , and  $\text{Li}_{14}(9,4,1)\text{-H}$  systems [the symbol  $\text{Li}_n(i,j,\dots)$ , where  $i,j,\dots$  is the number of atoms in the first, second, . . . layer]. An alternative algorithm to the Whitten procedure based on the simple overlap criterion using a projection operator over Löwdin orthogonalized orbitals (Löwdin procedure) has been proposed for localization of the one-electron functions employed in the configuration-interaction (CI) treatments. The selected one-electron functions have very similar composition for different chemisorption model clusters. In this manner only a small group of valence electrons which mostly contribute to the substrate-adsorbate interaction is selected for the truncated CI. Local properties of the chemisorption bond have been clearly demonstrated, particularly for the cage and bridge chemisorption sites. The chemisorption energy does not increase with increasing nuclearity of the cluster. The results are independent of both localization procedures used (employing projection or exchange operator).

## I. INTRODUCTION

In recent years, the cluster model of chemisorption has been widely used with the aim of developing a "molecular" description of the substrate-adsorbate bond.<sup>1</sup> This model is based on the assumptions that the chemisorption bond has essentially a local character and that several substrate atoms in the immediate neighborhood of the chemisorbate (adsorption site) play a dominant role in the substrate-adsorbate interaction. In this picture, the atoms surrounding the adsorption site contribute only with a nearly constant potential because their electronic structure is almost unaffected by the adsorption process. In order to describe approximately the influence of the neighborhood of the cluster modeling the adsorption site, this cluster can be embedded in another larger cluster, the atoms of which can be described at a lower-level theory (embedded-cluster versus isolated-cluster model). Several questions have been raised about the validity of the isolated-cluster model.<sup>2</sup> However, several theoretical investigations<sup>2</sup> have shown that clusters (of not too small size) can be considered an acceptable approximation for the real adsorption site, at least for predicting some specific physical quantities. In fact, within this model it is possible to predict optimum adsorbate-substrate relative geometry, values of vibrational frequencies, and interaction-energy values for some particular adsorption sites.<sup>3</sup>

It is important to realize that if the study of the chemisorption processes is carried out in the framework of the Hartree-Fock (HF) "ab initio" method, the lack of electronic correlation can substantially influence the reliability of the results. In several theoretical investigations

which explicitly consider the correlation effects, the correlation correction in simple cluster-adsorbate systems yields 30–50% of the chemisorption energy computed at the HF level.<sup>4</sup> As a consequence, the electronic theory of the chemisorption should be based on methods using correlated wave functions. However, due to the large size of the adsorbate-substrate system, a configuration-interaction (CI) calculation aiming to correlate all the electrons would not only be out of the present computational possibilities, but also the size-consistency error in the limited CI is expected to be large. Assuming that the chemisorption is basically a localized phenomenon, the correlation effects can be taken into account only for those electrons mainly involved in the substrate-adsorbate bond. The corresponding reduction of the active space in the CI calculation, however, can hardly be carried out by simple inspection of the canonical HF occupied and virtual orbitals, due to their delocalized character. On the contrary, the reduction is possible if a transformation of some occupied and virtual orbitals into localized one-electron functions is carried out. The localized orbitals building up the "active part" can be situated at so-called "chemisorption molecules" consisting of the cluster atoms modeling the chemisorption site and of the adsorbed molecule or atom.

Let us recall that the localized and delocalized one-electron functions connected by an appropriate unitary transformation are equivalent only in a CI procedure including all possible excitations of a given class. In the limited CI the use of the localized chemisorption molecule orbitals can be advantageous for correlating the electrons involved in a dominantly localized substrate-adsorbate interaction.

Along this line, the localization procedure proposed by Whitten<sup>5</sup> in the framework of embedded-cluster theory presently seems to be the only practical one if the correlation corrections are introduced by means of the CI method.

The aim of this paper is to show that CI calculations carried out with a reduced basis of localized occupied and virtual orbitals is a suitable tool for examining to what extent some physical quantities connected with the chemisorption phenomenon are transferable from one system to another, including clusters of increasing nuclearity. This is an important point since the transferability of such quantities can prove the local character of the chemisorption bond.

To answer the important question as to what extent the results are dependent on the particular localization procedure chosen, an alternative procedure to the Whitten algorithm is proposed which makes use of the simple projection operator defined over the subset of atomic functions centered at the "chemisorption molecule." For illustration, the calculations have been carried out for the series of lithium clusters Li<sub>8</sub>, Li<sub>10</sub>, Li<sub>12</sub>, and Li<sub>14</sub> interacting with a hydrogen atom, employing both localization procedures. The comparison shows that the main features of the curves for the cluster-hydrogen interaction as well as the calculated chemisorption energies are nearly independent of the localization method employed. Moreover, according to the results obtained from the CI treatments using appropriate localized orbitals, it is possible to predict to what extent a chemisorption bond involving a given chemisorption site is of a localized or delocalized nature.

## II. COMPUTATIONAL PROCEDURE

The aim of the desired procedure is a reliable description of the essential properties of the interaction between a larger and a relatively small system (e.g., the chemisorption site and the adsorbed molecule or atom) employing the limited configuration interaction. For this purpose it is first necessary to define in a suitable manner the "active" part of the chemisorption site which interacts "directly" with the chemisorbed species. Further, the canonical occupied orbitals should be transformed in such a way that they are mainly localized on the centers of the "active" chemisorption molecule (CM) according to a given criterion. Finally, the virtual orbitals are transformed to allow the selection of those transformed virtuals which can yield the excited configurations causing the largest correlation contributions to the chemisorption energy.

The chemisorption molecule (CM) can be characterized by a subset  $\{\chi^o\}$  ( $|\chi_i\rangle$ ,  $i=1,2,\dots,n_{\text{CM}}$ ) of the basis set  $\{\chi\}$  ( $|\chi_j\rangle$ ,  $j=1,2,\dots,n$ ), where  $n_{\text{CM}} < n$ . The functions from the subset  $\{\chi^o\}$  are supposed to be most directly involved in the interaction between both subsystems. An arbitrary one-electron function  $|\phi_j\rangle$  can be, of course, expanded in terms of  $\{\chi\}$ .

Therefore, the row vector of the HF solutions  $|\phi\rangle$  which can be partitioned in the occupied and virtual part  $|\phi^o; \phi^v\rangle$  can be written in terms of  $\{\chi\}$ :

$$|\phi\rangle = |\phi^o; \phi^v\rangle = |\chi\rangle \mathbf{T} = |\chi\rangle (\mathbf{T}^o; \mathbf{T}^v). \quad (1)$$

The occupied canonical HF orbitals  $|\phi^o\rangle$  can be transformed into the localized one-electron functions  $|\bar{\phi}^o\rangle$ :

$$|\bar{\phi}^o\rangle = |\phi^o\rangle \mathbf{U}^o = |\chi\rangle \mathbf{T}^o \mathbf{U}^o, \quad (2)$$

where  $\mathbf{U}^o$  is the eigenvector matrix of a suitable "localization" operator  $\hat{W}$ .

In the localization procedure proposed by Whitten<sup>5</sup> the operator  $\hat{W}$  is defined as a sum of the exchange operators  $\hat{K}_i$  for the subset  $\{\chi^o\}$  [the Whitten procedure (WP)]:

$$\hat{W} = \sum_{i=1}^{n_{\text{CM}}} \hat{K}_i. \quad (3)$$

Therefore, the matrix  $\mathbf{W}$  in the representation of occupied canonical orbitals is

$$\begin{aligned} W_{jk} &= \sum_{i=1}^{n_{\text{CM}}} \langle \phi_j^o(1) | \langle \chi_i(2) | r_{12}^{-1} | \chi_i(1) \rangle | \phi_k^o(2) \rangle \\ &\equiv \sum_{i=1}^{n_{\text{CM}}} (\phi_j^o \chi_i | \chi_i \phi_k^o). \end{aligned} \quad (4)$$

An alternative choice of the operator  $\hat{W}$  is the projector  $\hat{P}_{\text{CM}}$ , which guarantees a maximum overlap of the transformed occupied molecular orbitals (MO's) with the set  $\{\chi^o\}$  defining the chemisorption molecule.

In order to fulfill the idempotency requirements, it is convenient to build a projector using the Löwdin symmetrically orthogonalized orbitals associated with  $\{\chi^o\}$ :

$$\begin{aligned} \hat{W} &= \hat{P}_{\text{CM}} = |\chi\rangle \mathbf{S}^{-1/2} \mathbf{\Lambda} \mathbf{S}^{-1/2} \langle \chi | \\ &= \sum_{i=1}^{n_{\text{CM}}} \sum_{j,k=1}^n |\chi_j\rangle (S^{-1/2})_{ji} (S^{-1/2})_{ik} \langle \chi_k |, \end{aligned} \quad (5)$$

where  $\mathbf{\Lambda}$  is diagonal matrix with the nonzero elements equal to 1 only for the  $\{\chi^o\}$  basis functions. It is worth recalling that the Löwdin orbitals conserve the maximum atomic character. As a consequence, the orbitals entering the definition of  $\hat{P}_{\text{CM}}$  are strongly localized, apart from small oscillations outside the adsorption site, due to the orthogonality constraints. In the localization procedure making use of the  $\hat{P}_{\text{CM}}$  operator [the Löwdin procedure (LP)], the matrix  $\mathbf{W}$  is

$$\begin{aligned} \mathbf{W} &= \langle \phi^o | \chi \rangle \mathbf{S}^{-1/2} \mathbf{\Lambda} \mathbf{S}^{-1/2} \langle \chi | \phi^o \rangle \\ &= \tilde{\mathbf{T}}^o \mathbf{S}^{1/2} \mathbf{\Lambda} \mathbf{S}^{1/2} \mathbf{T}^o \end{aligned} \quad (6)$$

with elements

$$W_{pq} = \sum_{j,k}^n \sum_{i=1}^{n_{\text{CM}}} T_{pj}^o S_{ji}^{1/2} S_{ik}^{1/2} T_{kq}^o. \quad (7)$$

The LP matrix has  $n - n_{\text{CM}}$  zero eigenvalues, while the  $\mathbf{W}$  matrix of the WP is positive definite. In both cases, the eigenvalues  $\mathbf{U}^o$  of  $\mathbf{W}$  can be ordered according to the increasing magnitude of the associated eigenvalues and the transformed occupied orbitals are easily partitioned into two subsets  $\{\bar{\phi}_A^o\}$  and  $\{\bar{\phi}_B^o\}$  having small and large

exchange interaction (or overlap) with the reference subset  $\{\chi^o\}$ , respectively.

The occupied orbitals  $\{\bar{\phi}_B^o\}$  are those mostly involved in the description of the chemisorption process. In order to correct the Hartree-Fock description of the substrate-adsorbate interaction beyond the one-electron picture, the  $\{\bar{\phi}_B^o\}$  are the good one-electron functions used as the part of a basis in the CI calculations.

In this context, the canonical virtual HF orbitals are not suitable any longer for building up the CI spaces together with the  $\{\bar{\phi}_B^o\}$  occupied orbitals, which have lost their canonical character due to localization. As a consequence, a localization procedure should be also carried out for the virtual orbitals. This can be achieved in two different ways. In the WP the virtual orbitals are localized by the same operator  $\hat{W}$  used already for the occupied ones. In contrast, in the framework of the LP, the virtual orbitals are transformed so that the maximum of their exchange interaction with the occupied localized orbitals  $\{\bar{\phi}_B^o\}$  is obtained. The transformation matrix  $U^v$ :

$$|\bar{\phi}^v\rangle = |\phi^v\rangle U^v \quad (8)$$

is obtained from the diagonalization of the matrix  $W$  with elements

$$W_{ij} = \sum_{k=1}^{n_B^o} (\langle \phi_i^v \bar{\phi}_{B,k}^o | \bar{\phi}_{B,k}^o \phi_j^v \rangle). \quad (9)$$

As shown in a previous work,<sup>6</sup> this transformation yields localization of the virtual orbitals in the same spatial region of the occupied ones and can easily improve the CI energy convergence, especially when the virtual space is truncated.

Those transformed virtual orbitals  $\{\bar{\phi}_A^v\}$  which have a localization index (the exchange eigenvalue) lower than a chosen threshold can be discarded from the active CI space. The localization index (LI) can be defined as  $\varepsilon_i^v / \varepsilon_{\max}$ , where  $\varepsilon_i^v$  is the eigenvalue of the operator  $\hat{W}$  associated with  $\bar{\phi}_i^v$  and  $\varepsilon_{\max}$  is the largest eigenvalue.

In summary, the procedure yields four subsets of orbitals,  $\{\bar{\phi}_A^o\}$ ,  $\{\bar{\phi}_B^o\}$ ,  $\{\bar{\phi}_B^v\}$ , and  $\{\bar{\phi}_A^v\}$ .  $\{\bar{\phi}_A^o\}$  and  $\{\bar{\phi}_A^v\}$  have small amplitudes at the "chemisorption molecule" and are considered as frozen ("core") orbitals, and discarded orbitals, respectively, in the CI procedure.

The selected columns of the matrix  $S^{1/2}$  in Eq. (7) do not involve, in general, symmetry-adapted functions. These latter functions can be easily obtained by a suitable unitary transformation which leaves the projector  $\hat{P}_{CM}$  unaltered. The irreducible representation spanned by the selected functions in  $S^{1/2}$  depend only upon the characteristics of the functions centered at the chemisorption molecule. In other words, if the reducible representation of the CM subsystem  $\{\chi_o\}$  can be expressed as a superposition of all irreducible representations of the full cluster-adsorbate system, all occupied orbitals  $\{\phi^o\}$  of the whole cluster-adsorbate model are treated on the same footing during the localization process and no one-electron function  $\phi_j^o$  will be fully projected out by the operator  $P_{CM}$  for symmetry reasons. In order to conserve the full point-group symmetry and the energy invariance, the transformation of the original set of orbitals is carried out for

each irreducible representation and for each electronic shell separately.

The aim of the CI calculation carried out in the present context is to achieve a good correlation correction for the electrons directly involved in the substrate-adsorbate interaction which are essentially valence electrons. Accordingly, the occupied ( $\{\bar{\phi}_A^o\}$ ) and the virtual ( $\{\bar{\phi}_A^v\}$ ) sets of the one-electron functions are truncated. Note that  $\{\bar{\phi}_A^o\}$  contains occupied valence MO's which are not localized at the chemisorption site. In addition,  $\{\bar{\phi}_A^o\}$  must contain also the MO's mainly composed from core atomic orbitals because essentially only valence MO's localized at the chemisorption site should participate in developing the CI spaces. The core character of the MO's included in  $\{\bar{\phi}_A^o\}$  cannot be identified according to the values of their one-electron energies because the HF operator is no longer diagonal in the basis of the transformed  $\{\bar{\phi}^o\}$  orbitals. Moreover, if the localization procedure is carried out over the full set of the canonical HF MO's, the core-valence separation of the transformed MO's is partially lost in the case that the  $\{\chi^o\}$  orbitals have large orthogonality tails in the core region (LP) or large one-center exchange integral with the core atomic orbitals (WP). This means that the active part of the occupied space  $\{\bar{\phi}_B^o\}$  may contain some contributions from core MO's due to the characteristics of the localization operator. The resulting core-valence mixing does not affect the description of the chemisorption interaction *only* in the case that its extent is strictly constant along the interaction curve. If this is not fulfilled, the CI spaces at different points of the interaction coordinate include different contributions from core-valence excitations. Correspondingly, the computed correlation-energy values are affected by different contributions from the core-valence correlation, which is much smaller than the valence-valence one. This problem is explicitly illustrated on the example of a  $Li_2$  molecule in the Appendix.

If the localization procedure is carried out over the full set of HF canonical occupied orbitals and if some of the localized orbitals are excluded from the truncated CI, then the composition of the CI space is not constant along the interaction curve. In Sec. IV it will be shown that this effect is common to both localization procedures (LP and WP) and that reliable interaction energies can be obtained only if the "continuity" of the characteristics of CI space is guaranteed throughout the curve. A possible way of keeping the composition of the truncated CI space consistent along the chemisorption curve is to exclude the core HF orbitals from the localization procedures, as will be shown in Sec. IV and in the Appendix.

### III. TRANSFERABILITY OF LOCALIZED ORBITALS IN CLUSTERS OF INCREASING NUCLEARITY

In this section it will be shown to what extent the LP is effective in producing a subset of localized occupied orbitals which conserve the same spatial distribution when the cluster size increases. For this purpose, the series of lithium clusters  $Li_n$  ( $10 \leq n \leq 24$ ) derived from the bcc lattice

TABLE I. Mean value of overlap between corresponding projected MO's in a cluster of increasing nuclearity.

|                                | <i>A</i> | <i>B</i> | <i>C</i> | <i>D</i> | <i>E</i> |
|--------------------------------|----------|----------|----------|----------|----------|
| "Bridge" adsorption site       |          |          |          |          |          |
| (A) Li <sub>10</sub> (6,2,2)   | 1.000    | 0.967    | 0.896    | 0.793    | 0.761    |
| (B) Li <sub>14</sub> (6,6,2)   |          | 1.000    | 0.937    | 0.735    | 0.765    |
| (C) Li <sub>16</sub> (8,6,2)   |          |          | 1.000    | 0.800    | 0.867    |
| (D) Li <sub>20</sub> (8,6,6)   |          |          |          | 1.000    | 0.923    |
| (E) Li <sub>24</sub> (8,8,6,2) |          |          |          |          | 1.000    |
| "Cage" adsorption sites        |          |          |          |          |          |
| (A) Li <sub>14</sub> (6,6,2)   | 1.000    | 0.900    | 0.885    | 0.835    |          |
| (B) Li <sub>18</sub> (6,6,6)   |          | 1.000    | 0.952    | 0.872    |          |
| (C) Li <sub>20</sub> (6,6,6,2) |          |          | 1.000    | 0.929    |          |
| (D) Li <sub>24</sub> (8,8,6,2) |          |          |          | 1.000    |          |

has been considered for two different definitions of the adsorption site and the associated projector.

In the following, the structure of the clusters will be denoted by the symbol Li<sub>*n*</sub>(*i*,*j*,...), where *i*,*j*,... is the number of atoms in the first, second, ... layer.

The first adsorption site, the "bridge" (*B*), corresponds to the bond midpoint between two atoms of the cluster belonging to the first layer, while the "cage" (*C*) adsorption (or better absorption) site coincides with the center of a tetrahedral cavity formed by two atoms of the first and two atoms of the second layer. Two different series of clusters have been generated for *B* and *C* sites according to the criterion which selects those atoms of the bcc lattice having the average distance from all the atoms defining the absorption site smaller than a given threshold (see Table I). The analysis is carried out on the basis of the HF wave functions for the closed-shell ground state, computed with a minimal basis set.<sup>7</sup>

The projection operator associated with the site *B* is built only from the 2*s* orbitals of the two reference atoms. Therefore, the comparison between the MO's of the different clusters projected on the adsorption site can be simply carried out by computing a 2×2 overlap determinant *D*. For simplicity, the values of *D*<sup>1/2</sup>, which can be considered as a "mean" overlap value between two corresponding projected MO's for the series of clusters considered, are reported in Table I.

For the site *C* a four-dimensional projector is defined, and the comparison between the projected MO's of different clusters is given in Table I employing the values of *D*<sup>1/4</sup> of the corresponding overlap determinant.

The data of Table I show that the transferability of the projected MO's in clusters of increasing nuclearity can be considered quite satisfactory, especially if one considers that the localization procedure is of "symmetry-restricted" type (see Sec. II).

It is important to point out that the removal of the symmetry constraints would certainly produce MO's with a higher degree of localization, and a better index of transferability could be obtained for the series of clusters considered. However, this fully localized but not symmetry-adapted MO basis cannot be used in CI calculations without an important further computational cost.

#### IV. INVARIANCE OF THE CHEMISORPTION ENERGY FROM CLUSTER SIZE FOR A GIVEN CHEMISORPTION SITE

The interaction between the hydrogen atom and different chemisorption sites of lithium clusters which are part of the bcc lattice has been studied in order to test the validity of the concepts on which different localization procedures (WP and LP) are based.

First, the restricted HF calculations are carried out employing the minimal basis set (6*s*/2*s*) (Ref. 7) augmented by a *p* function for the lithium atom (Ref. 4) and the basis (4*s*/2*s*) plus a *p* function with the exponent equal to 1.0 for the hydrogen atom (Ref. 8). The chemisorption curves for the doublet states of the totally symmetric representation (<sup>2</sup>*A*<sub>1</sub>) have been investigated for all studied cluster-hydrogen systems. This is appropriate if the singlet represents the ground state of the bare cluster. In the case where the triplet is the ground state of the cluster, the corresponding doublet state for the composite system has been determined [for example, for Li<sub>8</sub>(6,2) + H]. The localization of occupied and virtual MO's will later be specified for each studied chemisorption site separately. In the CI calculations which utilize the local occupied and virtual orbitals the configurations obtained by single and double excitations with respect to the reference HF configuration are selected according to the energy threshold *T* = 10<sup>-6</sup> microhartree. Throughout the paper the energies obtained from the extrapolation technique<sup>9</sup> (*T* → 0) are reported.

Let us first discuss the results obtained for the "cage" (tetrahedral cavity) chemisorption site (*C*). Three systems involving Li<sub>8</sub>(6,2), Li<sub>12</sub>(6,6), and Li<sub>14</sub>(6,6,2) have been considered as representative of the site *C*. The subset of atoms which defines the chemisorption molecule for all three systems is [Li<sub>4</sub>(2,2,0) + H], while for Li<sub>14</sub>(6,6,2)-H the chemisorption molecule defined by [Li<sub>4</sub>(0,2,2), H] has also been studied. The first layer corresponds to the *xy* plane and the *z* coordinate is negative for the other layers. The localization of the occupied MO's is carried out with respect to a subset of orbitals composed from 2*s* valence atomic orbitals (AO's) of the four lithium atoms and from both 1*s* functions of the hy-

drogen atom. The localized occupied MO's [LMO's] obtained from both LP and WP are of a very similar nature. A nearly exact one-to-one correspondence between LMO's  $\{\bar{\phi}_B^o\}$  having large eigenvalues of the  $\hat{P}_{CM}$  and of  $\hat{K}$  operators has been found. For the C site of all three systems considered, there are four doubly occupied strongly localized orbitals with a large eigenvalue of the  $P_{CM}$  and  $K$  operators and one singly occupied orbital. For example, the eigenvalues of  $\hat{P}_{CM}$  and of  $\hat{K}$  for four doubly occupied orbitals of  $Li_{14}(6,6,2)$ -H with CM  $[Li_4(2,2,0)$ -H] are 0.132, 0.161, 0.239, 0.671 and 0.138, 0.141, 0.243, 1.205, respectively. The largest eigenvalues of  $\hat{P}_{CM}$  and  $\hat{K}$  for the MO which is not taken as an active orbital in the CI treatment is 0.00045 and 0.047, respectively. In contrast, the virtual spaces generated by the two procedures are slightly different. The eigenvalues of the WP exchange operator decrease more rapidly than those of the corresponding operator of the LP, so that the localization indexes (defined in Sec. II) of the LP virtual orbitals have a mean value much larger than the WP ones. In order to reduce the dimensions of the virtual space a common threshold for the localization index cannot be applied for both LP and WP virtual spaces. In the LP we have chosen to select only those virtual orbitals having a localization index not smaller than 10%. The resulting dimension of the virtual space is 32 for all three C-site systems studied. The same number of virtual orbitals has been selected for the CI carried out with WP localized orbitals. It is interesting to notice that also the number of selected virtual orbitals belonging to the different irreducible representation is the same in both procedures. Nevertheless, for the same number of virtual orbitals, i.e., similar sizes of the CI spaces ( $\sim 3500$  configurations), the LP accounts for more correlation than the WP.

This fact is responsible for differences obtained when the localization of virtual orbitals is carried out with respect to the fixed AO basis set (WP) or with respect to the transformed occupied orbitals (LP), the kernel in Eq. (9). A measure of the spatial extent of the occupied localized orbitals can be roughly estimated from the Mulliken population of the transformed occupied orbitals for the CM subsystem. For example, for the "on-top" cluster model  $Li_{14}(9,4,1)$ -H, Mulliken population yields 5.1 valence electrons instead of 6 in the CM subsystem  $Li(1,4) + H$ , while for the "cage" cluster model  $Li_{14}(6,6,2)$ -H there are 3.9 instead of 5 valence electrons in the  $Li(2,2,0) + H$  CM moiety.

The chemisorption curves for the  $Li_8(6,2)$ -H system are given in Fig. 1. The tetrahedral "cage" (C site) is formed from two Li atoms of the first layer and two "exposed" atoms of the second layer  $[Li_2(2,2) + H]$ . A comparison of the results obtained from different procedures has been made for the  ${}^2A_1$  state. In this case, the CI treatments employing only LP and WP valence LMO's (four doubly occupied and one singly occupied) yield results equivalent to the CI utilizing only valence canonical HF orbitals. These three sets of one-electron functions are equivalent, apart from the unitary transformation in this particular case of the eight valence Li electrons. Therefore, only one curve I for all three cases is drawn in Fig. 1.

If both the LP and WP are applied on all core-valence

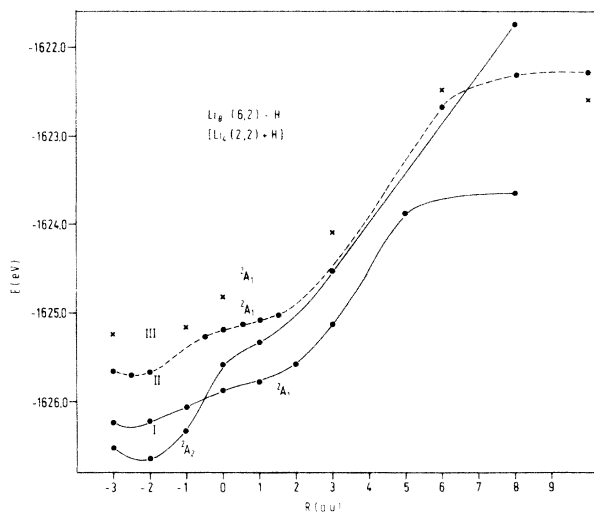


FIG. 1. Potential-energy curves for the  ${}^2A_1$  and  ${}^2A_2$  states of the  $Li_8(6,2)$ -H system for the "cage" chemisorption site C  $[Li_4(2,2) + H]$  as functions of the cluster-H distance  $R$  obtained from the CI treatments employing only valence LMO's (—) of LP localization procedure. The sizes of the CI spaces are  $\sim 3500$ . Curves II and III represent the  ${}^2A_1$  state obtained from the CI calculations with the LP (---) and WP (···) in which the localization is carried out for all core-valence canonical HF orbitals (all LMO's).

orbitals, the CI with all LMO's yields chemisorption curves with considerably higher energies, especially for the large  $Li_8$ -H distances (compare curves II and III of Fig. 1). Consequently, the reliable chemisorption energies can be obtained only from the valence-LMO CI treatments and they are listed in Table II. In addition, the chemisorption curve for the  ${}^2A_2$  state obtained from the CI using the LP valence LMO's is drawn in Fig. 1.

The chemisorption energy of 2.78 eV calculated for the  ${}^2A_1$  state has to be corrected for  $\sim 0.2$  eV because the  ${}^2A_2$  state lies lower than the  ${}^2A_1$  stated in the interval  $Z_H = [-3, -0.5]$ . The position of the hydrogen atom corresponding to the minimum energy is  $Z_H^{min} = -2.52$  a.u. for  ${}^1A_1$  and  $-2.12$  a.u. for the  ${}^2A_2$  state. The distance between the hydrogen atom and the Li atoms of the second layer is smaller than its distance from the Li atoms of the first layer (see Table II).

The next system considered is  $Li_{12}(6,6)$ -H. All the atoms which define the site C of the  $Li_4(2,2)$  subcluster have the same number of nearest neighbors. The triplet energy of the bare  $Li_{12}(6,6)$  cluster lies higher than the closed-shell singlet state; therefore, only the  ${}^2A_1$  of the composite system has been determined. The chemisorption curves for the  ${}^2A_1$  state obtained from LP and WP with (i) all LMO's and with (ii) only valence LMO's are drawn in Fig. 2. The WP accounts, in general, for less correlation than the LP for the similar sizes of the CI spaces. Both procedures with all LMO's yield higher energies than when only valence LMO's are employed, especially for larger  $Li_{12}$ -H distances (two curves with highest energies). The LP with only valence LMO's give rise to the lowest energies. The chemisorption energies listed in Table II obtained from only valence LMO's are very simi-

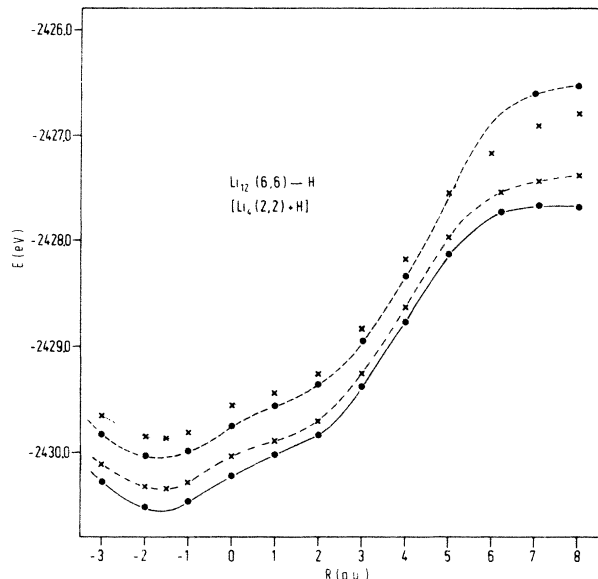


FIG. 2. Chemisorption curves for the  ${}^2A_1$  state of the  $\text{Li}_{12}(6,6)\text{-H}$  system for the "cage" site C [ $\text{Li}_4(2,2) + \text{H}$ ] obtained from the CI employing (i) only valence LMO's of the LP (—) and WP (---×---) and (ii) all LMO's of the LP (—) and WP (---×---) procedures.

lar for the LP and WP (2.84 and 2.96 eV) as well as the corresponding  $Z_{\text{H}}^{\text{min}}$  values (-1.69 and -1.57 a.u.).

For the  $\text{Li}_{14}(6,6,2)\text{-H}$  system two chemisorption molecules have been considered: [ $\text{Li}_4(2,2,0) + \text{H}$ ] and [ $\text{Li}_4(0,2,2) + \text{H}$ ]. Corresponding potential curves are given in Fig. 4 for the  ${}^2A_1$  state (triplet state  ${}^3A_2$  of the bare cluster lies slightly above the closed-shell singlet state). The chemisorption energies obtained from the LP and WP with only valence LMO's (cf. Table II) for both

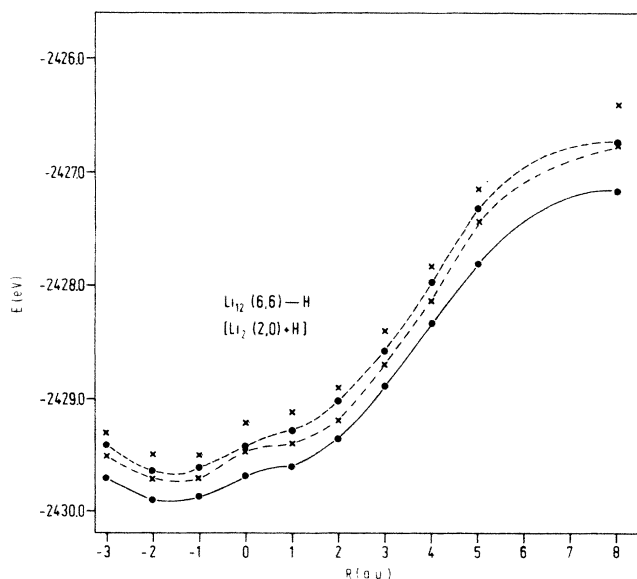


FIG. 3. Chemisorption curves for the  ${}^2A_1$  state of the  $\text{Li}_{12}(6,6)\text{-H}$  system for the bridge site B: [ $\text{Li}_2(2,0) + \text{H}$ ] obtained from the analogous CI treatments with localized orbitals as described in Fig. 2.

TABLE II. Chemisorption energies (eV) (all results are obtained from the CI calculations using only valence-localized orbitals of the LP and WP), minimum-energy position of the hydrogen atom (the Z axis is orthogonal to the layers; first, second, and third layers are at  $Z=0$ , -3.3, and -6.6 a.u., respectively) in  $\text{Li}_n + \text{H}$  systems (a.u.), vibrational frequencies ( $\text{cm}^{-1}$ ), and the number of nonactive  $\bar{\phi}_A^v$ ,  $\bar{\phi}_B^v$  and active  $\bar{\phi}_A^v$ ,  $\bar{\phi}_B^v$  localized orbitals.

| Cluster                 | Chemisorption molecule |      | $D_c$ |       | $Z_{\text{H}}^{\text{min}}$ |        | $\omega_e$ |    | $n(\bar{\phi}_A^v)$ |    | $n(\bar{\phi}_B^v)$ |    | $n(\bar{\phi}_A^v)$ |    |
|-------------------------|------------------------|------|-------|-------|-----------------------------|--------|------------|----|---------------------|----|---------------------|----|---------------------|----|
|                         | LP                     | WP   | LP    | WP    | LP                          | WP     | LP         | WP | LP                  | WP | LP                  | WP | LP                  | WP |
| $\text{Li}_8(6,2)$      | 2.78                   | 2.71 | -2.52 | -2.54 | 684.1                       | 639.2  | 4          | 5  | 32                  | 32 | 0                   | 0  | 4                   | 5  |
| $\text{Li}_8(6,2)$      | 2.99                   | 2.98 | -2.12 | -2.15 | 561.3                       | 524.8  | 4          | 5  | 32                  | 32 | 0                   | 0  | 4                   | 5  |
| $\text{Li}_{12}(6,6)$   | 2.84                   | 2.96 | -1.69 | -1.57 | 501.5                       | 583.8  | 14         | 5  | 32                  | 32 | 14                  | 14 | 14                  | 5  |
| $\text{Li}_{12}(6,6)$   | 2.74                   | 3.00 | -1.57 | -1.42 | 657.9                       | 588.2  | 15         | 4  | 24                  | 24 | 22                  | 22 | 15                  | 4  |
| $\text{Li}_{14}(6,6,2)$ | 2.92                   | 3.02 | -1.66 | -1.66 | 586.5                       | 446.2  | 17         | 5  | 32                  | 32 | 21                  | 21 | 17                  | 5  |
| $\text{Li}_{14}(6,6,2)$ | 2.80                   | 2.83 | -5.26 | -5.78 | 1536.3                      | 1513.2 | 17         | 5  | 32                  | 32 | 21                  | 21 | 17                  | 5  |
| $\text{Li}_{10}(5,4,1)$ | 0.79                   | 0.81 | 3.17  | 3.19  | 1504.0                      | 1515.4 | 10         | 6  | 39                  | 39 | 0                   | 0  | 10                  | 6  |
| $\text{Li}_{10}(5,4,1)$ | 0.81                   | 0.81 | 3.19  | 3.18  | 1373.7                      | 1363.8 | 10         | 6  | 39                  | 39 | 0                   | 0  | 10                  | 6  |
| $\text{Li}_{14}(9,4,1)$ | 1.20                   | 1.26 | 3.26  | 3.28  | 1409.8                      | 1322.8 | 16         | 6  | 40                  | 40 | 13                  | 13 | 16                  | 6  |
| $\text{Li}_{14}(9,4,1)$ | 1.07                   | 1.13 | 3.26  | 3.28  |                             |        | 16         | 6  | 39                  | 39 | 14                  | 14 | 16                  | 6  |

<sup>a</sup> Number of active doubly and singly occupied orbitals.

chemisorption sites are similar and have values between 2.8 and 3.02 eV. The barrier to penetration of the hydrogen atom into the tetrahedral cavity is located at the distance of the second layer for both chemisorption sites (cf. Fig. 3). For the  $[\text{Li}_4(2,2,0)\text{-H}]$  site the minimum of the chemisorption curve is at  $Z_{\text{H}}^{\text{min}} = -1.66$  for the LP and WP. The two procedures deviate more in predicting the distance for penetration of the hydrogen atom into the  $\text{Li}_4(0,2,2)$  cavity ( $Z_{\text{H}}^{\text{min}} = -5.26$  and  $-5.78$  a.u.) (cf. Table II). For the *C* site the chemisorption takes place under the "surface." Very low calculated vibrational frequencies (cf. Table II) indicate that the hydrogen atom moves very easily within the tetrahedral cavity.

An almost constant value of the chemisorption energy of  $\sim 3$  eV for the *C* site of  $\text{Li}_8\text{-H}$ ,  $\text{Li}_{12}\text{-H}$ , and  $\text{Li}_{14}\text{-H}$  shows strong transferability of the local properties of the chemisorption bond and demonstrates the conceptual advantage of the localization procedures.

Let us emphasize that already the inspection of the eigenvalues of the  $\hat{P}_{\text{CM}}$  or  $\hat{K}$  operator and of the localization indices of virtual orbitals has shown that the number of mostly localized occupied and virtual (cf. Table II) orbitals remains unchanged for the increasing nuclearity of the cluster for the chemisorption site *C*. This indicates that the characteristics of active orbitals remain unchanged with enlargement of the neighborhood of the chemisorption molecule beyond a certain number of surrounding atoms and that the local properties of the chemisorption bond are present.

The bridge chemisorption site *B* with chemisorption molecule  $[\text{Li}_2(2,0) + \text{H}]$  has been studied for the  $\text{Li}_{12}(6,6)\text{-H}$  system (cf. Fig. 3 and Table II). The projection operator  $\hat{P}_{\text{CM}}$  or exchange operator  $\hat{K}$  are defined over the  $2s$  orbitals of two Li atoms and both  $s$  orbitals of the hydrogen atom. The localization procedures yield in this case only three doubly occupied mostly localized orbitals, one

singly occupied orbital, and 24 virtual orbitals with localization index larger than 10% (cf. Table II). The CI calculations using only valence LMO's of the LP and WP yield 2.74 and 3.00 eV for the chemisorption energy (cf. Table II). It is interesting to note that the values of the chemisorption energy do not differ substantially from the values obtained for the "cage" chemisorption site *C*, although the definition of the chemisorption molecule is different and the number of the active localized orbitals employed in the CI treatments is different (cf. Table II).

The "on-top" chemisorption site has been studied for the  $\text{Li}_{10}(5,4,1)$  and  $\text{Li}_{14}(9,4,1)$  clusters interacting with the hydrogen atom (Figs. 5 and 6). Two types of chemisorption molecules have been chosen,  $[\text{Li}_5(1,4) + \text{H}]$  and  $[\text{Li}_5(5,0) + \text{H}]$ , in order to investigate the transferability of the localization concept. The localization of the occupied MO's is carried out with respect to a subset of orbitals composed from  $2s$  valence AO's of the five lithium atoms and from both  $1s$  functions of the hydrogen atom. For both "chemisorption molecules" and both systems considered, the localization procedures yield five of the most localized doubly occupied orbitals. Besides these LMO's and one singly occupied orbital, we selected, according to the same criterion as for the previous cases, 39 virtual orbitals for the CI treatments (cf. Table II for a number of active orbitals). It is worth mentioning that for the  $[\text{Li}_5(1,4) + \text{H}]$  chemisorption molecule the symmetry properties of localized MO's for  $\text{Li}_{10}\text{-H}$  and  $\text{Li}_{14}\text{-H}$  systems are different. A larger number of Li atoms in the first layer for the  $\text{Li}_{14}$  cluster results in one of the strongly localized orbitals belonging to the  $a_2$  irreducible representation of the  $C_{2v}$  symmetry point group; this is not the case for the  $\text{Li}_{10}\text{-H}$  system. This can also be an indication that the transferability of the local properties is perhaps less present for the  $[\text{Li}_5(1,4) + \text{H}]$  than for the  $[\text{Li}_5(5,0) + \text{H}]$  chemisorption molecule. Again, for the

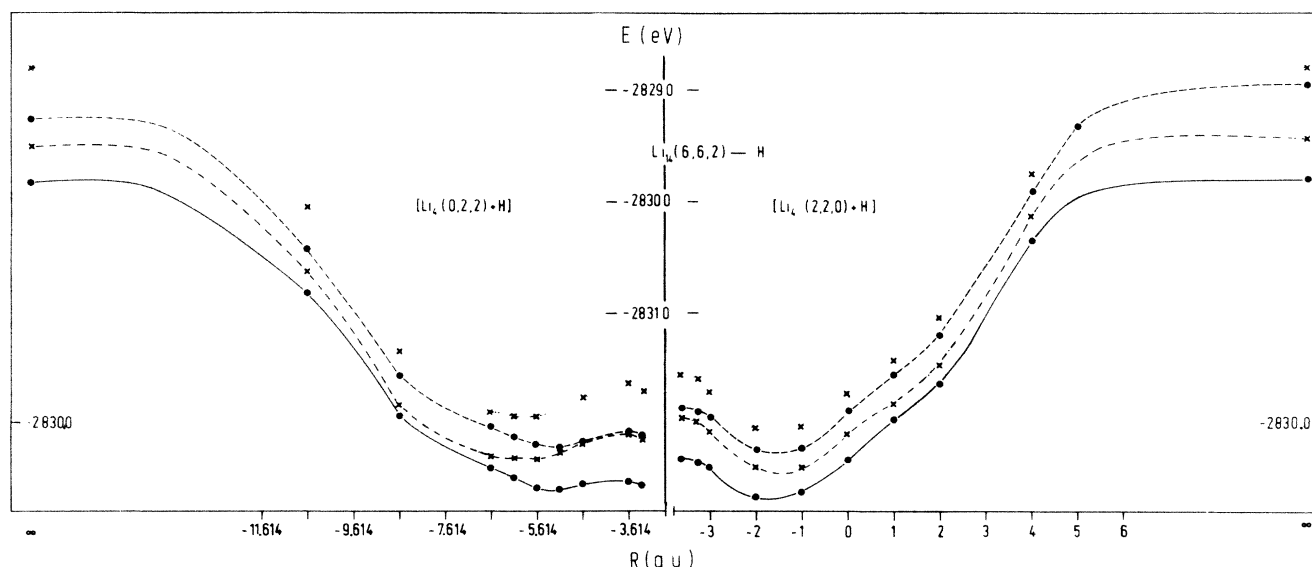


FIG. 4. Chemisorption curves for the  ${}^2A_1$  state of the  $\text{Li}_{14}(6,6,2)\text{-H}$  system for the two cage sites *C*:  $[\text{Li}_4(2,2,0) + \text{H}]$  and  $[\text{Li}_4(0,2,2) + \text{H}]$  obtained from the analogous CI treatments with localized orbitals as described in Fig. 2.



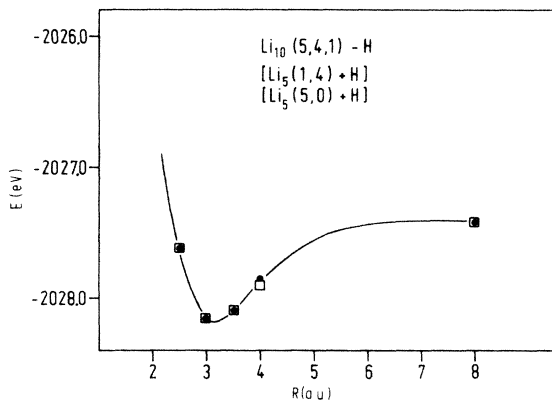


FIG. 5. Chemisorption curves for the  ${}^2A_1$  state of the  $\text{Li}_{10}(5,4,1)\text{-H}$  system for the two "on-top" chemisorption sites  $[\text{Li}_5(1,4) + \text{H}]$  ( $\square$ ) and  $[\text{Li}_5(5,0) + \text{H}]$  ( $\bullet$ ) obtained from the CI treatments using only valence LMO's of the LP and WP. The WP yields almost identical curves. The sizes of the CI spaces are  $\sim 6000$ .

same reasons as described for the cage and the bridge chemisorption sites, both the LP and WP with only valence LMO's yield reliable chemisorption curves.

In the case of  $\text{Li}_{10}\text{-H}$  systems for both on-top chemisorption sites, the chemisorption energies are similar,  $\sim 0.80$  eV (cf. Table II). The transferability of the local properties seems to be slightly better for the  $[\text{Li}_5(5,0) + \text{H}]$  on-top site because in this case the chemisorption energy for the  $\text{Li}_{14}(9,4,1)\text{-H}$  system is  $\sim 1.0$  eV, while for the  $[\text{Li}_5(1,4) + \text{H}]$  site  $D_e \sim 1.2$  eV (cf. Table II). The interaction energies are, in general, lower in the case of the localization with respect to the  $[\text{Li}_5(5,0) + \text{H}]$  chemisorption molecule.

The chemisorption energies and vibrational frequencies obtained for the on-top chemisorption site differ substantially from those obtained for the "cage" and "bridge" chemisorption sites (cf. Table II). The CI calculations

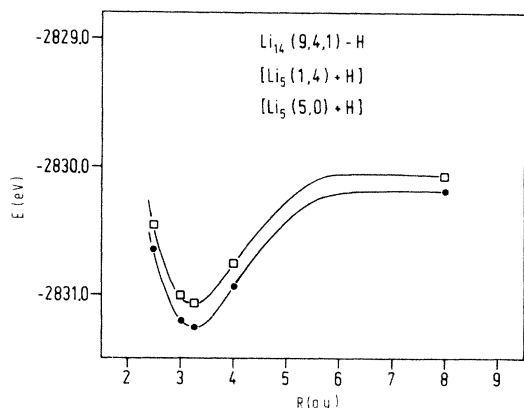


FIG. 6. Chemisorption curves for the  ${}^2A_1$  state of the  $\text{Li}_{14}(9,4,1)\text{-H}$  system for the two "on-top" chemisorption sites  $[\text{Li}_5(1,4) + \text{H}]$  ( $\square$ ) and  $[\text{Li}_5(5,0) + \text{H}]$  ( $\bullet$ ) obtained from the CI treatments using only valence LMO's of the LP. The WP yields analogous curves. The sizes of the CI spaces are  $\sim 6000$ .

employing localized orbitals yield very similar values for the chemisorption energies for all studied systems for which the chemisorption energy has been calculated using canonical HF orbitals in the CI procedure. The chemisorption energies for  $\text{Li}_8(6,2)\text{-H}$  and  $\text{Li}_{10}(5,4,1)\text{-H}$  systems obtained from all-electron MRDCI calculations without localization<sup>4</sup> are 2.97 and 1.2 eV, respectively. Embedded-cluster, all-electron, and pseudopotential MRDCI treatments without localization yield  $D_e = 2.91$  eV for the chemisorption energy for the  $\text{Li}_{12}(6,6)\text{-H}$  system.<sup>10</sup> In addition, the CI procedure using the Whitten localization algorithm in the framework of the embedded theory for the relatively large cluster-H system  $\text{Li}_{25}(9,16)\text{-H}$  yields, for the on-top chemisorption energy, 1.21 eV.<sup>11</sup>

## V. DISCUSSION AND CONCLUSIONS

It is worth mentioning that the study of transferability of the local properties of the chemisorption bond in the framework of the cluster models requires a systematic choice of the clusters with increasing nuclearity for each chemisorption site separately. One of the possible criteria for the construction of a series of clusters for such studies is surely the minimum distance between lattice atoms and each atom of the chemisorption molecule, so that with the growing size of the cluster the chemisorption molecule is surrounded by an increasing number of shells. All atoms of one shell contribute almost equivalently to the interaction with the adsorbate. Therefore, the convergence of the chemisorption properties should be reduced very rapidly with an increasing number of shells if the local properties of the chemisorption bond are present. Consequently, the cluster size is not the only important criterion for the suitability of a cluster to model the chemisorption site at the crystal surface.

The CI calculations employing two different localization techniques when appropriately applied yield the chemisorption energy of  $\sim 3$  eV for the "cage" (absorption) and "bridge" (adsorption) chemisorption sites of  $\text{Li}_n\text{-H}$  systems (with  $n \geq 8$ ) independent of the size of the cluster. For the on-top chemisorption site the chemisorption energy (0.7–1.2 eV) is smaller and its invariance on the size of the cluster is less evident than in the case of cage and bridge chemisorption sites. The chemisorption energies obtained from the truncated CI using both localization procedures, the LP and WP, are reliable only if the core orbitals are excluded from the localization, because in this case the characteristics of the selected CI spaces remain unchanged for short and large cluster-H distances. It has been demonstrated that the localization represents a useful and important tool in predicting not only chemisorption energies but mainly in characterizing the nature of the chemisorption bond. If the transferability of the local properties with increasing size of the cluster can be established, it is very likely that the chemisorption energy will be also invariant to the size of the cluster for the given chemisorption site. The validity of two of the most important concepts has been demonstrated employing the following localization procedures: (i) It is sufficient to correlate only those electrons which are directly involved in the chemisorption bond if this bonding is of localized



nature, and (ii) the enlargement of the neighborhood of the chemisorption site beyond a given size does not affect substantially the chemisorption bond and, consequently, chemisorption energies.

The question can be raised about the physical reasons for fairly good agreements between the WP and LP. Let us point out that both methods differ basically in two points: (i) The space of occupied orbitals is transformed according to the exchange and overlap maximization criteria, respectively, and (ii) although in *both procedures* the virtual orbitals are transformed according to the exchange maximization criteria, the maximization is carried out with respect to the fixed set of atomic orbitals in the former procedure and with respect to the transformed localized occupied orbitals in the latter procedure.

From a careful analysis of the results obtained from both methods the following conclusions can be drawn: A set of spatially well-localized orbitals of almost the same nature is obtained from the transformation which makes use of either a projector operator or an exchange operator, although the overlap criterion represents a somewhat stronger requirement than exchange criterion for spatial localization. Consequently, spatial localization which does not depend on energetics is not sensitive to the choice of localization operator. The localization employing a projector operator is advantageous from the computational point of view since it requires determination of some one-electron integrals due to the overlap between full basis and a selected set of orbitals defining the kernel of projector, while the WP localization requires arithmetic dealing with a large number of two-electron integrals. The choice of basis with respect to which the maximization of the exchange operator for virtual orbitals is carried out is more important for energetic selection of configurations in truncated CI. In the proposed procedure the kernel of the exchange operator includes localized MO's and from the perturbative point of view it is to be expected that more correlation will be accounted for than if the kernel of the exchange operator is a fixed set of AO's. Consequently, all chemisorption curves obtained for the same sizes of truncated CI spaces in the LP lie below those obtained from the WP. Several tests have been carried out to show that the smaller sizes of CI spaces of the LP give rise to the same results (energies) as the WP employing larger CI spaces. It is to be expected that both schemes will yield similar results for other systems than studied ones in this work if both of them will produce similar spatial forms of the localized occupied orbitals. This will always be the case if the exchange maximization gives rise to sufficiently localized orbitals. The overlap-maximization criterion might be advantageous for describing penetration of chemisorbate into the tetrahedral cavity for which a sensitive mixture of substrate and chemisorbate AO's enter into the localized orbitals especially if the chemisorbate is an open-shell system. The studied systems in this paper represent much more difficult cases and the only discrepancy between the two procedures that has been found is the minimum energy position of the hydrogen penetrating into the  $\text{Li}_4(0,2,2)$  cavity of the  $\text{Li}_4(6,6,2)$  system (cf. Table II). These problems are less pronounced in the case of "closed-shell" chemisorbate systems. The re-

sults obtained for the interaction between CO and  $\text{Li}_x$  or  $\text{Be}_x$  clusters employing the same localization techniques which are to be published elsewhere support the generality of the conclusions drawn here.

This work strongly supports the basic idea of the methods in which the surrounding of the cluster of a given size interacting with the adsorbate can be described in a more approximate manner [at the self-consistent-field (SCF) level or in the framework of embedded theory] than the kernel subsystem.<sup>1(d),5,10</sup>

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#### APPENDIX: CONSEQUENCES OF A CORE-VALENCE MIXING IN THE LOCALIZATION PROCEDURES ON THE CI

The importance of constant contribution of core-valence excitations along the interaction coordinate of the chemisorbate-substrate can be easily understood by considering the simple example of the  $\text{Li}_2$  molecule described with a minimal basis set. The HF configuration is  $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2$ . In the "only-valence" CI treatment the allowed excitation is  $2\sigma_g^2 \rightarrow 2\sigma_u^2$ , because the  $1\sigma_g$  and  $1\sigma_u$  are treated as frozen-core orbitals. Let us substitute the  $2\sigma_g$  orbital with a linear combination

$$\overline{2\sigma_g} = \sin\alpha(1\sigma_g) + \cos\alpha(2\sigma_g).$$

The frozen orbitals are now the  $1\sigma_u$  and the corresponding

$$\overline{1\sigma_g} = \cos\alpha(1\sigma_g) - \sin\alpha(2\sigma_g).$$

The excitation  $(\overline{2\sigma_g})^2 \rightarrow 2\sigma_u^2$  now contains some core-valence character and the resulting correlation correction is smaller than in the case of the canonical ( $\alpha=0$ ) orbitals. Typical values for the correlation energy [computed at  $R_{\text{Li-Li}}=5.05$  a.u., with a STO-3G basis (Slater-type orbital—three Gaussians)] are 0.0431, 0.0029, 0.0003, and 0.0001 a.u. for  $\alpha=0^\circ, 30^\circ, 60^\circ,$  and  $90^\circ$ , respectively.

For illustrative purposes, the parameter  $\alpha$  can be taken as the degree of core-valence mixing which actually can occur due to the localization procedure. A careful examination of the  $\{\overline{\phi}_B^0\}$  vectors showed that the extent of the core-valence mixing is much larger for large adsorbate-substrate distances than for short distances. This is not surprising considering that at a very large distance (no interaction) the localization matrix  $\mathbf{W}$  has the special block-diagonal structure. The  $\{\chi^0\}$  subset is actually composed from two orthogonal subsets  $\{\chi_{\text{adsorbate}}^0\}$  and

$\{\chi_{\text{substrate}}^o\}$ . In this case the maximization of the overlap (or exchange) interaction can evidently involve the core orbitals of the cluster to a different extent than at short distances for which the overlap (or exchange interaction) between the valence components of the substrate and the adsorbate is dominant.

The large core-valence mixing induced by the localization procedure for the two noninteracting subsystems is reduced (but not eliminated) as the adsorbate-substrate distance decreases.

In order to examine the effect of the core-valence mixing discussed in Sec. II, a localization for  $\text{Li}_x\text{-H}$  systems Sec. II has been carried out for (i) all the occupied HF canonical orbitals (all LMO's) and (ii) for only valence-occupied HF orbitals (valence LMO's) in the framework of the LP and WP (cf. Figs. 2–4). The localization of virtual orbitals has been described in Sec. II. It is important to realize that some localized occupied orbitals which are explicitly included in the CI treatments can change characteristics along the chemisorption curve of two subsystems. At short distances for which the interaction is switched on there is a large charge transfer from "cluster electrons" towards the hydrogen atom so that one doubly occupied strongly localized MO (with a large eigenvalue of the  $\hat{P}_{\text{CM}}$  and  $\hat{K}$  operators) contains large weights of the AO's of hydrogen atoms. The other three doubly occupied, most strongly localized orbitals and one singly occu-

ried orbital are of a valence nature. At large distances for which there is no interaction, all doubly occupied localized orbitals contain, of course, AO coefficients centered at the cluster atoms. One of the localized doubly occupied orbitals contains, besides valence AO contributions, non-negligible participation of core  $1s$  orbitals of Li atoms.

The eigenvalue of the  $\hat{P}_{\text{CM}}$  and  $\hat{K}$  operators for this orbital is smaller for larger distances than for short ones, but this localized orbital must be included in the CI treatment because the same number of electrons should be correlated for all distances. In this case the generated excited configurations contain core-valence excitations which are of high energy and therefore they do not contribute to the selected CI space. Consequently, the correlation correction is too low for the large cluster-H distances (cf. Sec. II). In contrast, for short cluster-H distances mainly valence-valence excitations contribute and a considerably larger amount of configurations are selected in the CI. Therefore, it is to be expected that if all LMO's are employed the selected CI spaces are unbalanced along the chemisorption curve. The chemisorption energy is therefore easily overestimated. If one uses only valence LMO's in the CI treatments the continuity of the characteristics of the CI space remains throughout the curve and chemisorption energies are more reliable.

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