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Journal of Electron Spectroscopy and Related Phenomena 69 (1994) 31–42

JOURNAL OF  
ELECTRON SPECTROSCOPY  
and Related Phenomena

# Density functional approach to moderately large cluster embedding for infinite metal substrates

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First received 29 June 1993; in final form 17 August 1993

## Abstract

A density functional implementation of the moderately large embedded cluster (MLEC) scheme is presented. The method has been modified to permit the application to metal substrates and to stabilize the cluster self-consistent field procedure. An approximate description of the substrate electronic structure is employed in combination with an accurate treatment of the embedded cluster to facilitate the use of flexible basis sets for the description of the local perturbation. Results are presented for hydrogen adsorption on different sites of a lithium monolayer. Free and embedded clusters are compared to demonstrate the effects of embedding and to explore the merits and drawbacks of the method in the regime of metallic systems.

*Keywords:* Adsorption; Cluster; DF; Embedding; MLEC; SCF

## 1. Introduction

A large number of investigations of local perturbations of crystalline solids and surfaces using cluster models has proven the reliability and the value of this approach [1–5]. For a successful application of this conceptually simple scheme it is mandatory to carefully take into account its known limits and deficiencies. Therefore, there is a growing interest in improvements of the cluster approach in order to extend its range of applicability and its accuracy [4,6–16]. Often, these improved schemes are based on heuristic or physically motivated modifications; some exploit the complete electronic structure of the surrounding substrate. The latter usually solve the coupling problem of the cluster

to its environment quite accurately by means of Green functions, albeit at the price of a demanding computational procedure [12–14].

The moderately large embedded cluster method (MLEC) [17,18] and its improvements [19,20] represent a compromise between formal accuracy and computational effort. The method is derived from an exact Green matrix formalism via approximations inspired by the general philosophy underlying the cluster model approach. A cluster embedding procedure results which is well suited for implementation in a computational scheme based on localized orbitals and which seems to be handy enough to promise the possibility of routine applications.

Up to now the MLEC method has been applied mainly to perturbations of covalent and ionic substrates [17,18,20–22]. In adsorption studies slabs

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were adopted for modelling the solid surface. The electronic structure of the substrate and the perturbed cluster were treated by equivalent methods. Only one test calculation, employing an s-band tight-binding model, dealt with a system intended to describe a metal substrate [23]. Instead of a two-dimensional (2D) periodic description of the cluster environment, large clusters have also been used to represent the unperturbed substrate. Two implementations of the original MLEC method are based on this approach [24,25]; a limited number of applications were presented for H and H<sub>2</sub> adsorption on Li(001).

The purpose of the present work is to extend the MLEC embedding scheme to metallic systems for which modifications of the formalism are necessary. Furthermore, we suggest that the cluster Fermi energy should be determined self-consistently, thus avoiding instabilities of the SCF procedure found by other authors [18,24,25]. For computational convenience and aiming at routine use, we adopt the original formulation of the MLEC method [17,18]. As the treatment of chemisorption problems at metal surfaces will be our main goal, a slab model representation of the substrate seems a natural choice. In the following, we will present the first implementation of the MLEC method for this computational framework.

Density functional theory in the local density approximation (LDF) [26] has been chosen to describe the many-electron system. An accurate all-electron implementation based on a linear combination of Gaussian-type orbital (LCGTO) procedure [5] is used to treat the perturbed cluster; the substrate is described by an approximate Slater-type orbital (STO) LDF method [27,28] with 2D periodic boundary conditions. As a first application, hydrogen adsorption on a Li(001) monolayer is investigated. These test calculations are used to validate the present implementation of the embedding scheme, to provide a comparison with calculations employing “naked” cluster models and to rationalize the observed effects of embedding. Moreover, we aim at a clarification of the cluster size required to meet the basic approximations underlying the MLEC method. The test system Li(001)/H is chosen because it allows calculations

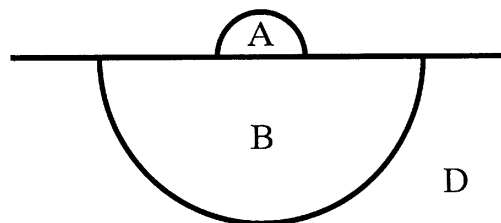


Fig. 1. Schematic representation of the partitioning of a chemisorption system: A, adsorbate; B, perturbed cluster; D, indented solid; chemisorption cluster  $C = A \cup B$ .

using flexible basis sets and rather large metal clusters without prohibitive computational expense.

In the first part of this paper we will sketch the MLEC formalism and describe the modifications as well as the main features of the present implementation. In the second part, H adsorption on a Li(001) monolayer is discussed, focussing on the effects of embedding and on cluster size effects.

## 2. Method

### 2.1. General theory

A detailed derivation of the MLEC formalism may be found at various places in the literature [17–19]. Here we will only give a short overview and present the modifications that allow the treatment of metallic systems. The general formalism is suited to various sorts of local perturbation problems; to be more specific we refer in our discussion to the chemisorption situation.

The chemisorption system under consideration is divided into three regions (Fig. 1): the adsorbate A, a cluster B which is considered as the perturbed part of the substrate, and the indented solid D which is assumed to be unaffected. The parts A and B together form the chemisorption cluster C. If all quantities of the corresponding electronic structure problem are represented in matrix form, using a basis set of local functions, this spatial partitioning is translated into a block matrix notation suited to the introduction of local approximations.

The cluster model is based on the assumption that all pertinent changes in the substrate

electronic structure due to the adsorbate are confined to a rather restricted surrounding of the adsorption site. In the MLEC approach, two fundamental assumptions are made concerning the cluster size: the cluster is large enough (1) to comprise all perturbations caused by the adsorbate, and (2) to afford a border region towards the substrate that is unaffected by the adsorbate. If one exploits these approximations in the Green matrix formulation of the self-consistent field (SCF) problem of the whole system using the Dyson equation, one achieves considerable simplifications. The following algebraic eigenvalue problem arises for the embedded chemisorption cluster:

$$\mathbf{H}_{CC}\bar{a}_i = \bar{e}_i \mathbf{S}_{CC}\bar{a}_i \quad (1)$$

where the cluster Hamiltonian

$$\mathbf{H}_{CC} = \bar{\mathbf{H}}_{CC}(\mathbf{P}_{CC}) + \Delta\mathbf{H}_{CC}^f \quad (2)$$

depends on a modified density matrix

$$\mathbf{P}_{\mu\nu} = \begin{cases} 2 \sum_i \bar{a}_{\mu i} \bar{a}_{\nu i} \Theta(E_f - \bar{e}_i) & \mu \in \mathbf{C}, \nu \in \mathbf{A} \\ 2 \sum_{i,\alpha \in \mathbf{B}} \bar{a}_{\mu i} \bar{a}_{\alpha i} M_{\alpha\nu}(\bar{e}_i) & \mu \in \mathbf{C}, \nu \in \mathbf{B} \end{cases} \quad (3)$$

In the first step of the SCF procedure the eigenvalue problem is solved for the isolated chemisorption cluster. The Hamiltonian matrix  $\mathbf{H}_{CC}$  is given by the C submatrix of the Hamiltonian of the whole system. The coupling of the resulting effective cluster electronic structure ( $\bar{a}_i =$  orbital coefficients,  $\bar{e}_i =$  orbital energies) to the surrounding substrate is achieved by modification of the density matrix  $\mathbf{P}_{CC}$ . The occupation numbers are partially modified by the energy and orbital dependent coupling matrix  $\mathbf{M}$ . Based on the perturbed cluster density, an effective cluster Hamiltonian  $\bar{\mathbf{H}}$  is constructed. To build up the C submatrix of the Hamiltonian of the extended system, the contributions of the nuclei and the electronic density of the indented solid have to be added. These corrections are formally summarized in the term  $\Delta\mathbf{H}$ . Although this term is independent of the adsorbate perturbation according to the MLEC approximation, it cannot be calculated directly. In density functional theory, as in most other

advanced electronic structure methods, the density enters the Hamiltonian in a nonlinear way. Thus, any attempt to determine  $\Delta\mathbf{H}$  directly from the wavefunctions of the free substrate [24] has to be regarded as an additional approximation. Using Eq. (2) as the defining relationship of  $\Delta\mathbf{H}$ , the correction term to the Hamiltonian is given by

$$\Delta\mathbf{H}^f = (\mathbf{H}^f(\mathbf{P}^f))_{\mathbf{BB}} - \bar{\mathbf{H}}_{\mathbf{BB}}^f(\mathbf{P}_{\mathbf{BB}}) \quad (4)$$

since the coupling to the indented solid is independent of the adsorbate according to the MLEC approximation.  $\bar{\mathbf{H}}_{\mathbf{BB}}$  denotes the effective Hamiltonian matrix of an unperturbed embedded cluster, the superscript f refers to the unperturbed substrate. Thus,  $\Delta\mathbf{H}$  can be determined for a given surface cluster once and for all.

The MLEC matrix  $\mathbf{M}$  depends only on the unperturbed host system

$$\begin{aligned} M_{\mu\nu}(e) = \mathcal{P} \int_{-\infty}^{+\infty} \frac{t S_{\mu\alpha} - H_{\mu\alpha}^f}{t - e} \rho_{\alpha\nu}^f(t) \Theta(E_f - t) dt \\ + \mathcal{P} \int_{-\infty}^{+\infty} \frac{e S_{\mu\alpha} - H_{\mu\alpha}^f}{e - t} \rho_{\alpha\nu}^f(t) \Theta(E_f - e) dt \end{aligned} \quad (5)$$

Here,  $\rho^f(t)$  denotes the projected density of states (PDOS) of the unperturbed substrate. The MLEC matrix is known to be a very smooth function of the energy [17,24,25], except for a logarithmic singularity at the Fermi level. This singularity originates in the discontinuity of the step function, used as the electronic distribution function in the definition of the density matrix of the unperturbed system, as the principal value integration is not defined for  $e = E_f$ . For insulating materials exhibiting a large bandgap no complications arise. A sufficiently large gap may also be found for most small metal clusters. For metal clusters that are large enough for the fundamental MLEC assumptions to hold, small gaps will occur as a rule for metal substrates, preventing a numerically stable SCF procedure [24,25].

In order to extend the applicability of the MLEC approach to metallic systems one is forced to remove the discontinuity of the step function. We decided to soften the step into a differentiable shape over a small energy interval of width  $\eta$

around the Fermi level, the principal value integration always then being well-defined. For a cosine-like step shape, simple trigonometric transformations yield slightly more complicated formulae for the coupling matrix in Eq. (5).

Summarizing the general MLEC formalism, the computational scheme results in the following steps (note that the various tasks are listed in the order of an increasing dependency on the specifics of the system):

- (1) Self-consistent determination of the substrate electronic structure.
- (2) Construction of the substrate projected density of states  $\rho^f$  and the Hamiltonian matrix  $H^f$  in a localized basis.
- (3) Choice of a surface cluster  $B$ , gathering of the corresponding submatrices of  $\rho^f$  and  $H^f$ , determination of the MLEC matrix and the correction to the Hamiltonian.
- (4) Specification of the adsorbate and self consistent treatment of the adsorption cluster.

## 2.2. Implementation

All previous implementations of the MLEC formalism [17,18,20,24,25] implicitly rely on a further assumption: the electronic structure description of the cluster and the (periodic) substrate have to be exactly equivalent, even to the point that the same localized basis set is used. Provided this prerequisite is met, then the MLEC formalism guarantees self-embedding consistency [17], i.e. the substrate electronic density is locally reproduced if an unperturbed cluster is embedded. From a theoretical point of view, this feature is desirable for any embedding method. In practice, one has to carefully adapt the electronic structure method and to judiciously choose computational parameters in order to achieve optimal results, both for the infinite substrate and for the cluster. This becomes quite obvious for the basis set. On the one hand, it should be localized enough to avoid overcompleteness problems in the treatment of the periodic substrate [27], on the other hand, enhanced flexibility is desirable for the description of the adsorbate–substrate interaction.

As our interest focusses on adsorption complexes we opted for an approximate description

of the substrate [27] to concentrate the computational effort on the cluster part. This approach is motivated by the observation that quantities entering the local SCF procedure are either of corrective character or do not depend on details of the substrate electronic structure. One is then free to adapt basis sets to the specific requirements of both the periodic and the molecular calculation. Furthermore, given the rather strong approximations that underly the MLEC formalism, a moderate additional approximation in the treatment of the substrate seems tolerable.

The partitioning of the chemisorption system into subsystems and the corresponding blocking of the matrix representations of all relevant quantities leads to a dependency of the MLEC method on the form of the basis set. The simplest procedure is to partition the function space according to atomic centres on which the basis functions are centred. It is known that this procedure leads to numerical problems [24,25] as elements of the coupling matrix may become fairly large, making a very accurate cancellation of terms in the determination of density matrix indispensable.

Moreover, our calculations on unperturbed Li(001) monolayer clusters showed that the electronic charge is distributed in an unbalanced way. Integration of the cluster submatrix of the substrate PDOS always yields less than 90% of the electronic charge of the corresponding neutral cluster. This loss of charge has to be ascribed to the lower coordination of atoms situated at the boundary of the cluster as they lack the contributions from the tails of basis functions anchored on atoms of the surrounding substrate. The resulting cluster electronic structure is an artifact and the corrective term to the Hamilton matrix has to be large enough to restore a substrate-like behaviour. This has two undesirable consequences. The large corrections tend to destabilize the SCF procedure and they render an interpretation of cluster-related quantities essentially impossible. For covalent substrates a transformation to hybridized orbitals has been proposed [22], for metallic systems orthogonalization procedures showed promising results [24,25]. To preserve the localization of the basis functions as much as possible we use a symmetric orthogonalization scheme. This procedure is

Table 1  
Total electronic charge  $Q^a$  (in a.u.) of various clusters constructed around the on-top and the bridge site of a Li(001) monolayer.

Cluster	$Q$
<b>On-top</b>	
Li <sub>5</sub>	15.002
Li <sub>9</sub>	27.003
Li <sub>13</sub>	39.004
Li <sub>21</sub>	63.007
Li <sub>25</sub>	78.009
Li <sub>29</sub>	87.010
<b>Bridge</b>	
Li <sub>8</sub>	24.003
Li <sub>12</sub>	36.004
Li <sub>16</sub>	48.005
Li <sub>22</sub>	66.007

<sup>a</sup> The charge is determined by integrating the cluster submatrix of the corresponding projected density of states; see Fig. 2 for the geometry of the various clusters.

known to result in functions which resemble most the original ones in a least-squares sense [29]. When defining the local cluster in terms of symmetric orthogonalized basis functions we find that charge is conserved and all quantities may be related to those of unperturbed clusters, permitting the familiar interpretation. As an example, we display in Table 1 values for the total charge of subclusters of a Li(001) monolayer, as determined by integrating the corresponding submatrix of the PDOS. For the on-top adsorption site the cluster series is constructed by increasing a Li<sub>5</sub> unit successively by shells of neighbours with increasing distance from the central atom (see the resulting numbering scheme in Fig. 2(a)). For the bridge site, the series starts with a Li<sub>8</sub> cluster (Fig. 2(b)). For all these monolayer clusters charge neutrality is conserved to a fraction of about  $10^{-4}$ .

While the determination of the coupling matrix only requires straightforward integration, the construction of the corrective term to the Hamiltonian is more involved because it is defined as the difference of quantities related to different functional spaces. In previous MLEC implementations this term either vanished due to intrinsic approximations of the adopted computational scheme [17] or it was treated in an approximate way [24,25].

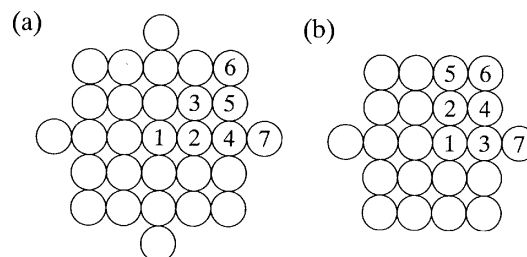


Fig. 2. Sketches of the largest clusters investigated, (a) Li<sub>29</sub> for the on-top site and (b) Li<sub>22</sub> for the bridge site. The numbering of the atoms indicates the shell of neighbours of increasing distance from the adsorption site.

Diagonalizing the submatrix  $(H^f)_B$  one obtains cluster orbitals which, when modified according to the coupling matrix (Eq. (5)), yield a local embedded density matrix. Based on this density, one now locally constructs the effective cluster Hamiltonian  $\bar{H}_B^f$ . While  $(H^f)_B$  is defined in the function space spanned by the slab basis,  $\bar{H}_B^f$  is represented in the local cluster space. Thus one has to project the effective cluster Hamiltonian onto the slab space before constructing the correction

$$\Delta H_B = (H^f)_B - P_S \bar{H}_B^f P_S \quad (6)$$

The self-consistent embedded cluster calculation proceeds by adding in each cycle this correction term to the Hamiltonian and by constructing the density matrix with the help of the coupling matrix  $M$  (Eq. (5)). The MLEC formalism in general does not guarantee the density matrix to be symmetric and positive definite; these fundamental properties are exactly satisfied only in the limit of infinite cluster size [17]. For large enough cluster models, both properties are fulfilled to a satisfactory degree. However, they are always enforced in the present implementation to guarantee meaningful results [30].

As a consequence of the fundamental assumptions underlying the MLEC approach no charge exchange is allowed between the perturbed cluster and its surroundings. However, the total charge of the cluster depends on the choice of Fermi energy and, as discussed earlier, on the details of partitioning of the basis set. As this feature is decisive for the significance of the cluster-related quantities and the

Table 2  
Variation of the broadening parameter  $\eta$  of the Fermi distribution function for on-top adsorption of H on Li<sub>9</sub>

$\eta/\text{eV}$	$d/\text{\AA}$	$\omega_0/\text{cm}^{-1}$	$E_b/\text{eV}$	$\mu/\text{Debye}$	$q(\text{H})/\text{a.u.}$
0.00	1.6795	1031	0.96	-0.1552	-0.023
0.05	1.6792	1033	0.99	-0.1557	-0.020
0.10	1.6792	1032	1.00	-0.1559	-0.019
0.25	1.6798	1031	1.00	-0.1563	-0.019

Key:  $d$ , Li–H distance;  $\omega_0$ , vibrational frequency;  $E_b$ , binding energy;  $\mu$ , normal component of the dipole moment;  $q(\text{H})$ , Mulliken charge of the adsorbate.

iterative stability of the SCF procedure, it deserves special attention. The natural choice for the Fermi energy is its substrate value. Employing a fixed Fermi energy runs the risk of charge oscillations during the SCF cycles, as found in other implementations [18,21,24]. There the convergence had to be stabilized by charge damping or even by renormalization procedures, despite the fact that the total cluster charge is tied to the Fermi energy. In addition to the partitioning problem, for metallic systems the details of the electronic structure near the Fermi energy will strongly influence the resulting cluster charge. The total electron number of the chemisorption cluster may even vary with adsorption geometry. Calculating the number of electrons of a subcluster of an extended system is in general a delicate task, as it is for ionic or covalent materials, because there is no unequivocal method to determine the charge related to a single atom in a compound system. We therefore refrain from introducing an ill defined computational parameter and fix the electron number of the chemisorption cluster, assuming it to be neutral. The Fermi energy is then computed self-consistently. This procedure is only exact for subclusters of elemental monolayers. For multilayered clusters small fractional atomic charges due to the surface polarization of the substrate may occur. The additional polarization due to the adsorbate is assumed to be located inside the chemisorption cluster if it is chosen in accord with the MLEC assumption.

### 2.3. Computational details

For the electronic structure calculations we use the density functional approach in the LDF approximation [26]. The exchange-correlation

potential is chosen according to the parametrization suggested by Vosko et al. [31]. The 2D-periodic substrate is treated with an approximative STO-LDF implementation [27,28]. Calculations on free and embedded clusters are performed with the accurate all-electron LCGTO-LDF method [5]. Flexible Gaussian basis sets, contracted according to atomic orbitals, are employed: (9s,4p)  $\rightarrow$  [4s,2p] for Li [32] and (6s,1p)  $\rightarrow$  [3s,1p] for H [33]. The band structure of the Li monolayer is calculated using 78 special points [34] in the irreducible wedge of the first Brillouin zone. The substrate PDOS is determined for 200 equidistant energy points in the valence band region. Core bands are treated separately. Based on these data, the MLEC matrix is calculated on an energy grid with quadratically increasing spacing centred at the Fermi level; 670 energy points are used.

The broadening parameter  $\eta$  is chosen to be 0.25 eV. This seems rather a large value, but it should be noted that the coupling matrix itself leads to an effective broadening of the one-electron spectrum and smoothing its energy dependence near the Fermi energy results in an effect of second order. In Table 2 the influence of  $\eta$  is shown for H adsorbed in the on-top position on a Li<sub>9</sub> cluster. Only for small clusters like this, is a calculation without broadening possible. For all displayed quantities the variation of  $\eta$  is found to have a negligible effect compared to the overall accuracy of the calculation and, especially, compared to those changes that occur with varying cluster size (see below).

Due to the self-consistent determination of the Fermi energy and the broadening of the occupation step function a very stable SCF procedure is achieved. The additional computational effort due

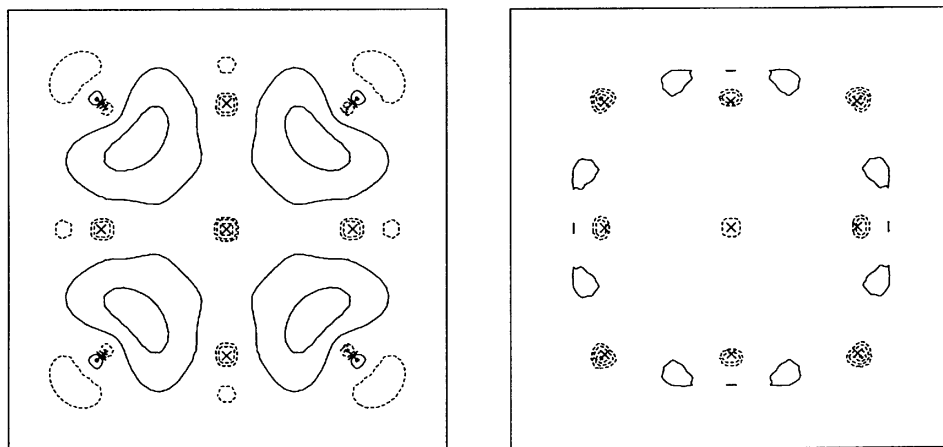


Fig. 3. Difference  $\Delta\rho = \rho(\text{Li}_9) - \rho(9\text{Li})$  of the electron density of a  $\text{Li}_9$  cluster and 9 superimposed atomic densities. Left panel: free cluster; right panel: embedded cluster. Contour lines are drawn for  $\pm 0.001$ ,  $\pm 0.0025$ ,  $\pm 0.005$  a.u. Continuous and dashed lines correspond to positive and negative values, respectively.

to the embedding is essentially compensated by the faster convergence of the calculations for embedded clusters, leading to comparable CPU times for free and embedded clusters.

### 3. H adsorption on Li monolayer

To test our implementation of the modified MLEC method, calculations have been performed modelling hydrogen adsorption on a lithium monolayer. This simple metallic system is well suited for methodical embedding studies because large clusters can be treated with a reasonable computational effort. H adsorption at the on-top and the bridge site is considered to provide examples of perturbations of differing strength. Results for adsorption on multilayer clusters will be presented elsewhere [30].

The geometry of the Li monolayer is chosen as in the top layer of the (001) surface of an ideally terminated bulk. The monolayer exhibits a square lattice with an interatomic spacing equal to that of the b.c.c. bulk (3.49 Å [35]).

The most pronounced embedding effect on monolayer clusters is expected to occur in the horizontal polarization of their electronic charge distribution. A Mulliken analysis may not be reliable enough to diagnose such changes, especially in

the case of lithium clusters with their delocalized nature of the bonding. Therefore we illustrate the differences in the cluster polarization by an electron density map of the cluster  $\text{Li}_9$  (see Fig. 3). The superposed electron density of nine free Li atoms is subtracted to provide an almost homogeneous background and to make the polarization more apparent. In the free cluster, edge polarization is strongest for the corner atoms. The electron density is enhanced in trapezoidal regions between three border atoms. This polarization of the density resembles the one found for small gas phase Li clusters in their equilibrium geometry [36]. These clusters are stabilized by three-centre bonds that become manifest in maxima of the electronic density located in Li triangles. This polarization, which is typical for free clusters, disappears totally when the cluster  $\text{Li}_9$  is embedded in a monolayer. In an infinite monolayer, density maxima of this type are forbidden by the point symmetry of the square lattice. The small features observed at the cluster edge have to be attributed partially to the inhomogeneity of the superimposed atomic densities. Additional small deviations from homogeneity at the boundary of the embedded cluster cannot be excluded. However, embedding succeeds in removing the artificial horizontal polarization of free monolayer clusters almost completely.

As far as cluster embedding is concerned, the on-

Table 3

Comparison of various characteristic quantities for free and embedded cluster models of on-top adsorption of H on a Li(001) monolayer

Cluster	$d/\text{Å}$	$\omega_0/\text{cm}^{-1}$	$E_b/\text{eV}$	$\Delta\mu/\text{Debye}$	$\partial\mu/\partial d/\text{a.u.}$
Free					
Li <sub>9</sub>	1.653	1122	2.05	-0.17	-0.18
Li <sub>13</sub>	1.657	1105	1.47	-0.21	-0.15
Li <sub>21</sub>	1.665	1091	1.27	-0.20	-0.21
Li <sub>25</sub>	1.658	1103	1.38	-0.21	-0.16
Li <sub>29</sub>	1.650	1123	1.91	-0.22	-0.16
Embedded					
Li <sub>9</sub>	1.680	1031	1.00	-0.16	-0.19
Li <sub>13</sub>	1.682	1053	1.37	-0.19	-0.17
Li <sub>21</sub>	1.678	1090	1.09	-0.21	-0.11
Li <sub>25</sub>	1.646	1083	1.19	-0.18	-0.15
Li <sub>29</sub>	1.659	1096	1.26	-0.17	-0.15

Key:  $d$ , Li–H distance;  $\omega_0$ , vibrational frequency;  $E_b$ , binding energy;  $\Delta\mu$ , change of the normal component of the dipole moment;  $\partial\mu/\partial d$ , dynamical dipole moment.

top site is clearly the most simple one of the three high symmetry adsorption sites on a Li(001) monolayer. Only one substrate atom is directly affected by the adsorption and the perturbation of the substrate will be weak in comparison to higher coordinated sites since the adsorbate–substrate distance will be large. The construction of clusters accounting for a large number of nearest-neighbour shells around the adsorption site is also easiest in this case. The clusters which comprise all second nearest-neighbours of those atoms forming an on-top, bridge, or hollow site are Li<sub>9</sub>, Li<sub>12</sub>, and Li<sub>16</sub>, respectively (see Fig. 2). Free and embedded cluster calculations were performed for on-top adsorption of hydrogen beginning with Li<sub>9</sub> up to Li<sub>29</sub> (sixth neighbour shell). The latter is shown in Fig. 2(a) together with the enumeration of atoms that will be used. In Table 3 we compare the results of the free chemisorption cluster models to those obtained from embedding calculations.

In the free cluster calculations a Li–H distance is obtained which is close to the one calculated for the LiH molecule (1.62 Å) the latter being in good agreement with experiment (1.60 Å [37]). The bond is significantly weaker than that for the diatomic molecule for which a binding energy of 2.54 eV and a vibrational frequency of 1380 cm<sup>-1</sup> is calculated, again in good agreement with experiment (2.43 eV and 1406 cm<sup>-1</sup>, respectively [37]).

For the free cluster models, the values of the adsorption bond length, of the corresponding vibrational frequency and of the binding energy fluctuate moderately with increasing cluster size, a phenomenon that is well documented in many other chemisorption cluster model studies [1]. The corresponding clusters embedded in a Li(001) monolayer yield quite comparable results, especially for the larger cluster models. In the embedded cluster series, a slight trend towards shorter distances and higher vibrational frequencies may be noted. The values of the binding energy obtained from the embedded models are in general lower than for the corresponding free cluster models.

Besides a more realistic modelling of the chemisorption interaction one expects an embedding scheme to improve the cluster convergence that is so difficult to achieve with free cluster models [4,38]. Obviously, the present MLEC results for Li(001)/H do not support this expectation (see Table 3). In the MLEC formalism there is one unavoidable cluster dependence that may easily be overlooked: the partitioning of the underlying substrate function space. In this way, the coupling matrix and the correction to the Hamiltonian will be affected by the selected part of the function space which actually defines the cluster model. One may also wonder whether the rigid coupling

Table 4  
Changes of the Mulliken populations due to the adsorption of H at the on-top site of the Li(001) monolayer<sup>a</sup>

Cluster	Li							H
	1	2	3	4	5	6	7	
<b>Free</b>								
Li <sub>9</sub>	-0.39	+0.13	-0.02					-0.04
Li <sub>13</sub>	-0.39	+0.10	-0.01	-0.01				-0.03
Li <sub>21</sub>	-0.39	+0.08	+0.02	-0.00	+0.01			-0.05
Li <sub>25</sub>	-0.37	+0.06	+0.02	+0.01	+0.00	+0.01		-0.03
Li <sub>29</sub>	-0.37	+0.06	+0.03	-0.01	+0.01	+0.00	+0.00	-0.02
<b>Embedded</b>								
Li <sub>9</sub>	-0.50	+0.10	+0.03					-0.02
Li <sub>13</sub>	-0.31	+0.09	+0.01	-0.00				-0.04
Li <sub>21</sub>	-0.42	+0.09	-0.00	-0.00	+0.03			-0.02
Li <sub>25</sub>	-0.39	+0.08	+0.00	+0.00	+0.01	-0.00		-0.02
Li <sub>29</sub>	-0.38	+0.07	+0.00	+0.00	+0.01	+0.00	-0.00	-0.02

<sup>a</sup> See Fig. 2(a) for the designation of the Li atoms.

of the embedded cluster to the substrate, independent of the adsorbate interaction, affects the results in an artificial fashion if the cluster models are not large enough. This effect may be invoked to rationalize the apparent weakening of the chemisorption bond found in smaller embedded clusters. For larger cluster models the corresponding assumption of the MLEC formalism should be fulfilled as may be deduced from the similarity of the results achieved for free and embedded clusters.

Changes of electronic density distribution due to adsorption may be monitored by the normal component of the cluster dipole moment and the dynamical dipole moment  $\partial\mu/\partial d$  at equilibrium separation. The latter may serve as a measure of the effective charge of the adsorbate, provided the dipole moment depends rather linearly on the bond distance. The latter condition is satisfied to a reasonable degree in the present systems. Free and embedded cluster results indicate a small transfer of electronic charge to the adsorbate. Especially for larger clusters the results for both types of models are in good agreement. An alternative, although only qualitative, analysis of the adsorption induced polarization is provided by the changes [sic] in Mulliken populations (see Table 4). The very small values calculated for the hydrogen atom should not be taken too seriously. It is well

known that absolute values of Mulliken charges may be misleading, especially if strongly overlapping atomic basis sets are used. The changes observed for the various types of Li atoms indicate a strong polarization of the adsorption site (atom 1) and of its nearest neighbours. With the exception of Li<sub>9</sub> the magnitude of the polarization is quite comparable with and without embedding. For larger clusters, the small changes for the atoms in the third and fourth shell of neighbours vanish completely for the embedded clusters. This observation confirms that embedded clusters are less polarized. Similar findings have been obtained for multilayered clusters [30]. In these systems the more effective screening of the local perturbation facilitates the fulfilment of the MLEC assumption.

The general homogeneity of the results for on-top adsorption of H shows that a reliable description of adsorption on metal surfaces is possible with the modified MLEC approach presented here. The close resemblance of the results for larger free and embedded clusters is only spoiled by the value of the binding energy of the free Li<sub>29</sub> cluster. However, the slow convergence of this quantity for free metal clusters is well known [4,38]. The small deviations of the MLEC results for Li<sub>9</sub> from those of the larger embedded clusters

Table 5  
Comparison of various characteristic quantities for free and embedded cluster models of bridge adsorption of H on a Li(001) monolayer

Cluster	$h/\text{Å}$	$\omega_0/\text{cm}^{-1}$	$E_b/\text{eV}$	$q(\text{H})/\text{a.u.}$
Free				
Li <sub>8</sub>	0.00	1062	2.77	0.07
Li <sub>12</sub>	0.00	1046	2.79	0.05
Li <sub>16</sub>	0.00		2.56	0.04
Li <sub>22</sub>	0.00	1071	2.61	-0.09
Embedded				
Li <sub>8</sub>	0.58	863	1.08	0.06
Li <sub>12</sub>	0.23	1184	2.60	0.04
Li <sub>16</sub>	0.00	1041	2.57	0.01
Li <sub>22</sub>	0.08	1214	2.41	0.03

Key:  $h$ , H adsorption height;  $\omega_0$ , vibrational frequency;  $E_b$ , binding energy;  $q(\text{H})$ , Mulliken charge of the adsorbate.

demonstrate that in case of a weak perturbation the inclusion of second nearest neighbours of the adsorption site already more or less satisfies the assumptions of the MLEC method.

On-top adsorption of H on Li(001) has previously been investigated by the MLEC method using a cluster-in-cluster approach [24]. Unfortunately a comparison with this work is not meaningful because their embedding effects were characterized only by means of Mulliken charges and a different type of basis set (STO) has been used.

As expected, we find more pronounced embedding effects for the adsorption at the bridge site. To demonstrate the failure of the MLEC method for clusters that are too small, we began the cluster series with Li<sub>8</sub>, a model that comprises only the first nearest neighbours of the adsorption site. The largest cluster (Li<sub>22</sub>) takes into account more than the third nearest neighbour shell (see Fig. 2(b)). The results are summarized in Table 5. For free clusters the adsorbate is always found in the plane of the monolayer, a location which corresponds to a Li–H distance of 1.75 Å. The binding energy is larger than for on-top adsorption in agreement with the observation that higher coordinated sites are generally favoured. However, the vibrational frequency is slightly smaller than for on-top adsorption, reflecting the shallow minimum of the potential energy surface. This fact complicates the accurate determination of the adsorption height and of the first vibrational excitation. To characterize the polarity of the LiH bond, only Mulliken charges are available due to

the particular geometric situation. Their values for H are slightly larger than those found for on-top adsorption where the Mulliken charge of H turned out to be somewhat smaller than the effective charge determined from the dynamical dipole moment. Thus, even for the bridge site, one may assume the adsorbate to be characterized by a small negative charge.

The corresponding embedded clusters show a quite different behaviour with respect to adsorption height and vibrational frequency. Only the larger clusters yield results roughly comparable to those of the free clusters. For corresponding clusters, one may note a tendency to a lower binding energy. Overall, the findings for the bridge site models demonstrate that for stronger perturbations more neighbouring shells have to be included in the cluster models in order to satisfy the fundamental MLEC assumptions. For Li<sub>8</sub> the failure of the embedding is obvious: the value of the adsorption height together with the very low value of the binding energy and the vibrational frequency indicate a considerable weakening of the LiH bond. These results may be rationalized by the rigid coupling of the cluster to the surrounding substrate. Consequently, for small clusters the adsorption interaction is weaker in the MLEC calculation because the polarizability of the adsorption site is artificially reduced. Similar observations have been made for H adsorption on small multilayered Li clusters [30]. The Mulliken charges of the adsorbate are more stable than those of free clusters, a manifestation of the removed edge polarisation due to embedding [30].

#### 4. Conclusions

The present work successfully demonstrates that the MLEC formalism may be appropriately modified for applications to metal substrates. The coupling of the cluster to its surrounding was stabilized by broadening the Fermi edge and by using symmetrically orthogonalized orbitals as the basis for the partitioning of the system into a perturbed cluster and its unaffected surrounding. A stable SCF procedure resulted from fixing the electronic charge on the cluster and from determining the cluster Fermi energy self-consistently. As a consequence, the SCF convergence was improved compared to the more polarizable free clusters. Owing to these methodological advances it was possible to embed rather large Li clusters, using a first principles LDF computational scheme and flexible basis sets.

H adsorption on different sites of a Li monolayer was chosen as a test system to validate our implementation. For unperturbed clusters it was demonstrated that embedding results in a rearrangement of the charge distribution toward a more surface-like behaviour. In the case of on-top adsorption, free and embedded clusters were extended until very similar results were achieved for several characteristic quantities, confirming the correctness of the MLEC approach in the limit of very large clusters. For all embedded clusters a tendency to lower binding energies was observed. For small clusters the basic assumptions of the MLEC method are clearly violated: a considerable weakening of the adsorbate–substrate bond results. Depending on the strength and the range of the substrate-induced perturbation suitable clusters have to be chosen for embedding. Our results indicate that at least the second nearest neighbours of the directly affected substrate atoms have to be taken into account when one wants to construct a “moderately large” cluster.

#### Acknowledgements

We thank B. Reichert for advising us in the use of the 2D STO-LDF method. This work was supported by the Deutsche Forschungsgemeinschaft

via SFB 338 and by the Fonds der Chemischen Industrie.

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