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Local-space approximation for treatment of chemisorption: Application to a model transition-metal system

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The *local-space* approximation (LSA) for the treatment of chemisorption is explored using a model system which consists of a hydrogen atom interacting with a semi-infinite one-dimensional chain of transition metal (tungsten) atoms within the Anderson-Newns approximation to the Hartree-Fock Hamiltonian. Convergence with respect to the size of the *local space* is much more rapid than for a finite-cluster calculation. In order to achieve the same accuracy, over twice as many atoms must be present in the latter case. Comparison with a standard Green's-function treatment confirms the importance of including self-consistent charge transfer between the surface complex and the neighboring substrate. Adsorbate-induced surface states are readily found and characterized by the LSA technique. In addition, we show how the effect of adsorption on the work function of the metal can be determined.

I. INTRODUCTION

It has been a long-held view that when an atom or molecule adsorbs on a metallic surface the perturbation is, ordinarily, not significant beyond a small number of neighboring atoms. In this way chemisorption is considered to be a local phenomenon, and theoretical investigations usually concentrate on the "surface complex," or cluster, comprising the adsorbate plus a few interacting neighbor substrate atoms.[1]

On the other hand, the fact that cluster calculations do not seem to converge rapidly with increasing size[2–5] highlights the importance of properly embedding the cluster within the entire system. This leads to the problem of handling—in a self-consistent way—a semi-infinite system with locally broken symmetry. As a result a variety of embedding methods have been proposed[6–9] including our own.[10] The former techniques often combine a simpler description of the periodic substrate outside the surface complex, with a higher level treatment of electronic interactions within this region. However, self-consistency is usually included in only a limited way and, at most, for just a couple of atoms in the surface complex. The transfer of electrons into or out of the surface complex is not correctly accounted for nor is the charge conserved as it should be.

Of the other embedding methods the closest in spirit to ours is that of Feibelman and co-workers[7] in the sense that both are matrix-oriented and that the density matrix, in particular, plays a central role. We also especially note the density-matrix procedure of Ying and co-workers[11] which has been applied to the formation of surfaces and vacancies in simple metals. As noted elsewhere[10] their method is based on a *local-space* approximation similar to ours. In contrast with them, however, we use a combination of fragments approach that allows for important simplifications without introducing further approximations. Additionally, both Ying *et al.* and Feibelman *et al.* are limited in *ab initio* calculations to density-functional (or Hartree-Fock) theory which is known to seriously underestimate binding energies.[12]

Our *local-space* approximation (LSA) for localized electronic interactions in extended systems was first presented[10] about five years ago. When used with the Hartree-Fock (HF) or $X\alpha$ model[13] this approximation is based on a density-matrix formulation[14] of the electronic structure problem. In the case of chemisorption our treatment allows the surface complex (i.e., the *local space*) to be fully coupled to the rest of the system and, at the same time, conveniently projects the HF problem onto the local region where the perturbation caused by the adsorbate is most felt. Therefore, subject to certain approximations presented in Sec. II, one gets a self-consistent solution for the entire semi-infinite system while the quantum chemistry calculation is reduced to molecular dimensions.

Previous applications of the LSA method include model calculations for the chemisorption of atomic hydrogen onto a tungsten (100) surface,[10] a treatment of the interaction between finite molecular fragments,[15] a study of the localizability of hydrogen bonds in large systems,[16] and an investigation of solitons in polyacetylene.[17] In all these problems it has been found that the method gives very good results for bond energies and for the projection of the density (or the charge and bond order) matrix on the local region.

In order to assess the efficiency of the LSA technique, it is necessary in each individual case to establish how fast the results converge with an increase in the size of the *local space*. From a practical point of view the calculations must converge—or, at least, one must be able to extrapolate reliably to the convergence limit—before the dimensions of the *local space* increase to the point of making the quantum chemistry treatment unmanageable. The purpose of the present paper is to carry out such a study for a model chemisorption system.

The particular model considered here is that of a hydrogen atom interacting with a semi-infinite one-dimensional chain of transition-metal (tungsten) atoms within the Anderson-Newns (AN) approximation[18,19] to the HF Hamiltonian. Due to the crudeness of the model we do not insist that the results agree with experiment. Instead we test the convergence of the LSA method and investigate its advantages and limitations relative to other approaches. In order to ascertain the importance of self-consistency throughout the entire system, our results are compared to ordinary cluster calculations as well as a typical Green's function scheme where self-consistency is imposed only on the surface complex. It turns out that a *local space* containing just 8 metal atoms yields essentially the same results as those obtained for a finite 20 atom metal cluster.

In addition to the adsorption energy, we examine the charge and magnetic moment of each individual atom in the surface complex. By considering charged hydrogen atoms we also determine the effect of adsorption on the work function of the metal. Finally, the presence of an adsorbate may induce the formation of surface states. The latter have been observed experimentally for hydrogen on metal surfaces[20] through the appearance of difference peaks in the photoemission spectra. Using our treatment we show how to find and characterize such states in a simple manner.

The organization of this paper is as follows. In Sec. II we present a short review of the theory on which the LSA method is based and, then, in Sec. III we give details of our model calculations. The results are shown in Sec. IV and a comparison with an alternative embedding treatment is presented in Sec. V.

II. THEORY

The Hartree-Fock LSA method has been presented previously.[10,15] Therefore, only a brief review is given here. For the chemisorption problem we start with the noninteracting subsystems A (for adsorbate) and M (for metal) which are described by their first-order density matrices, R^A and R^M, respectively. Our goal is to determine the self-consistent density matrix, R, for the entire system after the coupling between the hydrogen atom and the metal chain has been switched on. Let us call R_0 the combined density matrix for the noninteracting subsystems. Since the atomic orbitals are assumed to be orthogonal in the AN model, R_0 is just the direct sum $R^A + R^M$ of the two unperturbed density matrices.

In addition to the density matrices one must also know the unperturbed Hamiltonian matrices, h^A and h^M, each of which is a sum of occupied and unoccupied blocks, e.g., $h^A = R^A h^A R^A + (1^A - R^A) h^A (1^A - R^A)$, corresponding to the converged self-consistent solution for the independent subsystem. As in the case of the density matrix, the total zeroth-order Hamiltonian is $h_0 = h^A + h^M = R_0 h_0 R_0 + (1 - R_0) h_0 (1 - R_0)$.

After the interaction is switched on new terms will appear in the Hamiltonian matrix coupling the original occupied and unoccupied blocks. In the view, the final HF solution is found by diagonalizing the self-consistent Hamiltonian matrix into blocks corresponding to the new occupied and unoccupied spaces. It is useful to think of R and $U \equiv 1 - R$ as the respective projectors for these two spaces.

A fundamental property of the first-order HF density matrix is its idempotency,[14] i.e., $R^2 = R$. This condition plus the relation $\mathrm{tr}(R) = N$—where N is the total number of electrons in the combined system—assure both the representability of the density matrix in terms of an N electron (single determinant) wave function and charge conservation. In order to correctly describe the transfer of charge to and from the surface complex, these conditions have to be maintained for the entire system.

We define the local space as the set of atomic orbitals $|i\rangle$ which span the region where the effect due to the interaction will be most felt. In other words, these orbitals describe the surface complex (SC) formed by chemisorption. The corresponding projector (S is the overlap matrix)

$$\hat{Q} = \sum_{i,j \in \mathrm{SC}} |i\rangle (S^{-1})_{ij} < j| = \sum_{i \in \mathrm{SC}} |i\rangle\langle i|$$

plays a fundamental role in our treatment.

After the first self-consistent cycle the current density matrix, $R^{(1)}$, can be written in the general form:[14]

$$R^{(1)} = R_0 + \Delta R^{(1)} = (R_0 + v)(1 + v^\dagger v)^{-1}(R_0 + v^\dagger) , \qquad (1)$$

in which $v = U_0 X R_0$ and X is an arbitrary symmetric matrix that is ultimately determined by the stationary condition on the energy. It has been shown[10] that $\Delta R^{(1)}$ cannot be confined to the local space if the idempotency condition is to be satisfied. Hence, in the LSA we assume instead that X is confined to the local space, i.e., $X \simeq QXQ = X_Q$. Here Q is the matrix representation of $\hat{Q}$. Note that v still extends over the entire system due to the R_0 and U_0 projectors on either side of X_Q. Consequently, $\Delta R^{(1)}$ extends over the entire system as it must. Although arguments can be given to justify the LSA the most convincing rationale comes from actual calculations such as those presented here. It turns out that replacing X by X_Q reduces the HF problem to the dimension of the local space while self-consistent readjustments of charge remain possible over the entire interacting system.

In order to conveniently compute the updated density matrix we introduce the set of auxiliary matrices $(\sigma^R)_Q$, $(\sigma^{RU})_Q$, etc. defined such that

$$\Delta R = R_0(\sigma^R)_Q R_0 + R_0(\sigma^{RU})_Q U_0 + U_0(\sigma^{UR})_Q R_0 + U_0(\sigma^U)_Q U_0 \tag{2}$$

in which[15]

$$(\sigma^R)_Q = -(\sigma^{RU})_Q (U_0)_Q X_Q, \quad (\sigma^U)_Q = X_Q (R_0)_Q (\sigma^{RU})_Q \tag{3a}$$

and

$$(\sigma^{RU})_Q = X_Q[1_Q + (U_0)_Q X_Q (R_0)_Q X_Q]^{-1} = (\sigma^{UR})_Q^\dagger . \tag{3b}$$

Thus, once X_Q is obtained ΔR is readily evaluated and subsequent iterations may be treated similarly. The cumulative change in the density matrix, ΔR_T, is given by

$$\Delta R_T = R_0(\tau^R)_Q R_0 + R_0(\tau^{RU})_Q U_0 + U_0(\tau^{UR})_Q R_0 + U_0(\tau^U)_Q U_0 , \tag{4}$$

where each τ_Q is obtained by summing the corresponding σ_Q matrices over all iterations. Following this procedure we can relate all changes in the electronic structure due to the interaction between the adsorbate and the metal to the initial density matrix R_0.

The entire process is driven by successive optimizations of the matrix X_Q using the HF stationary condition on the energy which may be written as

$$\delta E = 2\,\mathrm{tr}[h(R)\delta R] = 0 , \tag{5}$$

where δR is a deviation from the exact density matrix and h is the effective one-electron Hamiltonian for the complete system. For idempotent linear variations [see Eq. (1)] $\delta R = RXU + UXR$. Using the LSA and the cyclic properties of the trace, one can express the above relation as

$$\delta E = 0 = 2\,\mathrm{tr}[(UhR + RhU)_Q X_Q] \tag{6a}$$

or, equivalently (since X_Q is arbitrary),

$$(UhR + RhU)_Q = 0 . \tag{6b}$$

Note the natural way in which the HF problem is projected onto the local space, even though the matrix $UhR + RhU$ remains nonlocal. In addition to R itself both h and U are functions of the density matrix. Since $R = R_0 + \Delta R_T$ the stationary condition (6b) depends upon X_Q, in a complicated manner, through Eqs. (2)–(4).

In previous papers[10,15] we have solved a linearized version of Eq. (6b) for X_Q. Sometimes, however, this procedure leads to a local energy minimum.[10] In order to ensure a global minimum and obtain the most rapid convergence it is preferable to employ the following two-step method. First, the system is driven to form the strongest bond possible between the adsorbate and the surface metal atom. That is done by choosing an X_Q which has unit elements in the bond positions and is zero everywhere else. The same X_Q is applied repeatedly[21] until the density matrix is no longer affected. Then, from this new starting point the method of conjugate directions[22] leads to the absolute minimum.

As discussed in Ref. 10 the chemisorption energy, ΔE, is calculated from

$$\Delta E = \mathrm{tr}(\{R_0[h(R_0)+h(R)]R_0\}_Q(\tau^R)_Q + \{U_0[h(R_0)+h(R)]R_0\}_Q(\tau^{RU})_Q + \{R_0[h(R_0)+h(R)]U_0\}_Q(\tau^{UR})_Q + \{U_0[h(R_0)+h(R)]U_0\}_Q(\tau^U)_Q) . \tag{7}$$

Clearly, once the self-consistent τ_Q matrices are known then ΔE can be evaluated by summing over just the local space.

Information about the electronic structure of the surface complex is contained in R_Q, the projected charge and bond order matrix. The diagonal element $(R_Q)_{ii}$ is the charge associated with the ith orbital of the surface complex, while $(R_Q)_{ij}$ is a measure of the bonding interaction between the orbitals i and j. Clearly the difference $\Delta n_{\mathrm{SC}} = \mathrm{tr}(R - R_0)_Q$ is the total amount of electronic charge transferred to the surface complex from the rest of the system due to the interaction.

One can carry this analysis a step further by diagonalizing R_Q. The resulting eigenvectors represent[23] localized orbitals of the surface complex which best approximate localized orbitals of the extended system. The corresponding eigenvalues give the (partial) occupancies of these surface complex orbitals; an eigenvalue equal to unity indicates a surface state.

III. CHARACTERIZATION OF A NONINTERACTING SYSTEM

We will consider here the chemisorption of a hydrogen atom onto a semi-infinite one-dimensional chain of transition-metal atoms. For this system the spin-polarized AN Hamiltonian can be written as

$$h = \sum_{\sigma} |\phi_{a\sigma}\rangle(\varepsilon_a + JR_{a-\sigma,a-\sigma})\langle\phi_{a\sigma}| + \sum_{k,\sigma} |\psi_{k\sigma}\rangle\varepsilon_{k\sigma}\langle\psi_{k\sigma}| + \sum_{\sigma}(|\phi_{a\sigma}\rangle V_{as}\langle\phi_{s\sigma}| + |\phi_{s\sigma}\rangle V_{as}\langle\phi_{a\sigma}|) , \tag{8}$$

where $\phi_{a\sigma}$ is the free adsorbate (i.e., hydrogen atom) atomic orbital of spin σ. $\psi_{k\sigma}$ is a pure metal eigenfunction; $\phi_{s\sigma}$ is the atomic orbital of the "surface" substrate atom which couples to the adsorbate; and V_{as} is the adsorbate-substrate interaction constant. The remaining metal atoms are involved in bonding to the adsorbate only indirectly. In Eq. (8), $\varepsilon_a = -13.6$ eV corresponds to the ionization potential of hydrogen and electron repulsion is included explicitly just for electrons of opposite spin on the adsorbate. The effect of the Coulomb potential $JR_{a-\sigma,a-\sigma}$ is to prevent an excess transfer of charge from the metal band to the adsorbate.[17] In the present case $J = 12.9$ eV which is the difference between the ionization potential and electron affinity of the hydrogen atom.

The term in Eq. (8) containing a sum over k introduces the dependence on the characteristics of the metal band. In order to compare with our previous results[10] we parametrize the semi-infinite chain to represent a tungsten surface. As a good approximation, then, the metal band is assumed to be half occupied with a total d-band width of 10 eV. The Fermi level is at -4.6 eV,[10,24] and the substrate is taken to be initially in a nonmagnetic state ($\varepsilon_{k\alpha}=\varepsilon_{k\beta}=\varepsilon_k$). Chemisorption induces spin polarization of the metal substrate as we will see shortly.

We seek the unrestricted HF solution for the AN Hamiltonian taking

$$(R_0)_{a\alpha,a\alpha}=1,\ (R_0)_{a\beta,a\beta}=0 \ . \tag{9}$$

Since $\phi_{a\sigma}$ is assumed to be orthogonal to all metal orbitals

$$R_0=R^A+R^M=|\phi_{a\alpha}\rangle\langle\phi_{a\alpha}|+\sum_{k,\sigma(\text{occ})}|\psi_{k\sigma}\rangle\langle\psi_{k\sigma}| \ . \tag{10}$$

In order to carry out the LSA treatment the density matrix of the metal must be transformed to a site representation. For this purpose we consider an infinite chain described by a tight-binding Hamiltonian with one orbital per site,

$$h^{\infty}=\sum_{i=-\infty}^{+\infty}|\phi_i\rangle\varepsilon_M\langle\phi_i|+|\phi_i\rangle V_M\langle\phi_{i+1}|+\text{H.c.} \tag{11}$$

Here ε_M is the self-energy of the atomic orbitals in the metal chain and V_M is the nearest-neighbor coupling. Following Kalkstein and Soven[25] the semi-infinite chain is imagined to result from slicing the entire chain in half. For consistency with the AN Hamiltonian no charge readjustment is considered at this stage. Thus, metal atoms in the surface region have the same charge as metal atoms in the bulk as we will see later.

The electronic structure of the semi-infinite chain, with Hamiltonian $h^{\infty/2}$, may be derived from a knowledge of the spectrum of the operator

$$G(\varepsilon)=(\varepsilon-h^{\infty/2})^{-1} \tag{12}$$

in the site representation. This spectrum is determined by means of the transfer-matrix (TM) method[26] which has proved to be very convenient for studying electronic structure of one-dimensional systems. The TM method takes advantage of the translational properties of the system by defining a transfer function

$$T(\varepsilon)=\frac{G_{i,j}(\varepsilon)}{G_{i,j-1}(\varepsilon)} \tag{13}$$

which can be used to decouple the set of equations obtained when one projects Eq. (12) in the site representation.[27] Thus, one can readily find any desired element $G_{ij}(\varepsilon)$ and, from

$$R_{ij}=-(1/\pi)\int^{\varepsilon_F}\text{Im}G_{ij}(\varepsilon)d\varepsilon \ , \tag{14}$$

the elements of the density matrix for the semi-infinite chain. It is easy to show that for the present model

$$R_{ij}=\begin{cases}\dfrac{1}{2}, & i=j\\ 0, & i-j \text{ even}\\ \dfrac{(-1)^{(i-j+3)/2}}{\pi}\dfrac{1}{i-j}+\dfrac{(-1)^j}{i+j+2}, & i-j \text{ odd}\end{cases} \tag{15}$$

where $i,j=0,1,2,\ldots$. Using the above values of R_{ij} together with $h_0=h^{\infty/2}$ it is straightforward to obtain the required matrices $(R_0h_0R_0)_Q$ and $(U_0h_0U_0)_Q$ for the semi-infinite chain. In order to reproduce the correct d-band width we take the coupling $V_M=-2.5$ eV; ε_F, of course, is the Fermi energy of -4.6 eV.

Once the coupling, V_{as}, between the hydrogen atom and the substrate is switched on, the system is perturbed and, after relaxation, will reach a new stationary state corresponding to the adsorbate chemisorbed on the metal chain. Since electron repulsion on the adsorbate is included explicitly in the AN Hamiltonian we must update this Hamiltonian after each self-consistent iteration by substituting into Eq. (8) the current values of the spin occupancies of the adsorbate orbital.

Since the variation of R is subject to the idempotency constraint, self-consistent readjustments will occur not just for $R_{a\sigma,a\sigma}$ but for *all* elements of the density matrix. This is the essential feature of the LSA method which makes it different from the usual embedding techniques. In the latter there is no simple way of accounting for relaxation of electronic charge beyond the surface complex. Furthermore, with the LSA method the usually tedious step of recalculating the Fermi level for the extended system is avoided; the idempotency condition (and charge conservation) automatically ensure that the proper number of energy levels are occupied.

IV. RESULTS

Chemisorption of a hydrogen atom will induce both charge and spin polarization in the metal substrate. In this connection, it is convenient to define

$$n_i=R_{ii}^{\alpha}+R_{ii}^{\beta}$$

and (16)

$$\mu_i=R_{ii}^{\alpha}-R_{ii}^{\beta}$$

as the charge and magnetic moment of atom i, respectively. We will examine the fluctuation of these quantities along the chain as a function of the number of metal atoms in the local space N_M.

First, the convergence of the binding energy and the atomic charges was investigated for a fixed coupling parameter $V_{as}=-4.156$ eV. This is the value of V_{as} which, for the largest N_M used (i.e., $N_M=8$), leads to a binding energy in agreement with the experimental value of 3.0 eV for hydrogen chemisorption on W(100).[28] We present in Table I the binding energy and atomic charges for $N_M\leq 8$. There is, clearly, significant electronic charge transfer from the metal to the hydrogen atom which increases with the dimension of the local space. Between $N_M=1$ and $N_M=8$ the net charge on hydrogen goes from $0.129e$ to $0.181e$ while the corresponding change in the

TABLE I. Variation of the binding energy (ΔE_b) as well as the electronic charge on hydrogen (n_{H}) and on the first seven atoms of the metal chain ($n_1, \ldots, n_7$) as a function of the number of metal atoms included in the local space (N_M). The energies are in eV; the charges in units of e. $\Delta n_{\mathrm{SC}} = \mathrm{tr}(R - R_0)_Q$ is the net amount of electronic charge transferred to the surface complex from the surrounding metal. The adsorbate-surface coupling is $V_{as} = -4.156$ eV; the Fermi level of the metal is at -4.6 eV; and the total d-band width is 10 eV.

N_M	ΔE_b	n_{H}	n_1	n_2	n_3	n_4	n_5	n_6	n_7	Δn_{SC}
1	2.560	1.129	0.959	0.936	1.000	0.990	1.000	0.996	1.000	0.089
2	2.776	1.156	0.937	0.985	0.975	0.979	0.999	0.991	1.000	0.078
3	2.869	1.164	0.922	1.000	0.981	0.963	0.997	0.992	0.999	0.067
4	2.924	1.170	0.917	1.013	0.980	0.987	0.977	0.988	0.997	0.066
5	2.957	1.174	0.912	1.019	0.978	0.993	0.988	0.974	0.996	0.064
6	2.980	1.177	0.909	1.025	0.976	0.999	0.988	0.989	0.983	0.062
7	2.995	1.179	0.906	1.029	0.974	1.002	0.987	0.992	0.991	0.061
8	3.013	1.181	0.903	1.033	0.973	1.006	0.986	0.996	0.991	0.059
∞ [a]	3.107	1.192	0.890							0.053

[a] Asymptotic values were obtained by extrapolation using Eq. (17) as discussed in text. The result given is the average of separate calculations on the even and odd series.

binding energy, ΔE_b, is 0.453 eV. As we have found previously,[10] for $N_M = 1$ the excess electronic charge on hydrogen comes primarily from beyond the neighboring metal atom. On the other hand, as the surface complex is enlarged the subsequent increase in negative charge on hydrogen is almost exactly balanced by a decrease on the first metal atom. The latter atom contributes a little over half the excess negative charge on hydrogen in the limit $N_M \rightarrow \infty$ which is obtained in the manner described below. Along the chain successive substrate atoms follow a pattern of alternating increase and depletion of charge reminiscent of Friedel oscillations.[29]

The atomic charges on the local space and the binding energy of the adsorbate vary monotonically with N_M, although there are two slightly different series (see below) depending upon whether N_M is even or odd. We have extrapolated these quantities to $N_M = \infty$ using a least-squares fit to the power series:

$$f(N_M) = a + \frac{b}{(N_M)^1} + \frac{c}{(N_M)^2} . \tag{17}$$

For even N_M the limiting values are $\Delta E_b = 3.111$ eV, $n_{\mathrm{H}} = 1.193e$, and $n_1 = 0.887e$. As a measure of the extrapolation error we may compare the corresponding results for odd N_M: $\Delta E_b = 3.102$ eV, $n_{\mathrm{H}} = 1.190e$, and $n_1 = 0.893$. In Table I we list the average values which should be correct[30] to about ± 0.014 eV in the energy and $\pm 0.009e$ in the number of electrons. This accuracy is certainly suitable for most purposes. Of course, the convergence properties for a three-dimensional substrate remain to be established but we are hopeful that a surface complex containing roughly the same number of atoms will show a similar degree of convergence.

Note that the net charge on the surface complex, Δn_{SC}, differs from zero even for an infinite local space. This difference is well beyond the estimated[30] extrapolation error and we will also see later on that an analogous, but even larger, effect occurs for spin polarization. So there is evidently some charge transfer across the boundary due to the LSA. In Table I a changing pattern in the calculated charge on a given atom is observed as one crosses over the dashed lines which represent the boundary between the local space and the remaining substrate. Within the local space, however, the variation of atomic charge with N_M is well behaved. Furthermore, for a given N_M these charges are virtually identical to those obtained by a cluster model calculation (using a much larger number of atoms) that will be discussed later.

It should be noted that the atomic charges outside the surface complex are determined by the LSA—through Eq. (4)—even though they do not appear directly in the treatment. We verified that charge is conserved for the entire system, as it must be, by going further into the bulk for $N_M = 7$. Contributions from the next 22 atoms (to make a total of 30 in the local space) reduces the total charge from $0.0608e$ to $0.0099e$; including the next set of 30 atoms reduces this figure further to $0.0050e$. Thus, the correct value of zero is being approached although the charge density wave persists for a long distance into the substrate.

Spin polarization behaves like charge polarization except that most aspects are exaggerated. The atomic magnetic moments in Table II, for example, converge much more slowly than the atomic charges as the size of the surface complex increases. Likewise, the spin oscillations are much larger than the charge oscillations. We have found[15] in previous (unrestricted HF) studies on closed shell systems that the LSA induces a small anomalous spin polarization. However, the effects seen here are of much larger magnitude and arise as a consequence of the Hamiltonian used (see also below).

An examination of the net magnetic moment for the surface complex, $\Delta\mu_{\mathrm{SC}}$, reveals that there are two different series of values depending upon the parity of N_M. (It was this observation that led us to do the separate even and odd N_M extrapolations described above.) Nonetheless both series lead to the same limit for $\Delta\mu_{\mathrm{SC}}$ within $0.002e$. The magnetic moment on the surface metal atom, i.e., μ_1, does not behave monotonically for odd N_M. Therefore, it

TABLE II. Variation of the magnetic moment on hydrogen (μ_H) and on the first seven atoms of the metal chain ($\mu_1, \ldots, \mu_7$) as a function of the number of metal atoms in the local space (N_M). The magnetic moments are in units of e and $\Delta\mu_{SC}$ is the net moment on the surface complex. See Table I caption for parameters used.

N_M	μ_H	μ_1	μ_2	μ_3	μ_4	μ_5	μ_6	μ_7	$\Delta\mu_{SC}$
1	0.604	−0.186	0.419	0.000	0.067	0.000	0.028	0.000	0.418
2	0.493	−0.188	0.283	0.114	0.120	0.006	0.050	0.001	0.587
3	0.436	−0.192	0.241	−0.016	0.245	0.013	0.080	0.003	0.470
4	0.402	−0.184	0.211	−0.031	0.164	0.080	0.106	0.009	0.562
5	0.377	−0.179	0.193	−0.040	0.146	0.007	0.180	0.015	0.503
6	0.355	−0.173	0.177	−0.043	0.129	−0.004	0.121	0.069	0.563
7	0.340	−0.168	0.166	−0.045	0.120	−0.013	0.110	0.014	0.525
8	0.322	−0.162	0.154	−0.045	0.110	−0.016	0.097	0.005	0.564
∞ [a]	0.239	−0.136[b]							0.576

[a] Asymptotic results for μ_H, μ_1, and $\Delta\mu_{SC}$ were found by extrapolation using Eq. (17) as discussed in text. The value given is the average of separate calculations on the N_M odd and even series. For μ_H the two extrapolations differ by $0.036e$; for μ_1 they differ by $0.017e$ (see also footnote b); for $\Delta\mu_{SC}$ by $0.002e$. In order to leave a margin for safety one should multiply these differences by 1.5 to establish the error bounds.

[b] Since the sum $\mu_H+\mu_1$ is better behaved than μ_1 itself we extrapolated the former to obtain the tabulated result.

turns out to be preferable to extrapolate the sum $\mu_H+\mu_1$ instead of μ_1 itself. The error bounds on the magnetic moments, which are reported in a footnote to Table II, are substantially broader than those for the corresponding charges.

As expected[17] the spin-density wave penetrates considerably further into the substrate than the charge density wave. We have previously mentioned calculations where the density matrix outside the local space was determined. In these calculations it was found that, for the first 30 atoms, the net charge in the surface region is $0.01e$. On the other hand the magnetic moment is only $0.91e$ and, therefore, the residual spin density in the surrounding substrate ($0.09e$) is 9 times larger than the charge density.

For comparison purposes we did a series of finite-cluster calculations using the AN Hamiltonian with the same parameters as above. In order to correspond with the local space treatment only clusters with an even number of metal atoms were considered. In Table III we present values of the binding energies, atomic charges and magnetic moments for a hydrogen atom interacting with a 2, 4, 6, 10, and 20 atom finite metal chain. The same *general* behavior of the atomic charges and magnetic moments is observed with or without embedding. Spin polarization effects are once again more pronounced confirming the earlier suggestion that they must be inherent to the model. Note, in particular, that the nonmonotonic behavior of μ_1 is again present. However, the rate of convergence is much slower for the cluster calculations; roughly twice as many atoms are needed to reproduce a given local space treatment. In fact, the cluster calculation for $N_M=20$ yields essentially identical results[31] to those obtained with the LSA for $N_M=8$. The slower convergence in the case of an isolated cluster is a consequence of the fact that the charge and spin disturbances introduced by chemisorption have to be damped over a much shorter range than in an embedded cluster.

We have also determined the effect of the adsorbate on the ionization potential of the metal. This was done by employing the same Hamiltonian and parameters to treat the chemisorption of H^+ (and, for comparison, H^-) on tungsten. From another point of view, after self-consistent charge readjustment this system may be described as the ion which results when an electron is re-

TABLE III. Finite-cluster calculations for chemisorption of atomic hydrogen on a tungsten linear chain containing N_M metal atoms. All other symbols, units, and parameter values are as given in the captions of Tables I and II.

N_M	ΔE_b	n_H (μ_H)	n_1 (μ_1)	n_2 (μ_2)	n_3 (μ_3)	n_4 (μ_4)	n_5 (μ_5)	n_6 (μ_6)
2	2.358	1.114 (0.665)	0.973 (−0.162)	0.913 (0.497)				
4	2.648	1.142 (0.557)	0.950 (−0.194)	0.963 (0.360)	0.996 (−0.022)	0.950 (0.300)		
6	2.776	1.155 (0.495)	0.936 (−0.198)	0.987 (0.295)	0.990 (−0.037)	0.969 (0.234)	0.998 (−0.007)	0.965 (0.218)
10	2.899	1.168 (0.419)	0.921 (−0.190)	1.011 (0.228)	0.982 (−0.048)	0.988 (0.172)	0.994 (−0.018)	0.982 (0.155)
20	3.011	1.181 (0.326)	0.904 (−0.164)	1.034 (0.157)	0.973 (−0.048)	1.007 (0.112)	0.987 (−0.025)	0.999 (0.098)

TABLE IV. Binding energy and atomic charges for chemisorption of a proton on a neutral metal chain as a function of the number of metal atoms in the local space. The binding energy is measured with respect to a neutral hydrogen atom and a charged metal surface. Otherwise all symbols, units, and parameter values are as defined in Table I.

N_M	ΔE_b^+	$n_{\rm H}$	n_1	n_2	n_3	n_4	n_5	n_6	n_7	$\Delta n_{\rm SC}^+$
1	1.755	1.080	0.805	0.362	1.000	0.898	1.000	0.958	1.000	0.885
2	2.412	1.140	0.837	0.730	0.726	0.836	0.984	0.932	0.996	0.706
3	2.593	1.154	0.848	0.809	0.926	0.616	0.978	0.908	0.994	0.738
4	2.723	1.164	0.855	0.872	0.940	0.812	0.804	0.876	0.980	0.644
5	2.786	1.169	0.859	0.900	0.948	0.849	0.946	0.732	0.972	0.670
6	2.843	1.173	0.862	0.928	0.951	0.884	0.956	0.854	0.846	0.609
7	2.875	1.176	0.864	0.942	0.953	0.901	0.966	0.876	0.954	0.631
8	2.911	1.179	0.866	0.958	0.954	0.919	0.968	0.901	0.963	0.587
∞ [a]	3.109	1.194	0.877							0.525

[a] Limiting values were obtained by extrapolation using Eq. (17) as described in the text and taking the average of the even and odd series. For ΔE_b^+ the two extrapolations differ by 0.024 eV; for $n_{\rm H}$ they differ by $0.002e$; for n_1 by $0.001e$; for $\Delta n_{\rm SC}^+$ by $0.021e$. In order to leave a margin for safety one should multiply these differences by 1.5 to establish the error bounds.

moved from a one-dimensional metal containing an adsorbed hydrogen atom. From the change in binding energy for ionic versus neutral adsorption one obtains the ionization potential of the metal with the adsorbate present. In general, there will be a change from the bare metal value due to the influence of the adsorbate on the surface dipole.

In Tables IV and V we present the results for H^+ and H^-, respectively. Note that the self-consistent treatment redistributes the initial charge so that $n_{\rm H}$ and n_1 are the same within extrapolation error[32] for H^+, H^-, and neutral adsorption. Plots of charge differences indicate that this is true of all atoms within the local space except that in H^- the charge oscillation might be slightly larger than the other two cases. Thus, for ionic adsorption, the excess positive or negative charge is completely delocalized.

It is convenient to measure the binding energy $\Delta E_b^\pm$ of the ion with respect to a separated neutral hydrogen atom and the appropriate charged metal surface. That is to say,

$$\Delta E_b^+ = \delta E^+ - \varepsilon_F + \varepsilon_a \tag{18}$$

and

$$\Delta E_b^- = \delta E^- + \varepsilon_F - \varepsilon_a - J \; , \tag{19}$$

where $\delta E^\pm$ is the electronic binding energy with respect to H^+ or H^- and the neutral metal surface. The energy difference $\Delta E_b - \Delta E_b^+$ is equal to the change in the ionization potential of the metal due to chemisorption. For the case at hand we find an insignificant change of 0.002 eV. The extrapolation errors are such that any value greater than 0.04—0.05 eV would be meaningful and this figure could be reduced by considering larger local spaces. Our result is reasonable but the model is too crude to permit a comparison with experiment especially in view of the fact that work function changes are very sensitive to surface structure.[33] The small change of 0.022 eV calculated for the electron affinity is consistent with that obtained for the ionization potential.

The degree to which the interaction between the adsor-

TABLE V. Binding energy and atomic charges for chemisorption of H^- on a neutral metal chain as a function of the number of metal atoms in the local space. The binding energy is measured with respect to a neutral hydrogen atom and a charged metal surface. Otherwise all symbols, units, and parameter values are as defined in Table I.

N_M	ΔE_b^-	$n_{\rm H}$	n_1	n_2	n_3	n_4	n_5	n_6	n_7	$\Delta n_{\rm SC}^-$
1	2.306	1.294	0.948	1.546	1.000	1.088	1.000	1.036	1.000	−0.758
2	2.690	1.246	0.924	1.299	1.188	1.130	1.010	1.054	1.002	−0.532
3	2.816	1.234	0.908	1.240	1.009	1.302	1.018	1.084	1.004	−0.609
4	2.896	1.226	0.902	1.198	0.991	1.178	1.134	1.096	1.020	−0.505
5	2.935	1.221	0.898	1.178	0.979	1.154	1.018	1.208	1.022	−0.550
6	2.969	1.218	0.895	1.160	0.975	1.132	1.005	1.131	1.104	−0.484
7	2.991	1.215	0.893	1.148	0.971	1.120	0.995	1.116	1.020	−0.520
8	3.010	1.213	0.892	1.138	0.969	1.109	0.991	1.101	1.010	−0.472
∞ [a]	3.129	1.201	0.881							−0.433

[a] Limiting values were obtained by extrapolation using Eq. (17) as described in the text and taking the average of the even and odd series. For ΔE_b^- the two extrapolations differ by 0.002 eV; for $n_{\rm H}$ they differ by $0.002e$; for n_1 by less than $0.001e$; for $\Delta n_{\rm SC}^-$ by $0.016e$. In order to leave a margin for safety one should multiply these differences by 1.5 to establish the error bounds.

bate and the metal chain gives rise to a localized surface complex can be put on a quantitative basis if one diagonalizes R_Q. Each eigenvector represents a localized orbital of the surface complex and the corresponding eigenvalue (between 0 and 1) gives the occupancy of that orbital. We have noted before[10] that one of the eigenvalues will always be unity. This is a consequence of the trapping of the occupied state originally associated with the hydrogen atom and it is due to the special form of the AN Hamiltonian. By the same token there will also be a trapped state of opposite spin which has zero occupancy. In addition, for every local space the occupancy of some of the orbitals will differ substantially from zero or unity. The freedom to have orbitals of the surface complex partially occupied is a major factor in the success of the LSA.

Besides the trapped state there may be others characterized by an eigenvalue essentially equal to unity[34] thereby identifying a candidate for a localized surface state. Such a state must, subsequently, prove to be an eigenfunction of the Hamiltonian as well. We find that as the dimension of the local space increases a second completely occupied orbital occurs, for the first time, at $N_M=3$. Its spin is opposite to that of the trapped state. When N_M is increased further more of these states appear. They are most often localized in the metal but they may also be adsorbate induced as indicated by a substantial contribution from the hydrogen atomic orbital.

Surface spectroscopy techniques are able to determine the existence and location of adsorbate-induced surface states. For instance, Plummer's[35] ultraviolet photoemission spectroscopy (UPS) measurement of saturated hydrogen chemisorption on tungsten (100) reveal two difference peaks due to the adsorbate at 1.6 and 4.7 eV below ε_F. On the other hand, angle-resolved photoemission studies[36] show three bands centered at 2, 6, and 12 eV below the Fermi level. Although the interpretation of these experiments may be difficult it is evident that the information of interest is present.

There have been numerous theoretical treatments of the effect of chemisorption on the surface density of states and, hence, on the UPS spectrum. An excellent review has been given by Muscat and Newns.[37] We also mention here the work of Anda and Ure[38] which explicitly takes into account adatom-plasmon interactions. Our approach to the calculation of adsorbate-induced surface states is straightforward. Let us denote the projector for the completely occupied local space states by G. Then the eigenvalues of GhG correspond to surface-state energies and the eigenvectors to surface state orbitals, ϕ_g, provided the Hamiltonian is block diagonal so that $gH(Q-g)=0=(Q-g)Hg$, where $g=|\phi_g\rangle\langle\phi_g|$. Of the true surface states, we have identified two as being adsorbate induced using the criterion that the magnitude of the hydrogen atomic orbital coefficient remains substantial (in both cases >0.4) as N_M increases. For chemisorption of a neutral hydrogen atom one of the two is the trapped state which describes, essentially, a diatomic molecule comprised of hydrogen and the first substrate atom. The other has the opposite spin and is more extended with a significant component on the second, third, and even the fourth metal atom.

In Table VI the orbital coefficients and the energy of the adsorbate-induced surface states are given as a function of N_M. We also present the norm of $gH(Q-g)$ which must vanish if ϕ_g is an eigenfunction of the entire system. From the convergence of the norm with increasing N_M and the fall-off in the coefficient as one goes deeper into the substrate we conclude that the orbitals listed represent true surface states. In the case of β spin an obvious discontinuity in the coefficients occurs at $N_M=6$ and, to a lesser extent, at $N_M=8$ owing to the introduction of a second and a third fully occupied state. The energy behaves more smoothly as do the coefficients for α spin despite the fact that, in the latter case, new fully oc-

TABLE VI. Adsorbate-induced surface states due to chemisorption of a neutral hydrogen atom as a function of the number of metal atoms in the local space, N_M. ε is the energy level with respect to ε_F; the norm refers to the projected Hamiltonian matrix $gH(Q-g)$; C_i is the coefficient of the ith metal orbital (C_H is the coefficient of hydrogen orbital) in the expansion of the corresponding state function. The majority spin is α; the minority spin β. All parameters are the same as in Table I; ε and the norm of $gH(Q-g)$ are in eV.

Spin	N_M	ε	C_H	C_1	C_2	C_3	C_4	C_5	C_6	Norm
α	1	−7.79	0.906	0.423						
	2	−7.34	0.855	0.506	0.119					0.434
	3	−7.10	0.825	0.537	0.172	0.034				0.305
	4	−6.96	0.806	0.553	0.205	0.060	0.010			0.186
	5	−6.85	0.780	0.564	0.247	0.103	0.036	0.008		0.054
	6	−6.76	0.772	0.570	0.254	0.111	0.044	0.014	0.003	0.037
	7	−6.69	0.767	0.573	0.259	0.116	0.049	0.018	0.005	0.013
	8	−6.62	0.761	0.577	0.263	0.120	0.055	0.025	0.010	0.010
β	3	−4.62	0.532	0.725	0.415	0.137				0.504
	4	−4.76	0.517	0.705	0.442	0.195	0.048			0.448
	5	−4.85	0.506	0.688	0.457	0.234	0.084	0.017		0.372
	6	−4.99	0.411	0.591	0.505	0.390	0.246	0.113	0.030	0.214
	7	−5.01	0.410	0.582	0.495	0.392	0.267	0.144	0.055	0.184
	8	−5.04	0.411	0.576	0.488	0.392	0.277	0.161	0.072	0.117

cupied states appear at $N_M=5$ and $N_M=8$. Due to the simplicity of the model used in this work and problems of interpreting the UPS spectra (which include, for example the effect of lateral interactions) we make no attempt at this time to correlate theory with experiment. But we do call attention to the fact that within the LSA method it is a simple matter to predict the existence of adsorbate-induced surface states, to obtain their positions, and to determine the corresponding state functions.

V. COMPARISON WITH ALTERNATIVE EMBEDDING TREATMENT

The most important feature of the LSA is that it allows self-consistent charge and spin-density readjustments over the entire system after introduction of a localized perturbation. This occurs even in the Anderson-Newns model because of the idempotency condition on the total density matrix. It is of interest to compare our results to those of earlier embedding treatments in which charge and spin readjustments are allowed only in a more local region. Consider, for example, a calculation using the same AN Hamiltonian but with just the hydrogen atom electronic charge adjusted self-consistently. This is akin to the cluster Bethe lattice treatments of chemisorption on two-dimensional substrates,[8,39,40] wherein the contribution to the chemisorption energy arising from atomic orbitals located outside the surface complex is neglected. Within this approximation a single transfer function, $T(\varepsilon)$, can be introduced and one can obtain the Green's function for the adsorbate as

$$G_{aa}(\varepsilon)=\frac{(\varepsilon-\varepsilon_M)-V_M T}{(\varepsilon-\varepsilon_a)[(\varepsilon-\varepsilon_M)-V_M T]-(V_{as})^2}\,, \qquad (20)$$

where

$$T(\varepsilon)=\frac{(\varepsilon-\varepsilon_M)\pm[(\varepsilon-\varepsilon_M)^2-4(V_M)^2]^{1/2}}{2V_M}\,. \qquad (21)$$

Two contributions to the occupancy of the adsorbate orbital arise from Eq. (20). The first one, associated with the pole of G_{aa}, comes from the localized atomic state below the band. The other, related to the tail of the imaginary part of G_{aa} within the band, is due to delocalized states. Assuming that the Fermi level is invariant, the binding energy can be computed by including contributions from all the atoms which adjust their populations[8,19] during the self-consistency process (in this case only the hydrogen atom).

If the same parameters are used as in the LSA treatment, a second localized state appears and unreasonable results are obtained particularly for the binding energy. So we chose instead, after some trial and error, to take the coupling parameter as $V_{as}=-3.757$ eV. In a spin-polarized calculation this value yields good agreement with the extrapolated LSA binding energy (3.119 eV versus 3.107 eV for LSA) and with the charge on hydrogen ($1.181e$ versus $1.192e$ for LSA). However, the net spin on hydrogen is $0.421e$ as compared to the LSA result $\mu_H=0.239e$. Thus, after modifying V_{as}, there remains a significant discrepancy for the magnetic moment on the adsorbate. As far as the substrate is concerned the errors are magnified owing to the constraint of periodicity which is imposed even after chemisorption. For the first metal atom one gets an electronic charge of $0.919e$ and a magnetic moment equal to $-0.215e$ instead of $0.890e$ and $-0.136e$. Of course, this approach could be improved by self-consistently determining the charges of the metal atoms within a given cluster surrounding the adsorbate. However, the larger the cluster the more cumbersome it becomes to determine the occupancy of each orbital in the self-consistent loop.[8] We note that in the LSA method the occupancies of all orbitals are simultaneously readjusted in each self-consistent cycle.

In spite of the simplicity of the model used in this paper we believe that the potential usefulness of the LSA method for the treatment of chemisorption has been revealed. In fact, the AN model probably[41] overestimates charge delocalization and, therefore, constitutes a worse case scenario as far as convergence is concerned. In order to obtain results of reliable accuracy more realistic calculations will have to be carried out. It is important to realize in this connection that our method is not limited to the semiempirical Anderson-Newns Hamiltonian nor, indeed, to the Hartree-Fock approximation. The treatment has been presented[10] in an *ab initio* framework and it has been generalized to include electron correlation according to the $X\alpha$,[10] generalized valence bond,[42] and even CI or coupled cluster[43] methods. As discussed before,[10,15,16] different levels of approximation can be used to describe the local space than the rest of the system. In this vein a long-range program to combine Nesbet's[44] linearized atomic cell orbital band-structure method (which is based on density-functional theory) with any of the various quantum chemical procedures mentioned above has been initiated.

It is easy to envision application of the LSA method to other chemisorption probleme beyond simple atomic adsorption. For example, the method can be used to treat dissociative adsorption; photoionization spectra of chemisorbed molecules; interactions between adsorbed atoms mediated by the substrate. We have already started exploratory work along these lines. For the dissociative chemisorption of H_2 on nickel surfaces a simple cubium description of the substrate is being combined initially with a semiempirical intermediate neglect of differential overlap (INDO) unrestricted Hartree-Fock treatment of H_2 which correctly reproduces the potential energy curve for the isolated molecule. Using a similar approach we are also obtaining shifts in the photoionization spectrum of chemisorbed CO. Once the localized molecular state of interest is identified, the ionization potential can be determined either by Koopmans's theorem or by the ΔE_{SCF} method.

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