PHYSICAL REVIEW B VOLUME 58, NUMBER 8 15 AUGUST 1998-II

Interaction between atoms and surfaces: A bond-pair description based on an extended Anderson model

P. G. Bolcatto
Facultad de Formación Docente en Ciencias and Facultad de Ingeniería Química, Universidad Nacional del Litoral (UNL),
9 de Julio 2655, 3000 Santa Fe, Argentina

E. C. Goldberg and M. C. G. Passeggi
Instituto de Desarrollo Tecnológico para la Industria Química (CONICET-UNL) and Facultad de Bioquímica y Ciencias Biológicas
UNL, P.O. Box 91, 3000 Santa Fe, Argentina

(Received 30 September 1997; revised manuscript received 8 April 1998)

A bond-pair model Hamiltonian developed previously for systems consisting of interacting atoms is applied to describe atom-surface interactions. By proposing a mixed basis set involving localized adatom orbitals $\{\phi_\alpha\}$ and extended surface states $\{\varphi_{\mathbf{k}}\}$, and by application of a mean-field approximation, the Hamiltonian is reduced to the form of the single-particle Anderson model. The resulting model Hamiltonian is free from adjustable parameters. These parameters include both the effects of electronic interactions between the atom and the solid and those arising from the lack of orthogonality between the adsorbate and substrate orbitals. The nonlocal exchange contributions are treated consistently within the Hartree-Fock method, while valencelike and corelike band states are also taken into account. This model is applied to consider the interaction of hydrogen with metals (Al, Li, and Na). The results for chemisorption are in good agreement with those obtained by other theoretical approaches based on either the density functional theory or embedding cluster methods, as well as with existing experimental data. In addition, the calculation of the shifts and widths of the adsorbate levels in an ample range of separation distances are also in good agreement with those obtained by using atomic physics techniques. [S0163-1829(98)10031-0]

I. INTRODUCTION

The description of the effects caused by interactions between atoms or molecules with solid surfaces, that are involved in an ample variety of physical and chemical phenomena, are of great intrinsic interest. Thus different kinds of experiments directed at dealing with processes either of a static or dynamical nature, such as those produced in the adsorption or in the scattering of atoms and ions from metal surfaces, can be understood in terms of the details of the solid surface electronic structure.[1–3] In many cases it is possible to identify whether the dominant effects are caused by substrate factors (such as its local and partial density of state, including the presence of deep-level states), or those due to the adsorbate structure (such as its electronegativity, closed shell structure, etc.), or both. Theoretical efforts have been progressively directed at describing not only the possible adsorption mechanisms[1,4–9] but also at identifying those constituents that may be relevant to account for atom-surface collision processes.[10–13]

Concerning adsorption processes, numerous theoretical attempts based on *ab initio* calculations exist in the literature, the density functional theory[14] (DFT) being the most frequently used method that focuses on the geometry of a single adsorbate interacting with an extended substrate. The local-spin-density approximation[15] (LSDA) for the exchange and correlation is generally adopted in order to obtain a tractable mainframe description of the adatom-jellium interacting system. Although it has been pointed out that by using the LSDA one can expect very accurate predictions for equilibrium distances and vibration frequencies, this has not been the case when binding energies are concerned, which are overestimated in general.[15,16] It has been also suggested that the main source of inaccuracy in the LSDA is due to an inappropriate treatment of the exchange potential.[16] Several authors[17–20] indicated that is necessary to depart from the LSDA because of abrupt changes in the electronic density that occur at the interface region. Actually, better results can be obtained by going beyond the LSDA to take into account nonlocal exchange-correlation terms, such as in the generalized gradient approximation[21] (GGA). Thus quantitative results for the adsorption processes are clearly improved. Cluster methods[22–24] appear as an alternative approximation to the DFT picture. These prominent molecular-physics-based approaches involve the use of the Hartree-Fock (HF) self-consistent approximation (with the open possibility of adding perturbative corrections to the correlation effects), and lead in general to results that are strongly dependent on the cluster size. Different kinds of embedding techniques have been developed, however, to avoid this undesired effect.[8,25]

A suitable framework for describing the interaction between atoms and surfaces is provided by the Anderson-Newns (AN) Hamiltonian.[26] The calculation is usually performed within the HF approximation,[27] it being possible to incorporate the intra-atomic correlation into the adsorbate site by using perturbation techniques.[28–30] In most cases, semiempirical parametrization of the Hamiltonian terms is mainly due[31,32] to the difficulties related to *ab initio* calculations of the on-site energy and hopping contributions. Many works conclude that very accurate results can be obtained even within a HF approximation in the strong interaction region, provided that a consistent selection of the Hamiltonian parameters is performed.[8,29,31,33–37] For instance, it has been pointed out that more realistic values of charge on the adatom may be obtained by adding terms to the AN

0163-1829/98/58(8)/5007(15)/$15.00

Hamiltonian that emerge naturally on an *ab initio* basis.[31] It has also been found that an exact treatment of the exchange terms gives a description of the interaction between a metal surface and a low-energy helium atom able to produce highly satisfactory results, provided that the van der Walls interaction is added to account for the remaining correlation effects.[35]

Based on these facts, the aim of the present paper is to describe the atom-surface interaction within a single particle approximation without requiring the use of semiempirical parameters. From a bond-pair model Hamiltonian developed in previous works for a system of interacting atoms,[38,39] the AN Hamiltonian is recovered for the atom-surface interacting system. The on-site energy and hopping terms are calculated in terms of both the local density of states of the surface and the atomic properties of the one- and two-electron interactions. As a consequence of this mixed treatment, the extended nature of the surface states and the localized features of the atom-atom interactions are naturally accounted for. Thus in our model Hamiltonian each interaction parameter (obtained from an *ab initio* basis) have a clear physical meaning, and can be manipulated very easily to allow for a quick identification of the bond system involved in the absorption process. This is also relevant in order to facilitate the understanding of related phenomena such as dynamic charge-exchange processes[40] or the calculation of the repulsive contribution (short range effects) to the physisorption potential. It can be also pointed out that the computational effort involved in the whole calculation is modest. Our code program, including the computation of the atomic integrals[41] in an orthonormalized basis set (within an adequate reference frame) as well as the self-consistent procedure (involving averages of diagonal and crossed products of creation and annihilation operators) as required by the calculation, can be run in just a few minutes on a PC486 computer.

This paper is organized as follows: in Sec. II, the theoretical steps leading to buildup the single particle interaction Hamiltonian, and the self-consistent procedure followed to calculate the interaction energy as well as the charge and the on-site width and shift of the adatom level, are given in detail. In Sec. III, the results obtained for the H adsorption on metal surfaces (Li, Na, Al) are discussed. The possibilities to include the long-range interactions effects to account for correlation effects at the surface are also discussed and compared with other existing results in this section. Final remarks are given in Sec. IV.

II. THEORY

A. A model for the atom-surface interaction

A suitable scheme to describe either the adsorption of atoms or the dynamical charge-transfer processes occurring between scattered atoms and surfaces, is based on the Anderson (or Anderson-Newns) model. The model Hamiltonian reads

$$H=H^{\mathrm{ads}}+H^{\mathrm{sub}}+H^{\mathrm{int}}=\sum_{\alpha\sigma}(\varepsilon_{\alpha}^{\sigma}+\tfrac{1}{2}U_{\alpha}\hat{n}_{\alpha-\sigma})\hat{n}_{\alpha\sigma}+\sum_{\mathbf{k}\sigma}E_{\mathbf{k}}^{\sigma}\hat{n}_{\mathbf{k}\sigma}+\sum_{\mathbf{k}\alpha\sigma}(T_{\alpha\mathbf{k}}^{\sigma}\hat{c}_{\alpha\sigma}^{\dagger}\hat{c}_{\mathbf{k}\sigma}+\mathrm{H.c.}), \tag{1}$$

where, as in the original proposal, $|\alpha\rangle$ represents the adsorbate (or the state at the ''impurity'' site) and $|\mathbf{k}\rangle$ labels the bandlike eigenstates corresponding to the solid substrate. The third term is the hopping between the atom and the band states. In previous works,[38,39] a Hamiltonian to describe an interacting atom system has been developed. Starting with a full many-body Hamiltonian written in second-quantized language, our approximation consists of retaining terms leading to the following form:

$$H=\sum_{i\sigma}\left[\varepsilon_{i}+\tfrac{1}{2}U_{i}\hat{n}_{i-\sigma}+\tfrac{1}{2}\sum_{j(\neq i)}(J_{ij}\hat{n}_{j-\sigma}+G_{ij}\hat{n}_{j\sigma})\right]\hat{n}_{i\sigma}+\sum_{i\neq j,\sigma}\hat{T}_{ij}^{\sigma}\hat{c}_{i\sigma}^{\dagger}\hat{c}_{j\sigma}+V_{n-n}. \tag{2}$$

V_{n-n} represents the nuclear repulsion terms, while all the remaining parameters are assumed to be defined in terms of an orthonormal set of functions $\{\phi_i\}$. These parameters are given by

$$t_{ij}=\langle\phi_{i(\bar{r})}|-\frac{\nabla^{2}}{2}-\sum_{v}\frac{Z_{v}}{|\bar{r}-\bar{R}_{v}|}|\phi_{j(\bar{r})}\rangle,\quad \varepsilon_{i}=t_{ii},$$

$$h_{kij}=V_{kkij}=\langle\phi_{k(\bar{r})}\phi_{i(\bar{r}')}|\frac{1}{|\bar{r}-\bar{r}'|}|\phi_{j(\bar{r}')}\phi_{k(\bar{r})}\rangle,$$

$$J_{ij}=h_{ijj}\quad\text{and}\quad U_{i}=h_{iii},$$

$$h_{kij}^{x}=V_{kikj}=\langle\phi_{k(\bar{r})}\phi_{i(\bar{r}')}|\frac{1}{|\bar{r}-\bar{r}'|}|\phi_{k(\bar{r}')}\phi_{j(\bar{r})}\rangle, \tag{3}$$

$$G_{ij}=V_{iijj}-V_{ijij},$$

$$l_{kij}=h_{kij}-h_{kij}^{x},$$

$$\hat{T}_{ij}^{\sigma}=t_{ij}+\sum_{k}(h_{kij}\hat{n}_{k-\sigma}+l_{kij}\hat{n}_{k\sigma}).$$

Equation (2), that was previously applied to consider pairs of atoms, may be generalized to any atom-surface system if one assumes that one of the two atoms consists of a system having a quasicontinuum basis of states $\{\varphi_{\mathbf{k}}\}$ (including extended valence and ''localized'' or corelike flatband states). In fact, starting with Eq. (2) and transforming indexes to allow for a quasicontinuum of states in one of the subsystems will strictly produce terms in the atom-surface Hamiltonian containing both adsorbate-adsorbate ($\hat{c}_{\alpha\sigma}^{\dagger}\hat{c}_{\beta\sigma}$) and solid-solid ($\hat{c}_{\mathbf{k}\sigma}^{\dagger}\hat{c}_{\mathbf{k}'\sigma}$) state transitions that are induced on each subsystem by the presence of the other. Usually in the AN picture of the interacting system, these transitions are considered to be of second order as compared to those directly coupling the adsorbate and substrate subsystems (given in terms of $\hat{c}_{\alpha\sigma}^{\dagger}\hat{c}_{\mathbf{k}\sigma}$ or $\hat{c}_{\mathbf{k}\sigma}^{\dagger}\hat{c}_{\alpha\sigma}$ products).[27] Following the same scheme we will ignore those transitions, and arrive at a many-body Hamiltonian in which three kinds of typical contributions can be recognized in parallel to the Anderson's model:

$$H=H^{\mathrm{ads}}+H^{\mathrm{sub}}+H^{\mathrm{int}}=\sum_{\alpha\sigma}\left[\varepsilon_{\alpha}-\sum_{\overline{\overline{R}}_s}V^{Z_{Rs}}_{\alpha\alpha}+\tfrac{1}{2}U_{\alpha}\hat{n}_{\alpha-\sigma}+\tfrac{1}{2}\sum_{\beta(\neq\alpha)}(J_{\alpha\beta}\hat{n}_{\beta-\sigma}+G_{\alpha\beta}\hat{n}_{\beta\sigma})+\tfrac{1}{2}\sum_{\mathbf{k}}(J_{\alpha\mathbf{k}}\hat{n}_{\mathbf{k}-\sigma}+G_{\alpha\mathbf{k}}\hat{n}_{\mathbf{k}\sigma})\right]\hat{n}_{\alpha\sigma}$$
$$+\sum_{\mathbf{k}\sigma}\left[\varepsilon_{\mathbf{k}}-\sum_{\overline{\overline{R}}_a}V^{Z_{Ra}}_{\mathbf{kk}}+\tfrac{1}{2}U_{\mathbf{k}}\hat{n}_{\mathbf{k}-\sigma}+\tfrac{1}{2}\sum_{\mathbf{k}'(\neq\mathbf{k})}(J_{\mathbf{kk}'}\hat{n}_{\mathbf{k}'-\sigma}+G_{\mathbf{kk}'}\hat{n}_{\mathbf{k}'\sigma})+\tfrac{1}{2}\sum_{\alpha}(J_{\alpha\mathbf{k}}\hat{n}_{\alpha-\sigma}+G_{\alpha\mathbf{k}}\hat{n}_{\alpha\sigma})\right]\hat{n}_{\mathbf{k}\sigma}$$
$$+\sum_{\mathbf{k}\alpha\sigma}\left\{\left[t_{\alpha\mathbf{k}}+\sum_{\beta}(h_{\beta\alpha\mathbf{k}}\hat{n}_{\beta-\sigma}+l_{\beta\alpha\mathbf{k}}\hat{n}_{\beta\sigma})+\sum_{\mathbf{k}'}(h_{\mathbf{k}'\alpha\mathbf{k}}\hat{n}_{\mathbf{k}'-\sigma}+l_{\mathbf{k}'\alpha\mathbf{k}}\hat{n}_{\mathbf{k}'\sigma})\right]\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}+\mathrm{H.c.}\right\}. \tag{4}$$

In Eq. (4), **k** includes state and band indexes, and the summation runs over all bands of the solid (including the inner ones). The α and β indexes label states which may correspond to one or more adatoms, i.e., Eq. (4) can also be used to consider the adsorption of molecules. In the first term of Eq. (4) we have explicitly separated the diagonal contributions produced by the electrostatic potentials caused by the nuclei of the solid ($V^{Z_{Rs}}_{\alpha\alpha}=\langle\phi_\alpha|Z_{Rs}/|r-R_s||\phi_\alpha\rangle$). Thus ε_α involves contributions of the adsorbate only, i.e., the kinetic energy and the electrostatic interaction with its nucleus. Similarly, the substrate $\varepsilon_{\mathbf{k}}$ terms do not include the corresponding effects of the adsorbate nuclei. By contrast, the remaining one-electron parameters ($t_{\alpha\mathbf{k}},t_{\alpha\beta},t_{\mathbf{kk}'}$) include all the electron-nuclei interactions.

B. Overlap expansion and mean-field approximation

So far, the procedure chosen has consisted of retaining the dimeric picture by associating an orthonormal set involving the extended and localized states of each of the ''atoms'' or subsystems. Strictly, all these states form an orthonormal set, and consequently these functions are no longer eigenstates of either of the two isolated subsystems. Thus the localized nature of the adsorbed atom states as well as the translational symmetry along the surface are lost. Therefore the subindexes α and **k** only represent labels that remind us of the nonorthonormal eigenstates of the isolated subsystems from which these states are mainly derived, with the underlying assumption that small overlaps will subsequently be involved. We have adopted a description based on the symmetric orthogonalization procedure,[42] although other alternatives have been used for that purpose.[4] Starting from a nonorthogonal basis set $\{\psi_\alpha,\psi_{\mathbf{k}}\}$ (where ψ_α and $\psi_{\mathbf{k}}$ correspond to states of the isolated subsystems), the application of $(1+S)^{-1/2}_{\alpha\mathbf{k}}$ produces the desired orthonormal $\{\varphi_\alpha,\varphi_{\mathbf{k}}\}$ set. Obviously, to obtain a complete orthogonalization between the adsorbate-substrate original states is out of the question, and it is then natural to appeal to an expansion in terms of the overlap $S_{\alpha\mathbf{k}}$. Previous works,[38,39] dealing with molecular or adsorbed systems, have shown that the overlap expansion of $(1+S)^{-1/2}$ can be reliably used even if overlap integrals are large (≈ 0.7 as in H_2). In addition to the overlap expansion, and after applying the HF approximation to Eq. (4), the effective one particle Hamiltonian looks like a generalized HF version of Anderson's model:

$$H=H^{\mathrm{ads}}+H^{\mathrm{sub}}+H^{\mathrm{int}}+V_{n-n}-[X],$$

where $[X]$ represents the whole of double-counted terms to be subtracted, and

$$H^{\mathrm{ads}}=\sum_{\alpha\sigma}E^{\sigma}_{\alpha}\hat{n}_{\alpha\sigma}=\sum_{\alpha\sigma}\left\{\varepsilon^{\sigma^{\mathrm{HF}}}_{\alpha}-\sum_{\overline{\overline{R}}_s}V^{Z_{Rs}}_{\alpha\alpha}+\sum_{\mathbf{k}}(J^{0}_{\alpha\mathbf{k}}\langle n_{\mathbf{k}-\sigma}\rangle+\tilde{G}_{\alpha\mathbf{k}}\langle n_{\mathbf{k}\sigma}\rangle)-\sum_{\mathbf{k}}S_{\alpha\mathbf{k}}\tilde{T}^{\sigma}_{\alpha\mathbf{k}}+\tfrac{1}{4}\sum_{\mathbf{k}}S^{2}_{\alpha\mathbf{k}}\left[\left(\varepsilon^{\sigma^{\mathrm{HF}}}_{\alpha}-\sum_{\overline{\overline{R}}_s}V^{Z_{Rs}}_{\alpha\alpha}\right.\right.\right.$$
$$\left.\left.\left.+\sum_{\mathbf{k}'}J^{0}_{\alpha\mathbf{k}'}\langle n_{\mathbf{k}'-\sigma}\rangle+\sum_{\mathbf{k}'(\neq\mathbf{k})}G^{0}_{\alpha\mathbf{k}'}\langle n_{\mathbf{k}'\sigma}\rangle\right)-\left(\xi_{\mathbf{k}}-\sum_{\overline{\overline{R}}_a}V^{Z_{Ra}}_{\mathbf{kk}}+\sum_{\beta}J^{0}_{\beta\mathbf{k}}\langle n_{\beta-\sigma}\rangle+\sum_{\beta(\neq\alpha)}G^{0}_{\beta\mathbf{k}}\langle n_{\beta\sigma}\rangle\right)\right]\right\}\hat{n}_{\alpha\sigma}, \tag{5}$$

$$H^{\mathrm{sub}}=\sum_{\mathbf{k}\sigma}E^{\sigma}_{\mathbf{k}}\hat{n}_{\mathbf{k}\sigma}=\sum_{\mathbf{k}\sigma}\left\{\xi_{\mathbf{k}}-\sum_{\overline{\overline{R}}_a}V^{Z_{Ra}}_{\mathbf{kk}}+\sum_{\alpha}(J^{0}_{\alpha\mathbf{k}}\langle n_{\alpha-\sigma}\rangle+\tilde{G}_{\alpha\mathbf{k}}\langle n_{\alpha\sigma}\rangle)-\sum_{\alpha}S_{\alpha\mathbf{k}}\tilde{T}^{\sigma}_{\alpha\mathbf{k}}+\tfrac{1}{4}\sum_{\alpha}S^{2}_{\alpha\mathbf{k}}\left[\left(\xi_{\mathbf{k}}-\sum_{\overline{\overline{R}}_a}V^{Z_{Ra}}_{\mathbf{kk}}\right.\right.\right.$$
$$\left.\left.\left.+\sum_{\beta}J^{0}_{\beta\mathbf{k}}\langle n_{\beta-\sigma}\rangle+\sum_{\beta(\neq\alpha)}G^{0}_{\beta\mathbf{k}}\langle n_{\beta\sigma}\rangle\right)-\left(\varepsilon^{\sigma^{\mathrm{HF}}}_{\alpha}-\sum_{\overline{\overline{R}}_s}V^{Z_{Rs}}_{\alpha\alpha}+\sum_{\mathbf{k}'}J^{0}_{\alpha\mathbf{k}'}\langle n_{\mathbf{k}'-\sigma}\rangle+\sum_{\mathbf{k}'(\neq\mathbf{k})}G^{0}_{\alpha\mathbf{k}'}\langle n_{\mathbf{k}'\sigma}\rangle\right)\right]\right\}\hat{n}_{\mathbf{k}\sigma}, \tag{6}$$

$$H^{\mathrm{int}}=\sum_{\mathbf{k}\alpha\sigma}(T^{\sigma}_{\alpha\mathbf{k}}\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}+\mathrm{H.c.})=\sum_{\mathbf{k}\alpha\sigma}[(\tilde{T}^{\sigma}_{\alpha\mathbf{k}}-\tilde{G}_{\alpha\mathbf{k}}\langle c^{\dagger}_{\mathbf{k}\sigma}c_{\alpha\sigma}\rangle)\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}+\mathrm{H.c.}]. \tag{7}$$

In Eqs. (5)–(7) the parameters with superscript zero are formally defined as in Eq. (3), but with the orthogonal functions replaced by the ''atomic'' ones. The parameter $\xi_{\mathbf{k}}$ now concerns the electronic structure of the isolated surface and

$$\varepsilon_{\alpha}^{\sigma^{\mathrm{HF}}}=\varepsilon_{\alpha}^{0}+U_{\alpha}^{0}\langle n_{\alpha-\sigma}\rangle+\sum_{\beta(\neq\alpha)}(J_{\alpha\beta}^{0}\langle n_{\beta-\sigma}\rangle+G_{\alpha\beta}^{0}\langle n_{\beta\sigma}\rangle),$$

$$\tilde{G}_{\alpha\mathbf{k}}=G_{\alpha\mathbf{k}}^{0}+S_{\alpha\mathbf{k}}^{2}J_{\alpha\mathbf{k}}^{0},$$

$$\tilde{T}_{\alpha\mathbf{k}}^{\sigma}=t_{\alpha\mathbf{k}}+\sum_{\beta}(h_{\beta\alpha\mathbf{k}}\langle n_{\beta-\sigma}\rangle+l_{\beta\alpha\mathbf{k}}\langle n_{\beta\sigma}\rangle)$$

$$+\sum_{\mathbf{k}'}(h_{\mathbf{k}'\alpha\mathbf{k}}\langle n_{\mathbf{k}'-\sigma}\rangle+l_{\mathbf{k}'\alpha\mathbf{k}}\langle n_{\mathbf{k}'\sigma}\rangle).$$

It may be noted that the overlap expansion has been performed only on H^{ads} and H^{sub}, while H^{int} has been unaltered, being only affected by the renormalization of the exchange contribution in the HF approximation. Equations (5)–(7) represent our basic expressions to describe the atom-surface interaction. The main differences from the AN model are as follows: (i) The adsorbate-substrate two-electron interactions are explicitly considered within the mean-field approximation. (ii) The entire adsorbate and substrate levels are modified by the orthogonalization effects. (iii) H^{sub} includes the inner energy bands. (iv) Consistently with the overlap expansion and the HF approximation, the hopping term results from the addition of two contributions: $\tilde{T}_{\alpha\mathbf{k}}^{\sigma}$, which is the standard hopping between orthogonalized functions; and $-\tilde{G}_{\alpha\mathbf{k}}\langle c_{\mathbf{k}\sigma}^{\dagger}c_{\alpha\sigma}\rangle$, which accounts for the correct nonlocality of the exchange interaction within a HF. This latter point is crucial to allow for an adequate description of the interacting system. Details on its calculation are given in Sec. II C.

C. LCAO expansion

1. Adsorbate level E_{α}^{σ}

In order to solve Eqs. (5)–(7), we use a local combination of atomic orbitals (LCAO) expansion for the substrate states. As an example we consider the term associated with the Coulombic integral $J_{\alpha\mathbf{k}}^{0}$ given by

$$\sum_{\mathbf{k}\sigma}J_{\alpha\mathbf{k}}^{0}\langle n_{\mathbf{k}-\sigma}\rangle=\sum_{\mathbf{k}\sigma}\left\langle\psi_{\alpha}(\bar{r}-\bar{R}_{a})\psi_{\mathbf{k}}(\bar{r}')\left|\frac{1}{|\bar{r}-\bar{r}'|}\right|\psi_{\mathbf{k}}(\bar{r}')\psi_{\alpha}(\bar{r}-\bar{R}_{a})\right\rangle\langle n_{\mathbf{k}-\sigma}\rangle$$

$$=\sum_{\mathbf{k}\sigma}\left[\sum_{ij\bar{R}_{s}\bar{R}_{s'}}c_{i(\bar{R}_{s})}^{\mathbf{k}*}c_{j(\bar{R}_{s'})}^{\mathbf{k}}\left\langle\psi_{\alpha(\bar{r}-\bar{R}_{a})}\psi_{i(\bar{r}'-\bar{R}_{s})}\left|\frac{1}{|\bar{r}-\bar{r}'|}\right|\psi_{j(\bar{r}'-\bar{R}_{s'})}\psi_{\alpha(\bar{r}-\bar{R}_{a})}\right\rangle\right]\langle n_{\mathbf{k}-\sigma}\rangle,$$

where the $c_{i}^{\mathbf{k}}(\bar{R}_{s})$'s are the coefficients of the LCAO expansion, while i and j label the states of a substrate atom located at the R_s site. Neglecting the nondiagonal density-matrix elements $[c_{i}^{\mathbf{k}*}(\bar{R}_{s})c_{j}^{\mathbf{k}}(\bar{R}_{s'}),i\neq j$, and $\bar{R}_{s}\neq\bar{R}_{s'}]$, this term is approximated by

$$\sum_{\mathbf{k}\sigma}J_{\alpha\mathbf{k}}^{0}\langle n_{\mathbf{k}-\sigma}\rangle\cong\sum_{i\bar{R}_{s}\sigma}\left[\sum_{\mathbf{k}}|c_{i}^{\mathbf{k}}(\bar{R}_{s})|^{2}\langle n_{\mathbf{k}-\sigma}\rangle\right]J_{\alpha i}^{0}(\bar{R}_{a}-\bar{R}_{s})$$

$$=\sum_{i\bar{R}_{s}\sigma}J_{\alpha i}^{0}(\bar{R}_{a}-\bar{R}_{s})\langle n_{i-\sigma}(\bar{R}_{s})\rangle. \tag{8}$$

$\langle n_{i-\sigma}(\bar{R}_{s})\rangle$ is the occupation number associated with the i state with spin-σ at the R_s site. These numbers are, in principle, different from those of the unperturbed solid, because the presence of the adsorbate modifies the occupation of the $\mathbf{k}$ states. As this represents a minor order change, $\langle n_{i-\sigma}(\bar{R}_{s})\rangle$ will be obtained by integrating the local and partial densities of states corresponding to the isolated solid. Fixing the occupation numbers of the substrate at their values of the isolated solid implies the assumption of a complete screening of the adsorbate effects when interacting with the surface, and represents the major constraint we are imposing on our calculation. This assumption is also consistent with the neglect of nondiagonal terms in the density matrix, as stated above. The R_s dependence results as a consequence of the variations of the local density of states in each of the crystalline planes parallel to the surface. With regard to the parameters that define E_{α}^{σ} we proceed likewise, except for those terms proportional to a $S_{\alpha\mathbf{k}}^{2}$ involving only a single sum over $\mathbf{k}$, in which case the following approximation is performed:

$$\sum_{\mathbf{k}}|c_{i}^{\mathbf{k}}|^{4}\langle n_{\mathbf{k}\sigma}\rangle\cong\sum_{\mathbf{k}}|c_{i}^{\mathbf{k}}|^{2}\langle n_{\mathbf{k}\sigma}\rangle=\langle n_{i\sigma}\rangle.$$

After all these approximations, Eq. (5) becomes, in the LCAO expansion,

$$H^{\mathrm{ads}}=\sum_{\alpha\sigma}E_{\alpha}^{\sigma}\hat{n}_{\alpha\sigma}\cong\sum_{\alpha\sigma}\Bigg\{\varepsilon_{\alpha}^{\sigma^{\mathrm{HF}}}-\sum_{\bar{R}_{s}}V_{\alpha\alpha}^{Z_{Rs}}+\sum_{i\bar{R}_{s}}(J_{\alpha i}^{0}\langle n_{i-\sigma}\rangle+\tilde{G}_{\alpha i}\langle n_{i\sigma}\rangle)-\sum_{i\bar{R}_{s}}S_{\alpha i}\tilde{T}_{\alpha i}^{\sigma}+\tfrac{1}{4}\sum_{i\bar{R}_{s}}S_{\alpha i}^{2}\Bigg[\Bigg(\varepsilon_{\alpha}^{\sigma^{\mathrm{HF}}}-\sum_{\bar{R}_{s'}}V_{\alpha\alpha}^{Z_{Rs}}$$

$$+\sum_{j\bar{R}_{s'}}J_{\alpha j}^{0}\langle n_{j-\sigma}\rangle+\sum_{j(\neq i)\bar{R}_{s'}}G_{\alpha j}^{0}\langle n_{j\sigma}\rangle\Bigg)-\Bigg(\bar{\varepsilon}_{i}-\sum_{\bar{R}_{a}}V_{ii}^{Z_{a}}+\sum_{\beta}J_{\beta i}^{0}\langle n_{\beta-\sigma}\rangle+\sum_{\beta(\neq\alpha)}G_{\beta i}^{0}\langle n_{\beta\sigma}\rangle\Bigg)\Bigg]\Bigg\}\hat{n}_{\alpha\sigma}. \tag{9}$$

The $\overline{\varepsilon}_i$'s correspond to the energy levels of the isolated solid states. These will be selected as follows: for the inner states we will use experimental values obtained from x-ray photoemission spectroscopy (XPS) data,[43] while for the valence states we will use the corresponding average values

$$\overline{\varepsilon}_i=\begin{cases}\varepsilon_i^{\text{XPS}}, & i\equiv\text{inner states}\\ \displaystyle\int_{\varepsilon_{Bi}}^{\varepsilon_f}\varepsilon\rho_{i\overline{R}_s}(\varepsilon)d\varepsilon, & i\equiv\text{valence states,}\end{cases}$$

where $\rho_{i\overline{R}_s}(\varepsilon)$ is the local and partial density of states. Equation (9), as well as all other terms in the model Hamiltonian, exhibit in a transparent way the localized-extended nature of the interaction parameters, involving contributions from atom-atom integrals appropriately weighted by occupation numbers obtained from the corresponding local and partial densities of states.

2. Hopping terms $T^{\sigma}_{\alpha\mathbf{k}}$

The LCAO expansion of the hopping term requires a special consideration, as this results from two different contributions: (i) the coupling between orthogonalized functions ($\tilde{T}^{\sigma}_{\alpha\mathbf{k}}$), and (ii) the exchange term defined with the functions of the nonperturbed system $(-\tilde{G}_{\alpha\mathbf{k}}\langle c^{\dagger}_{\mathbf{k}\sigma}c_{\alpha\sigma}\rangle)$. The LCAO expansion over the latter is performed in the same way as for E^{σ}_{α}. Concerning (i), as the LCAO expansion must be done over the states of the isolated subsystems, this is accomplished by an overlap expansion. As an example, we show the result for the one-electron terms. For the two-electron terms the procedure is essentially the same:

$$\sum_{\mathbf{k}\sigma} t_{\alpha\mathbf{k}}\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}=\sum_{\mathbf{k}\sigma}\left[t^{0}_{\alpha\mathbf{k}}-\tfrac{1}{2}S_{\alpha\mathbf{k}}(t^{0}_{\alpha\alpha}+t^{0}_{\mathbf{kk}})\right]\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}.$$

After separating explicitly the dimeric from the three-center contributions, one obtains

$$\begin{aligned}\sum_{\mathbf{k}\sigma}\sum_{i\overline{R}_s} c^{\mathbf{k}}_i(\overline{R}_s)\Bigg\{ & t^{0\,\text{dim}}_{\alpha i}-\tfrac{1}{2}S_{\alpha i}(\varepsilon^{0}_{\alpha}-V^{Z_{Ra}}_{\alpha\alpha}+\overline{\varepsilon}_i-V^{Z_{Ra}}_{ii})\\ &-\sum_{\overline{R}_{a'}(\neq\overline{R}_a)}\left[V^{Z_{Ra'}}_{\alpha i}-\tfrac{1}{2}S_{\alpha i}(V^{Z_{Ra'}}_{\alpha\alpha}+V^{Z_{Ra'}}_{ii})\right]\\ &-\sum_{\overline{R}_{s'}(\neq\overline{R}_s)}\left[V^{Z_{Rs'}}_{\alpha i}-\tfrac{1}{2}S_{\alpha i}(V^{Z_{Rs'}}_{\alpha\alpha}+V^{Z_{Rs'}}_{ii})\right]\Bigg\}\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}.\end{aligned}\tag{10}$$

The three-center integrals $V^{Z_{Ra'}}_{\alpha i}$ and $V^{Z_{Rs'}}_{\alpha i}$, are approximated according to the proposal of Ref. 44, and consistently with the overlap expansions

$$\begin{aligned}V^{Z_{Ra'}}_{\alpha i}&\cong\frac{1}{2}\left(\sum_j S_{\alpha j}V^{Z_{Ra'}}_{ij}+\sum_{\beta}S_{\beta i}V^{Z_{Ra'}}_{\alpha\beta}\right)\\ &\cong\frac{1}{2}S_{\alpha i}(V^{Z_{Ra'}}_{ii}+V^{Z_{Ra'}}_{\alpha\alpha}),\\ V^{Z_{Rs'}}_{\alpha i}&\cong\frac{1}{2}\left(\sum_j S_{\alpha j}V^{Z_{Rs'}}_{ij}+\sum_{\beta}S_{\beta i}V^{Z_{Rs'}}_{\alpha\beta}\right)\\ &\cong\frac{1}{2}S_{\alpha i}(V^{Z_{Rs'}}_{ii}+V^{Z_{Rs'}}_{\alpha\alpha}),\end{aligned}\tag{11}$$

where j and β run over the states of the R_s and R_a sites, respectively. Replacing Eq. (11) in Eq. (10), we obtain an expression in which the nondimeric contributions are canceled:

$$\sum_{\mathbf{k}\sigma}\Bigg\{\sum_{i\overline{R}_s} c^{\mathbf{k}}_i(\overline{R}_s)\times\left[t^{0\,\text{dim}}_{\alpha i}-\tfrac{1}{2}S_{\alpha i}(\varepsilon^{0}_{\alpha}-V^{Z_{Ra}}_{\alpha\alpha}+\overline{\varepsilon}_i-V^{Z_{Ra}}_{ii})\right]\Bigg\}\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}.$$

The final step consists of recovering the parameters defined with orthogonalized functions, so that the hopping is a superposition of those defined only with functions orthogonalized in each dimeric subspace (R_a, R_s),

$$\begin{aligned}\sum_{\mathbf{k}\sigma}\tilde{T}^{\sigma}_{\alpha\mathbf{k}}\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}&\cong\sum_{\mathbf{k}\sigma}\left[\sum_{i\overline{R}_s}c^{\mathbf{k}}_i(\overline{R}_s)\tilde{T}^{\sigma\,\text{dim}}_{\alpha i}\right]\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}\\ &=\sum_{\mathbf{k}\sigma}\Bigg\{\sum_{i\overline{R}_s}c^{\mathbf{k}}_i(\overline{R}_s)\Bigg[t^{\text{dim}}_{\alpha i}+h^{\text{dim}}_{\alpha\alpha\mathbf{i}}\langle n_{\alpha-\sigma}\rangle\\ &\quad+\sum_j\left(h^{\text{dim}}_{j\alpha i}\langle n_{j-\sigma}\rangle+l^{\text{dim}}_{j\alpha i}\langle n_{j\sigma}\rangle\right)\Bigg]\Bigg\}\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}.\end{aligned}\tag{12}$$

Therefore, the interaction term of the model Hamiltonian in the LCAO version is finally approximated by (hereafter we omit the superscript dim)

$$\begin{aligned}H^{\text{int}}=\sum_{\mathbf{k}\alpha\sigma}(T^{\sigma}_{\alpha\mathbf{k}}\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}+\text{H.c.})=\sum_{\mathbf{k}\alpha\sigma}\sum_{i\overline{R}_s}c^{\mathbf{k}}_i(\overline{R}_s)\\ \times[(\tilde{T}^{\sigma}_{\alpha i}-\tilde{G}_{\alpha i}\langle c^{\dagger}_{i\sigma}c_{\alpha\sigma}\rangle)\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}+\text{H.c.}].\end{aligned}\tag{13}$$

The approximation of the three-center atomic integrals is crucial in the modeling of the atom-surface complex, since it allows one to redefine the hopping only with dimeric contributions, i.e., the whole system is rebuilt from the calculation of each elemental dimer. Expressions (9) and (13) are the fundamental equations that define our model. While these expressions are approximated, they have a clear *ab initio* character. Each term of the Hamiltonian is calculated in terms of atomic functions (those that determine the corresponding integrals), and in terms of the density of states which characterizes the band structure of the surface (which fix the values of $\langle n_{i-\sigma}\rangle$ and $\langle c^{\dagger}_{i\sigma}c_{\alpha\sigma}\rangle$).

3. Occupation number $\langle n_{\alpha\sigma}\rangle$

Using standard methods based on Green's-function techniques,[45] the calculation of the occupation number is reduced to solve

$$\begin{aligned}\langle n_{\alpha\sigma}\rangle&=-\frac{1}{\pi}\int_{-\infty}^{\varepsilon_f}\text{G}^{\sigma}_{\alpha\alpha}(\varepsilon)d\varepsilon\\ &=-\frac{1}{\pi}\text{Im}\int_{-\infty}^{\varepsilon_f}[\varepsilon-E^{\sigma}_{\alpha}-\Lambda^{\sigma}(\varepsilon)+i\Delta^{\sigma}(\varepsilon)]^{-1}d\varepsilon,\end{aligned}$$

where the chemisorption function $\Delta^{\sigma}(\varepsilon)$ is separated into the inner- and valence-band contributions

$$\begin{aligned}\Delta^{\sigma}(\varepsilon)&=\pi\sum_{\mathbf{k}}|T^{\sigma}_{\alpha\mathbf{k}}|^{2}\delta(\varepsilon-E^{\sigma}_{\mathbf{k}})\\&\cong\pi\sum_{\mathbf{k}}\sum_{i\bar{R}_s}|c^{\mathbf{k}}_{i}(\bar{R}_s)|^{2}|T^{\sigma}_{\alpha i}|^{2}\delta(\varepsilon-E^{\sigma}_{\mathbf{k}})\\&=\pi\sum_{i\bar{R}_s}\rho^{\sigma}_{i\bar{R}_s}(\varepsilon)|T^{\sigma}_{\alpha i}|^{2}\end{aligned}\tag{14}$$

and

$$\Lambda^{\sigma}(\varepsilon)=P\sum_{\mathbf{k}}\frac{|T^{\sigma}_{\alpha\mathbf{k}}|^{2}}{\varepsilon-E^{\sigma}_{\mathbf{k}}}=\frac{1}{\pi}P\int_{-\infty}^{\infty}\frac{\Delta^{\sigma}(\varepsilon')}{(\varepsilon-\varepsilon')}d\varepsilon'$$

$$(P\equiv\text{principal value}).\tag{15}$$

Assuming a δ-like form for the density of states of inner bands, and a semielliptical function for the valence ones,[27] the occupation number is obtained as

$$\langle n_{\alpha\sigma}\rangle=-\frac{1}{\pi}\int_{-\infty}^{\varepsilon_f}G^{\sigma}_{\alpha\alpha}(\varepsilon)d\varepsilon=-\frac{1}{\pi}\sum_{i\bar{R}_s}\int_{\varepsilon_{Bv}}^{\varepsilon_f}\frac{\rho^{\sigma}_{i\bar{R}_s}(\varepsilon)|T^{\sigma}_{\alpha i}|^{2}}{\{[\varepsilon-E^{\sigma}_{\alpha}-\Lambda^{\sigma}(\varepsilon)]^{2}+[\Delta^{\sigma}(\varepsilon)]^{2}\}}d\varepsilon.\tag{16}$$

Equation (16) corresponds to cases where E^{σ}_{α} is resonant with the valence band, while for $G^{\sigma}_{\alpha\alpha}$, having a simple pole, i.e., $\Lambda^{\sigma}(\varepsilon)=\varepsilon-E^{\sigma}_{\alpha}$ and $\Delta^{\sigma}(\varepsilon)=0$, and $\langle n_{\alpha\sigma}\rangle$ is given by

$$\langle n_{\alpha\sigma}\rangle_{l}=[1-\Lambda'^{\sigma}(\varepsilon_{l})]^{-1},\quad\text{where }\Lambda'^{\sigma}(\varepsilon_{l})=\left.\frac{d\Lambda^{\sigma}(\varepsilon)}{d\varepsilon}\right|_{\varepsilon=\varepsilon_{l}}.\tag{17}$$

4. Crossed average expectation values $\langle c^{\dagger}_{\alpha\sigma}c_{i\sigma}\rangle$

Within the HF scheme, the calculation of the exchangelike contributions requires the knowledge of the nondiagonal average expectation values $\langle c^{\dagger}_{\alpha\sigma}c_{i\sigma}\rangle$. How to obtain these cross-average terms is not obvious and, in order to arrive at a tractable formula, we will make use of the contribution to the mean energy related to the hopping term:

$$\sum_{\mathbf{k}\sigma}T^{\sigma}_{\alpha\mathbf{k}}\langle\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}\rangle\cong\sum_{\mathbf{k}\sigma}\left[\sum_{i\bar{R}_s}c^{\mathbf{k}}_{i}(\bar{R}_s)T^{\sigma}_{\alpha i}\right]\langle\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}\rangle=\sum_{i\bar{R}_s\sigma}T^{\sigma}_{\alpha i}\langle\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{i\sigma}\rangle=\sum_{i\bar{R}_s\sigma}(\tilde{T}^{\sigma}_{\alpha i}-\tilde{G}_{\alpha i}\langle c^{\dagger}_{i\sigma}c_{\alpha\sigma}\rangle)\langle c^{\dagger}_{\alpha\sigma}c_{i\sigma}\rangle\tag{18}$$

where we have used $\Sigma_{\mathbf{k}}c^{\mathbf{k}}_{i}(\bar{R}_s)\;\langle\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}\rangle=\langle c^{\dagger}_{\alpha\sigma}c_{i\sigma}\rangle$.

On the other hand, averages of the kind $\langle\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}\rangle$ can also be written in terms of the corresponding matrix element of the Green's function $G^{\sigma}_{\alpha\mathbf{k}}(\varepsilon)$:[45]

$$\langle\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}\rangle=-\frac{1}{\pi}\int_{-\infty}^{\varepsilon_f}G^{\sigma}_{\alpha\mathbf{k}}(\varepsilon)d\varepsilon=-\frac{1}{\pi}\int_{-\infty}^{\varepsilon_f}\frac{T^{\sigma}_{\alpha\mathbf{k}}}{\varepsilon-E^{\sigma}_{\mathbf{k}}+\imath\eta}G^{\sigma}_{\alpha\alpha}(\varepsilon)d\varepsilon.$$

From the definition of $G^{\sigma}_{\alpha\alpha}(\varepsilon)$ and remembering that $\Sigma_{\mathbf{k}}[|T^{\sigma}_{\alpha\mathbf{k}}|^{2}/(\varepsilon-E^{\sigma}_{\mathbf{k}}+\imath\eta)]=\Lambda^{\sigma}(\varepsilon)-\imath\Delta^{\sigma}(\varepsilon)$, one obtains

$$\sum_{\mathbf{k}\sigma}T^{\sigma}_{\alpha\mathbf{k}}\langle\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}\rangle=\frac{1}{\pi}\sum_{i\bar{R}_s}\int_{\varepsilon_{Bv}}^{\varepsilon_f}\frac{\Delta^{\sigma}(\varepsilon)(\varepsilon-E^{\sigma}_{\alpha})}{[(\varepsilon-E^{\sigma}_{\alpha}-\Lambda^{\sigma}(\varepsilon)]^{2}+[\Delta^{\sigma}(\varepsilon)]^{2}\}}d\varepsilon.$$

Replacing $\Delta^{\sigma}(\varepsilon)$ [see Eq. (14)], the contribution of the interaction term to the energy is

$$\sum_{\mathbf{k}\sigma}T^{\sigma}_{\alpha\mathbf{k}}\langle\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}\rangle=\sum_{i\bar{R}_s}\left[(\tilde{T}^{\sigma}_{\alpha i}-\tilde{G}_{\alpha i}\langle c^{\dagger}_{i\sigma}c_{\alpha\sigma}\rangle)\int_{\varepsilon_{Bv}}^{\varepsilon_f}\frac{(\tilde{T}^{\sigma}_{\alpha i}-\tilde{G}_{\alpha i}\langle c^{\dagger}_{i\sigma}c_{\alpha\sigma}\rangle)\rho^{\sigma}_{i\bar{R}_s}(\varepsilon)(\varepsilon-E^{\sigma}_{\alpha})}{\{[\varepsilon-E^{\sigma}_{\alpha}-\Lambda^{\sigma}(\varepsilon)]^{2}+[\Delta^{\sigma}(\varepsilon)]^{2}\}}d\varepsilon\right].\tag{19}$$

Comparing Eqs. (18) and (19) term by term, the average $\langle\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{i\sigma}\rangle$ can be obtained from the following recurrent relationship

$$\langle c^{\dagger}_{\alpha\sigma}c_{i\sigma}\rangle^{\text{out}}=\int_{\varepsilon_{Bv}}^{\varepsilon_f}\frac{(\tilde{T}^{\sigma}_{\alpha i}-\tilde{G}_{\alpha i}\langle c^{\dagger}_{i\sigma}c_{\alpha\sigma}\rangle^{\text{in}})\rho^{\sigma}_{i\bar{R}_s}(\varepsilon)(\varepsilon-E^{\sigma}_{\alpha})}{\{[\varepsilon-E^{\sigma}_{\alpha}-\Lambda^{\sigma}(\varepsilon)]^{2}+[\Delta^{\sigma}(\varepsilon)]^{2}\}}d\varepsilon,\tag{20}$$

When localized states appear, i.e., when $G^{\sigma}_{\alpha\alpha}(\varepsilon)$ has a simple pole, their contributions to the interaction energy are given by

$$\sum_{\mathbf{k}\sigma} T^{\sigma}_{\alpha\mathbf{k}}\langle\hat{c}^{\dagger}_{\alpha\sigma}\hat{c}_{\mathbf{k}\sigma}\rangle = -\frac{1}{\pi}\mathrm{Im}\left\{-\imath\pi\frac{\Lambda^{\sigma}(\varepsilon_l)}{[1-\Lambda'^{\sigma}(\varepsilon_l)]}\right\}$$
$$=\Lambda^{\sigma}(\varepsilon_l)\langle n_{\alpha\sigma}\rangle_l=(\varepsilon_l-E^{\sigma}_{\alpha})\langle n_{\alpha\sigma}\rangle_l\,. \tag{21}$$

Replacing $\Lambda^{\sigma}(\varepsilon)$ by Eq. (15) and comparing Eqs. (18) and (21) term by term, we obtain the contribution of $\langle c^{\dagger}_{\alpha\sigma}c_{i\sigma}\rangle$ when localized states are present:

$$\langle c^{\dagger}_{\alpha\sigma}c_{i\sigma}\rangle^{\mathrm{out}}_{l}=\frac{\Lambda^{\sigma}_{i}(\varepsilon_l)}{(\tilde{T}^{\sigma}_{\alpha i}-\tilde{G}_{\alpha i}\langle c^{\dagger}_{i\sigma}c_{\alpha\sigma}\rangle^{\mathrm{in}})[1-\Lambda'^{\sigma}(\varepsilon_l)]}\,. \tag{22}$$

5. Self-consistent procedure

The self-consistent procedure to solve the bond-pair Hamiltonian consists of the following stages: (i) The initial value for $\langle n_{\alpha\sigma}\rangle$ is taken as that corresponding to the isolated atom and $\langle c^{\dagger}_{\alpha\sigma}c_{i\sigma}\rangle=0$. (ii) Subsequently E^{σ}_{α}, $T^{\sigma}_{\alpha i}$, and E^{σ}_{c} [Eqs. (9), (13), and (6)] are calculated. These magnitudes define the chemisorption function $\Delta^{\sigma}(\varepsilon)$ and its Hilbert transform $\Lambda^{\sigma}(\varepsilon)$ [Eqs. (14) and (15)]. (iii) $\langle n_{\alpha\sigma}\rangle$ and $\langle c^{\dagger}_{\alpha\sigma}c_{i\sigma}\rangle$ are obtained according to Eqs. (16), (17), (20), and (22). This iterative input-output procedure is repeated until convergence is achieved. The interaction energy E_{int} is calculated subsequently. At this point it is worth stressing that for the problem under consideration two simplifying assumptions were made from the start: internal transitions within each subsystem have been ignored, implying that averages of the kind $\langle\hat{c}^{\dagger}_{\mathbf{k}\sigma}\hat{c}_{\mathbf{k}'\sigma}\rangle=\langle c^{\dagger}_{\alpha\sigma}c_{\beta\sigma}\rangle=0$ and also the occupation number of the states in the solid are kept fixed along the whole procedure, i.e.,

$$\langle n_{i\sigma}\rangle=\begin{cases}1, & i\equiv\text{inner states}\\ \int_{\varepsilon_{Bi}}^{\varepsilon_f}\rho_{i\bar{R}_s}(\varepsilon)d\varepsilon, & i\equiv\text{valence states,}\end{cases}$$

where $\rho_{i\bar{R}_s}(\varepsilon)$ is the local and partial density of states corresponding to the unperturbed solid. Thus $\langle n_{\alpha\sigma}\rangle$ and $\langle c^{\dagger}_{\alpha\sigma}c_{i\sigma}\rangle$ are the only density-matrix elements that are allowed to vary in each iteration stage. Strictly, changes on these averages along the self-consistent loop will not only modify the adsorbate level and the effective hopping [Eqs. (9) and (13)] but will also redefine the energies associated with the states of the solid [see Eq. (6)]. In this last respect we adopted a distinct treatment for the inner and valence bands. As the inner bands have a narrow width, they were considered localized states. This implies that the location of the inner levels E^{σ}_{c} will become shifted due to the orthogonality requirements and their interactions with the adsorbate states. Therefore the chemical shifts λ of the inner levels ($\lambda=E^{\sigma}_{c}-\varepsilon^{\mathrm{XPS}}_{i}$) can be obtained as a byproduct of the whole calculation. On the other hand, as we are considering the adsorption of a single adatom, we will assume that the electronic structure of the valence band remains unaltered in the self-consistent calculation. Freezing the occupation of the valence-band states can be considered as a first-order approximation that will be kept along the self-consistent stages. In the calculation of the interaction energy (see Sec. III) all the changes due to orthogonalization effects, the electron-nucleus interaction, and the electron-electron interaction between adsorbate and all surface states are included.

6. Interaction energy

The interaction energy is obtained as the difference between the average of the Hamiltonian for a given distance R of the adsorbate from the surface and that corresponding to the subsystem at infinite separation

$$E_{\mathrm{int}}=(\langle H^{\mathrm{ads}}\rangle+\langle H^{\mathrm{sub}}\rangle+\langle H^{\mathrm{int}}\rangle+[X]+V_{n-n})_R$$
$$-(\langle H^{\mathrm{ads}}\rangle+\langle H^{\mathrm{sub}}\rangle+[X])_{\infty};$$

when $R\rightarrow\infty$, both $\langle H^{\mathrm{int}}\rangle$ and V_{n-n} vanish. The explicit LCAO expression for the interaction energy is

$$E_{\mathrm{int}}=\sum_{\alpha\sigma}(E^{\sigma}_{\alpha}\langle n_{\alpha\sigma}\rangle-\varepsilon^{\sigma\mathrm{HF}}_{\alpha}\langle n_{\alpha\sigma}\rangle_{\infty})-\tfrac{1}{2}\sum_{\alpha\sigma}\left\{U^{0}_{\alpha}\langle n_{\alpha-\sigma}\rangle+\sum_{\beta(\neq\alpha)}(J^{0}_{\alpha\beta}\langle n_{\beta-\sigma}\rangle+\tilde{G}_{\alpha\beta}\langle n_{\beta\sigma}\rangle)\right\}\langle n_{\alpha\sigma}\rangle$$
$$+\tfrac{1}{2}\sum_{\alpha\sigma}\left\{U^{0}_{\alpha}\langle n_{\alpha-\sigma}\rangle_{\infty}+\sum_{\beta(\neq\alpha)}(J^{0}_{\alpha\beta}\langle n_{\beta-\sigma}\rangle_{\infty}+\tilde{G}_{\alpha\beta}\langle n_{\beta\sigma}\rangle_{\infty})\right\}\langle n_{\alpha\sigma}\rangle_{\infty}+\sum_{i\bar{R}_s\sigma}\left\{-\sum_{\bar{R}_a}V^{Z_{Ra}}_{ii}-\sum_{\alpha}S_{\alpha i}\tilde{T}^{\sigma}_{\alpha i}\right.$$
$$\left.+\tfrac{1}{4}\sum_{\alpha}S^{2}_{\alpha i}\left[\left(\bar{\varepsilon}_i-V_{ii}+\sum_{\beta}J^{0}_{\beta i}\langle n_{\beta-\sigma}\rangle+\sum_{\beta(\neq\alpha)}G^{0}_{\beta i}\langle n_{\beta\sigma}\rangle\right)-\left(\varepsilon^{\sigma\mathrm{HF}}_{\alpha}-\sum_{\bar{R}_{s'}}V^{Z_{Rs'}}_{\alpha\alpha}+\sum_{j\bar{R}_{s'}}J^{0}_{\alpha j}\langle n_{j-\sigma}\rangle+\sum_{j(\neq i)\bar{R}_{s'}}G^{0}_{\alpha j}\langle n_{j\sigma}\rangle\right)\right]\right\}$$
$$\times\langle n_{i\sigma}\rangle+\sum_{\alpha\sigma}\sum_{i\bar{R}_s}(\tilde{T}^{\sigma}_{\alpha i}-\tilde{G}_{\alpha i}\langle c^{\dagger}_{i\sigma}c_{\alpha\sigma}\rangle)\langle c^{\dagger}_{\alpha\sigma}c_{i\sigma}\rangle+V_{n-n}\,. \tag{23}$$

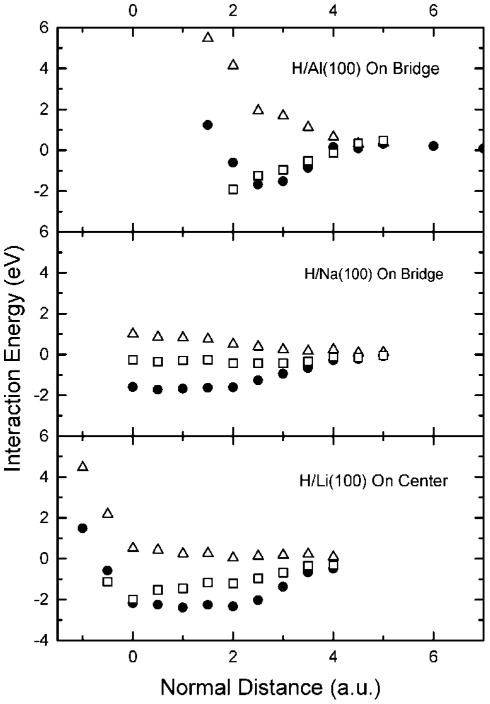

FIG. 1. Interaction energy as a function of the distance between the adsorbate and the first plane of surface atoms. Circles: HF calculation that includes the renormalization of the hopping term through the nonlocal exchange interaction [Eq. (13)], and the atomic $T_{\alpha i}^{\sigma}$ parameters calculated with reference to an orthonormalized set of functions for each dimeric subsystem [Eq. (12)] [option (a)]. Triangles: results obtained by neglecting the exchange contribution to the hopping term ($\langle c_{\alpha\sigma}^{\dagger} c_{i\sigma} \rangle \equiv 0$) [option (b)]. Squares: complete HF calculation, but considering an overlap expansion up to second order in defining the atomic couplings $T_{\alpha i}^{\sigma}$ [option (c)].

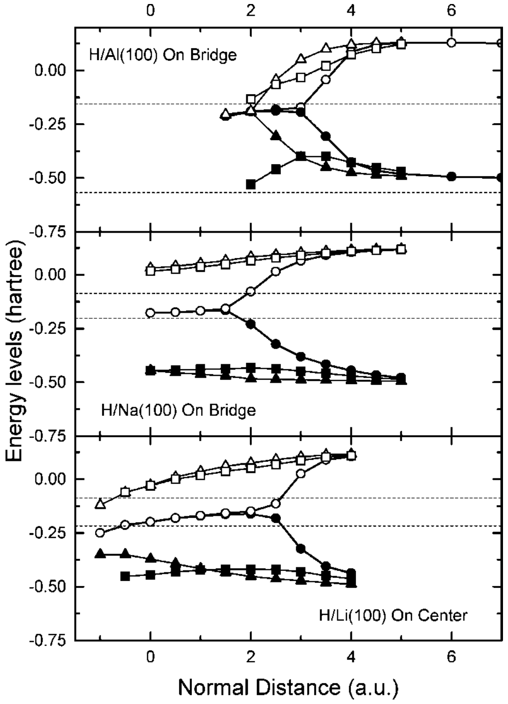

FIG. 2. Variation of the hydrogen levels vs atom-surface distance. The symbols correspond to the cases included in Fig. 1. Solid and open symbols indicate spin-up and -down, respectively.

Again, not only do the hybridizations effects on the adsorbate contribute, but the corresponding changes for direct interactions and orthogonalization in the solid are also included. Otherwise the fourth term in Eq. (23) (the sum over i, R_s, and σ) vanish identically.

III. RESULTS AND DISCUSSION

A. Interaction energy, energy levels, and occupation numbers of the adsorbate

To test the possibilities of the bond-pair Hamiltonian proposed to describe the atom-surface interaction, we have applied the formalism to the following H-metal systems: H/Li(100), H/Na(100), and H/Al(100). Several adsorption sites and crystallographic faces for these systems were examined with results that show the same kinds of general trends in all cases.[46] With regards to the electronic structure of each substrate, surfaces with growing degrees of complexity were considered in going from Li to Al. In the Li case, only s-like valence and inner bands are considered; while for Na p-like inner bands are also included. In the case of Al, s- and p-like valence and core bands are involved. In our simplified description, the sp-band states will be assumed to be nonhybridized.

It is worth comparing the effects of some of the different approximations on the hopping term against that leading to a good description of the adsorption process [Eq. (13)]. Figure 1 shows results of the interaction energy as a function of the distance between the adsorbate and the first surface plane of atoms for the three systems under consideration. Three situations are examined: (a) HF calculation including the renormalization of the hopping term through the nonlocal exchange interaction [Eq. (13)], with the atomic $T_{\alpha i}^{\sigma}$ parameters calculated with reference to an orthonormalized set for each dimeric subsystem [Eq. (12)]. (b) The same as (a), but neglecting in the hopping term the exchange contribution $\langle c_{\alpha\sigma}^{\dagger} c_{i\sigma} \rangle = 0$. (c) HF results obtained by an overlap expansion up to second order to define the atomic couplings $T_{\alpha i}^{\sigma}$. From the comparison among these alternatives, it becomes clear that option (a) is the only one that leads to a physically acceptable description of the interaction between H and the metal surfaces. We observe that the exchange interaction enhances the hybridization between the adsorbate and the surface states, resulting in an attractive contribution to the interaction energy. On the other hand, the calculation of $T_{\alpha i}^{\sigma}$ using an overlap expansion [option (c)] leads to unphysical results for these interacting systems. This shows that our HF model calculation, without using semiempirical parameters, is very sensitive to the contributions that define the hopping term. The same conclusions can be extracted from an analysis of the variation of the hydrogen up and down level positions against the atom-surface distance (Fig. 2). At large separation distances and assuming that $\langle n_{\alpha\uparrow} \rangle = 1$ ($\langle n_{\alpha\downarrow} \rangle = 0$), $E_{\alpha}^{\uparrow}$ tends to the ionization level $I = -0.5$ hartree, while $E_{\alpha}^{\downarrow}$ goes to the affinity level $A = I + U^0 = 0.125$ hartree. At closer distances and under option (a), one observes that $E_{\alpha}^{\uparrow}$ is shifted upward while the $E_{\alpha}^{\downarrow}$ goes downward, showing the expected correspondence with $\langle n_{\alpha\downarrow} \rangle$ and $\langle n_{\alpha\uparrow} \rangle$, respectively (Fig. 3), predicted by the HF approximation of the Coulomb term within the usual AN model.[27] At short distances, where

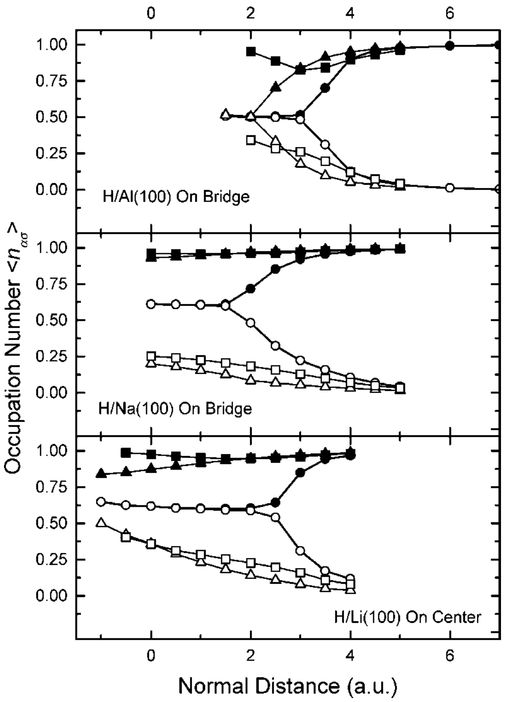

FIG. 3. Variation of the occupation number with the atom-surface distance. The symbols are the same as in Fig. 1. Solid and open symbols indicate spin-up and -down, respectively.

the hybridization between the atom and the surface states become large, the two levels merge into a degenerated level. Within this range, their broadening, caused by interactions with the surface, do not allow one to distinguish between them. This correlated behavior of the hydrogen levels is lost or poorly described when an incorrect prescription is used for the hopping term. This is illustrated in Fig. 4, which shows the variation of the hydrogen levels as a function of the average occupation number $[E_\alpha^\sigma = E_\alpha^\sigma(\langle n_{\alpha-\sigma}\rangle)]$ for the H/Li(100) on-center case. Each point corresponds to a different atom-surface distance. The linear relationship $E_\alpha^\sigma = \varepsilon_\alpha^0 + U_\alpha^0\langle n_{\alpha-\sigma}\rangle$ ($\varepsilon_\alpha^0 = -0.5$ hartree and $U^0 = 0.625$ hartree) is also plotted in this figure. One observes that a hopping term, renormalized by the exchange contributions selected consistently with the mean-field approximation, produces a behavior of the diagonal term E_α^σ having the usual functional form $E_\alpha^\sigma = \varepsilon_\alpha^0 + U_\alpha^0\langle n_{\alpha-\sigma}\rangle$ given by the AN model, within an ample range of distances. Omitting these contributions to the hopping term gives rise to an incorrect balance among the diagonal and nondiagonal Hamiltonian parameters, leading to inconsistencies in the behavior of the hydrogen level positions. We suggest this is a relevant result that confirms the importance of adopting a unified treatment to construct, from an *ab initio* basis, the whole set of parameters that enter into the effective mean-field Hamiltonian. Fedyanin *et al.*[31] arrived at similar conclusions by analyzing an extension of the standard AN model, that includes a parametrized hopping term depending on the occupation of the adatom. They found that for some selected sets of parameter values, a HF calculation of the charge-transfer process can be favorably improved as compared with calculations that include perturbative corrections caused by the residual electronic correlation. They emphasized the importance of defining the hopping term as derived from a HF approximation on a first-principles basis consistently with other terms,[50] as to ensure a good description of charge transfer processes.

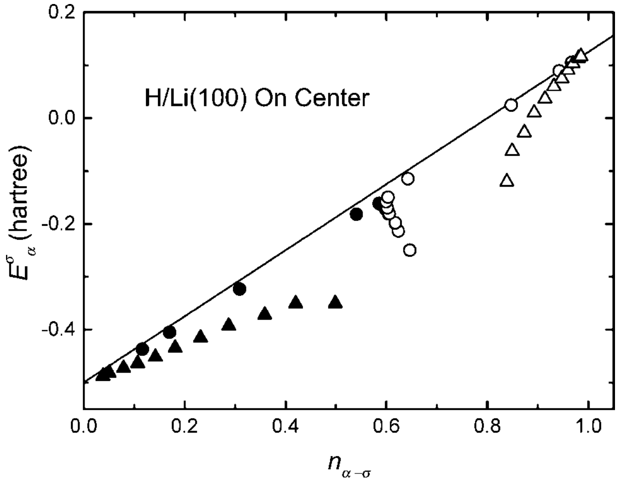

FIG. 4. Variation of the hydrogen levels as a function of the average occupation number. Circles: option (a). Triangles: option (b). Solid and open symbols correspond to spin-up and -down, respectively. The solid line represents the function $E_\alpha^\sigma = \varepsilon_\alpha^0 + U_\alpha^0\langle n_{\alpha-\sigma}\rangle$ ($\varepsilon_\alpha^0 = -0.5$ hartree and $U_\alpha^0 = 0.625$ hartree).

B. Joining the different interaction regions

Figure 5(a) shows that the HF results fail when R is increased, since they assume small positive values corresponding to a barrier. In contrast to the case of hydrogen dissociative adsorption, in atomic adsorption no barrier is to be expected. However, this it is not surprising in view of the fact that long-range effects have been ignored in our calculation. The ample range of distances involved in the description of the atom-surface interaction requires a detailed balance of the contributions to the basic potential terms and, depending on the distances of interest, different theoretical approaches have been proposed.[1] Thus, in the range of large distances ($z \geqslant 4-5$ a.u.), the position and width of the hydrogen level are calculated including potential terms that describe the electron scattering by the surface in the presence of the proton.[10,11] Basically, the interaction between the electron and the proton electrical image is the potential that accounts for electron correlation at the surface. The atom-surface potential interaction behaves as the classical image potential at large distances, while, at intermediate distances, a smeared surface charge density is induced by the positive core, as well as by the change in the exchange-correlation potential.[10,11] In these kinds of calculations, it has been found that the level width is very sensitive to the details of the potential in the surface region. In the case of physisorbed species, well-behaved interaction energies can be obtained by adding the attractive long-range van der Waals potential[33–35] to the repulsive short-range contributions. Zaremba and Kohn[33] found that, to lowest order in the overlap between the metal and atom states, the HF interaction energy provides an accurate description of the short-range interaction between the metal surface and a low-energy helium atom. Harris and Liebsch[35] argued that the neglected correlation terms are small as compared with the corresponding

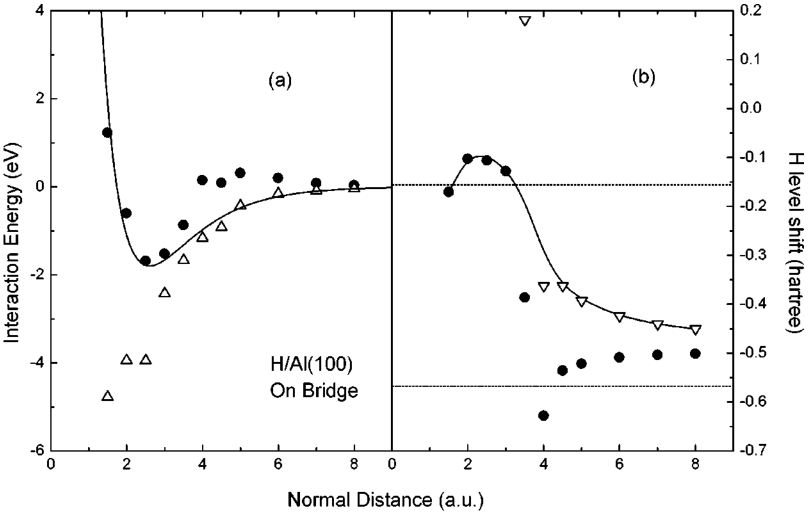

FIG. 5. Joining the results obtained from (a) (circles) and (b) (triangles) calculation prescriptions. (a) Interaction energy. (b) H level shift.

exchange contributions that are treated exactly in this approximation. In the case of chemisorption, reactive adsorbates are characterized by the fact that new electronic configurations are required in order to describe the sharing of electrons between an adsorbate and substrate. Thus an empty (filled) electron state of the adsorbate at large separation from the surface may become shifted to energies either below or above the Fermi level of the solid as the adsorbate becomes closer to the substrate. Consequently, as long as the substrate acts as an electron reservoir, the adsorbate occupancy will change accordingly. All these effects are fairly well described by a HF approximation in the chemisorption region. However, at medium and large separations, the long-range effects due to electronic correlation become important. Thus, a calculation that allows for a description of the adsorption process covering the entire range of distances represents a very hard task.[1] Many authors have put efforts into including features that are relevant in the chemisorption region, while renouncing to consider those which become important at large distances.[3,27,47–49] On the other hand, model calculations leading to well-behaved interaction potentials, able to provide a good description of shifts and widths of the adsorbate levels, are only valid at large separations ($z \gtrsim 4-5$ a.u.).[10,11]

Analyzing our results [Fig. 5(a)] for the interaction energy, we observe that the expected behavior is well described in the strong interaction region ($z \lesssim 3$ a.u.), where it is expected that short-range contributions dominate. For distances larger than 3–4 a.u., our model calculation seems to fail in giving an adequate description of the transition between the chemisorption (strong interaction) and the asymptotic or weak-interacting region. This failure is more evident in H/Al than in H/Li and H/Na (see Fig. 1) because of the increased complexity in the electronic structure of Al surfaces. Consequently, short-range contributions such as hybridizations, charge exchange, etc., become more relevant. As the collective effects involved in the surface response are ignored in our model, the net result is to produce an undesirable unbalance between short- and large-range contributions in the intermediate-distance region. To avoid this we propose to adapt our model calculation to distances far from the surface. Obviously if we neglect those contributions mainly responsible for the strong hybridization and mixing at short distances, we will arrive at a very poor description of the chemisorption but at the same time eliminate the source of unbalance in the asymptotic region. Thus in our prescription the terms that will not be considered are those that redefine the exchange interaction $(-\tilde{G}_{\alpha\mathbf{k}}\langle c^{\dagger}_{\mathbf{k}\sigma}c_{\alpha\sigma}\rangle)$, and also those related to the shift of the substrate valence levels caused by the orthogonalization requirements [Eq. (9)]. The results obtained under this prescription are also included in Fig. 5(a), showing a more adequate behavior for distances larger than 3–4 a.u. Our final suggestion is to join the results obtained under both prescriptions by fitting them with a smooth curve like that shown in Fig. 5(a).

The same sort of failure of our model calculation is reflected by the asymptotic behavior of the shift of the hydrogen energy levels by the interaction with the surface. Again, this can be attributed to the neglected electron-correlation effects in the solid. It is known that the correct behavior of the level shift at large distances should follow a classical image potential $1/4(z-z_0)$, where z_0 is the distance measured from the image plane.[11] We found that by adding the image potential to our self-consistent HF results of $E^{\sigma}_{\alpha}+\Lambda^{\sigma}(E^{\sigma}_{\alpha})$, we can reproduce a well-behaved adjustment at larger distances [Fig. 5(b)]. A matching of this result with the complete HF calculation of $E^{\sigma}_{\alpha}+\Lambda^{\sigma}(E^{\sigma}_{\alpha})$, assumed to give the correct answer for distances within the typical chemisorption region, is then performed. In this form, a satisfactory description of the adsorbate energy level variation can be obtained over an ample range of distances, as shown in Fig. 5(b).

C. Dependence on the number of adsorbate neighbors

As in our proposal the interaction energy results from the superposition of bond-pair interactions between the adsorbate and the atoms of the solid, one immediate question concerns the dependence on the number of substrate atoms included in the calculation. Our results in Fig. 6 show that, on practical terms, rapid convergence in the sum over bond pairs can be achieved by retaining only contributions coming from the nearest neighbors to the adsorbate. Thus our modeling supports the localized nature of the adatom adsorption process.

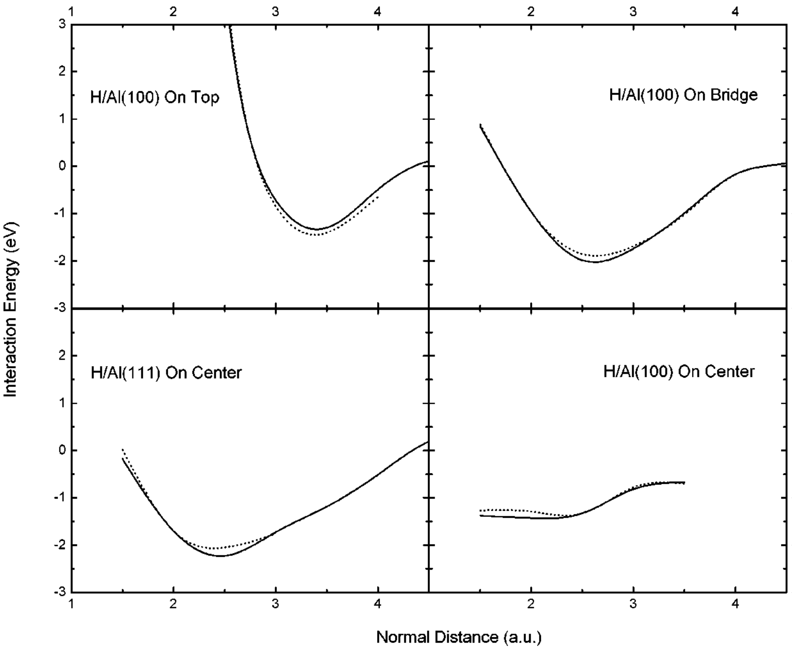

FIG. 6. Dependence on the number adsorbate neighbors. (———), next-nearest neighbors. (. . . . . . .), second-nearest neighbors.

D. Comparison with other existing results

The combinations of adatom and substrate systems studied in this paper have been considered by other authors under different theoretical approaches. These go from extended models for the substrate within a LSDA or GGA to the very localized clusterlike picture of the solid, passing through embedding cluster methods. Also the results obtained by García-Vidal *et al.*[39] (GV), based on a tight-binding model Hamiltonian, involve the same general ideas applied in this work.[50,51] Apart from the fact that these authors were limited to considering only a fraction of an adsorbate monolayer interacting with the surface as a result of their calculation technique, the most noticeable differences with our procedure come from (i) their local approximation of the exchange term in order to simulate correlation effects, and (ii) the fact that their hopping term is obtained by resorting to the Bardeen tunneling current concept.

1. H/Al(100)

The interaction energy for the on-bridge adsorption site on this system, after the joining procedure described in Sec. III B, is compared with that obtained by Hjelmberg[3] within a LSDA and also with results by GV (Ref. 39) in Fig. 7(a). Binding energies, equilibrium distances, and vibrational frequencies for different adsorption sites (on-top, on-bridge, and on-center) are compared in Table I, in which we also include the GGA results.[52] An overall agreement can be observed among the different calculations. In coincidence with the other authors, and with the existent experimental data on this system[53] we found that the on-bridge adsorption site is the most stable. In particular, it is interesting to compare our results with those obtained under the LSDA and GGA methods: the GGA binding energy is -2.13 eV when the coverage is 1 ML, with a tendency to decrease to about -2.07 eV for <1 ML.[52] The LSDA result (-2.3 eV) differs from the GGA up to 25%, this being expected as the LSDA tends, in general, to overestimate binding energies. The difference between our results and those of the GGA is smaller than 0.1 eV at low coverage. We believe that this small difference (near to the numeric rounding errors) is an encouraging result, particularly if one takes into account the simplicity and transparency of this method against that involved in the DFT, LSDA, and GGA approaches.

Better agreement with GV is found for the on-bridge site than for the on-center site. This can be attributed to the fraction of the adsorbate monolayer they considered. In this case the repulsion between the hydrogen atoms will lower the binding energy more markedly for the on-center site, where the adsorbate-substrate atom distances became larger. Concerning the transferred charge, our results predict a charge excess on the hydrogen by 0.05, 0.05, and 0.01 electron for the on-center, on-bridge, and on-top adsorption sites, respec-

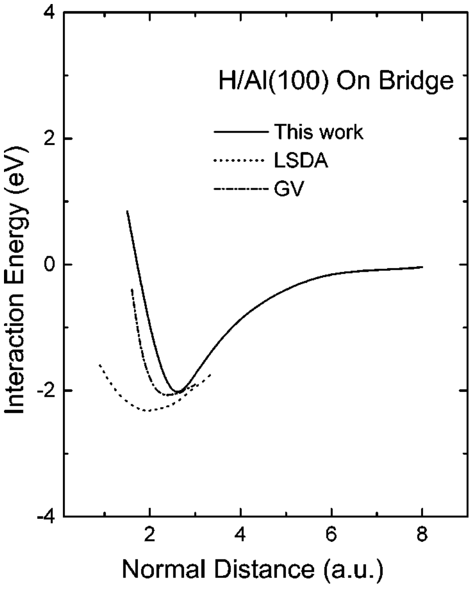

Figure 7/10 Ref.: BJ6653 P.G. Bolcatto et al

FIG. 7. Interaction energy as a function of the atom-surface distance. (———), present work. (- - - -), Ref. 3 (-·-·-), Ref. 39.

TABLE I. Binding energies E_B (eV), equilibrium distances R_e (a.u.), and vibrational frequencies ω_e (meV) for the H/Al(100) and H/Na(100) systems. The reference data were extracted from Refs. 3 (LSDA), 39 (GV), and 52 (GGA).

			E_B (eV)	R_e (a.u.)	ω_e (meV)
H/Al (100)	Top	This work	-1.5	3.39	199
		LSDA	-1.9	3.0	210
	Bridge	This work	-2.0	2.60	167
		LSDA	-2.3	2.0	130
		GGA	-2.13		
		GV	-2.07	2.4	
	Center	This work	-1.4	2.33	68
		LSDA	-1.4	2.4	70
		GV	-0.8	2.0	
H/Na (100)	Bridge	This work	-1.8		
		LSDA	-2.4		
	Center	This work	-1.8		
		LSDA	-2.1		

tively. These results are also in agreement with the values reported by GV.

The corresponding vibrational frequencies have been calculated by fitting the interaction energy curves along the whole separation range with a Morse-like potential, and performing a harmonic approximation around the equilibrium distances. The values 167 and 199 meV obtained for the on-bridge and on-top positions, respectively, are in fairly good agreement with the values assigned to the vibrational modes obtained from electron-energy-loss spectroscopy[53] data (139 and 226 meV, respectively). Our calculated frequencies are somewhat larger than LSDA results for the on-bridge and on-center sites, while for the on-top position a smaller value was obtained. In any case, for all the analyzed surface faces we checked that $\omega_e^{\mathrm{Top}} > \omega_e^{\mathrm{Bridge}} > \omega_e^{\mathrm{Center}}$. This provides another indication of the localized nature of the interactions involved. The equilibrium properties of a chemisorbed system emerge from the balance of two competitive effects: (i) the kinetic repulsion due to the overlap between the adsorbate and substrate electronic densities, and (ii) the Coulombic attraction between the substrate nuclei and the adsorbate electrons. If the former becomes the dominant interaction, it may be anticipated that the adsorbate will ''see'' the solid as some sort of jellium, and consequently the vibrational frequencies should be practically independent of the adsorption site. Conversely, if the second kind of interaction dominates, a marked dependence of the vibrational frequency on the adsorption site is expected. Taking into account that as the adsorbate goes away from the surface, atom-atom distances vary more slowly in the on-center case than for the on-bridge site, it turns out that the expected sequence should be $\omega_e^{\mathrm{Top}} > \omega_e^{\mathrm{Bridge}} > \omega_e^{\mathrm{Center}}$. Again these results are indicative of the role played by the localized nuclei-electrons interactions in the chemisorption process.

Figure 8(a) shows the hydrogen level shifts in front of an Al(111) face, obtained by joining our HF results with the corrected behavior by the image potential contribution at large distances, as discussed previously (Fig. 5). Distances are measured with reference to the first plane of substrate atoms. The comparison with other existing results in the literature[9–11,13,54] shows that after adding the image potential term to the calculated HF level shifts, good agreement is

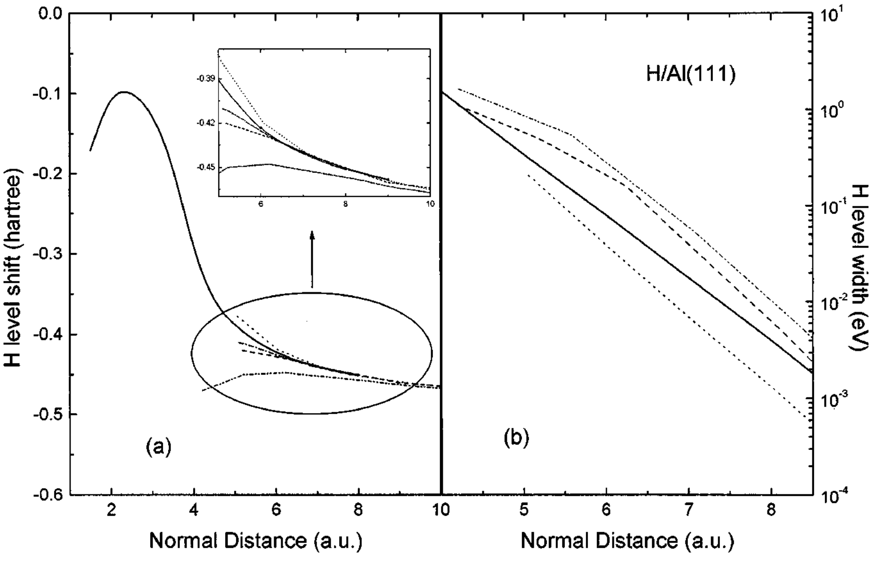

FIG. 8. (a) Ionization hydrogen level shifted by the interaction with an Al(111) surface. (b) Ionization hydrogen level width. (———), present work. (.........), Ref. 11. (- - - - -), Ref. 10. (-·-·-), Ref. 54. (-··-··-), Ref. 13.

achieved with some authors[10,11] [see the inset in Fig. 8(a)].

The H level widths obtained at large distances are plotted in Fig. 8(b). The agreement with other authors' results[10,11,13,54] enforce the argument that the HF approximation is also adequate in the range where correlation effects are expected to be important. As can be observed from Fig. 8, this gives rise to a large distance behavior comparable to that obtained by considering a detailed analysis of the different potential terms for an electron in the presence of a proton and a surface.

The widths and shifts of the adsorbate level vs distance can be easily transferred to a semiclassical description of collision processes between atoms and surfaces, to calculate ionization and/or neutralization probabilities of the projectile.[10,11] Our results prove to be as good as the other ones for this purpose. However, our model calculation also provides the distance-dependent Hamiltonian parameters required to perform a full quantum-mechanical formulation of the time-dependent collision processes within an AN picture.[40]

2. H/Na(100)

The interest in this system relies on the contrasting differences with respect to the H/Al(100) one. The Na metallic surface is a more open surface (bcc) with a smaller electronic density ($r_s = 3.99$), and theoretically[2,3] and experimentally[55] existent information point out the possibility of hydrogen diffusion. Also, strong relaxation of the Na surface due to its small cohesive energy can occur when hydrogen is adsorbed. This leads to the formation of NaH units with a crystalline fcc structure. In Fig. 9, the calculated interaction energy for the on-bridge adsorption site is compared with results of Ref. 3. The lack of a manifest barrier at distances close to the surface suggests the possibility of hydrogen diffusion in both calculations. However, neither our calculation nor Hjelmberg's includes surface relaxation effects that can be of importance in this case. In Table I, values of the binding energies and equilibrium distances are compared for the on-bridge and on-center adsorption sites.

3. H/Li(100)

The adsorption of hydrogen by a Li surface has been treated on the basis of a cluster description of the Li surface by Beckman and Koutecky[22] (BK) and by Hira and Ray[23] (HR). In essence these works considered clusters of up to ten Li atoms, performing an unrestricted HF calculation corrected by correlation effects. Bonacic-Koutecky *et al.*[24] (BGGCK) also performed a cluster calculation, but allowed for relaxation so as to minimize the total energy. As convergence with respect to the number of atoms in the cluster was not properly achieved, alternatives were proposed by Casassa and Pisani[8] (CP) based on an embedded cluster model within a restricted HF approximation, and others by Krüger and Rösch[25] which employ the moderately large embedded cluster (MLEC) formalism. This system has also been studied within the local-density-functional framework in Ref. 56 using the FILMS code.[57]

In Table II, our results for the binding energies, equilibrium distances, and charge transfer to the hydrogen atom are compared for an on-center adsorption site. One can observe how the BK and HR calculations greatly depend on the size of the cluster considered. The differences in the sign of the corrections due to correlation effects are indicative of the instabilities associated with the small cluster descriptions. The binding energy obtained with our bond-pair Hamiltonian is in good overall agreement with the HF values obtained by BK and HR, and it can also be observed that these results tend toward ours as the size of the cluster size is increased. The CP and BGGCK binding energies show the largest discrepancy with reference to our results, and these differences can be attributed to either the embedding technique used by CP calculation, or to the geometry optimization performed in

TABLE II. Binding energies E_B (eV), equilibrium distances R_e (a.u.), and charge transfer n for the H/Li(100) system. The reference data were extracted from Refs. 8 (CP), 22 (BK), 23 (HR), 24 (BGGCK), 25 (MLEC), 39 (GV), and 56 (FILMS). In CP, BK, HR, and BGGCK, the number of Li atoms in the first, second, and third crystalline planes used in the definition of the cluster are indicated. In CP, Sn denotes the number of slabs of the crystalline substrate. Value between parentheses in the binding-energy column correspond to a calculation including correlation effects.

		E_B (eV)	R_e (a.u.)	Δn
On center	This work	-2.4	0.3	-0.21
	CP (4,1,4) $S3$	-3.3	0.0	-0.46
	(4,1,4) $S5$	-3.6	0.0	-0.46
	BK (4,0)	-1.7 (-1.4)	0.0	
	(4,5)	-2.2 (-2.7)	0.5	
	HR (4,0)	-1.9 (-2.0)	0.45	-0.44
	(4,5)	-2.2 (-3.0)	0.5	-0.36
	MLEC Li_{26}	-2.48	0.34	-0.12
	Li_{30}	-2.32	0.34	-0.22
	FILMS $\Theta = 1$ ML	-2.99	0.25	-0.31
	$\Theta = \frac{1}{2}$ ML	-2.90	0.28	-0.28
	GV	-2.0	-0.5	-0.60
Optimized geometry	BGGCK (5)	-2.7 (-3.0)		
cluster	(7)	-2.8 (-2.7)		

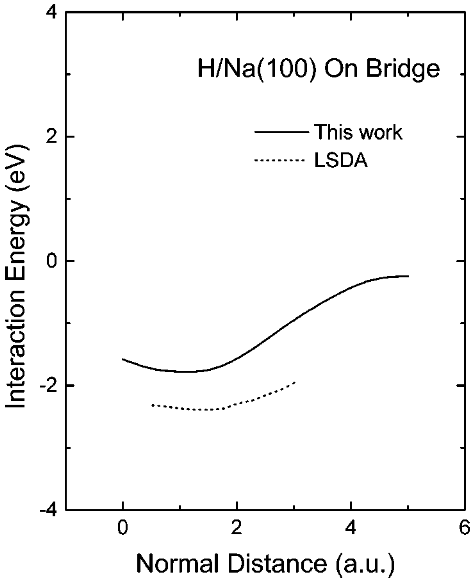

FIG. 9. Interaction energy for the H/Na(100) on-bridge site. (———), present work. (.........), Ref. 3.

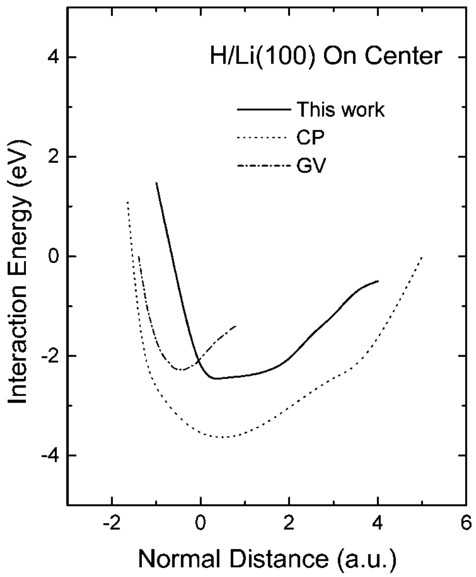

FIG. 10. Interaction energy for the H/Li(100) on-center site. (———), present work. (.........), Ref. 8. (-·-·-), Ref. 39.

the BGGCK case. The value of GV is smaller than our result, and this can be understood by taking into account the repulsion effects between adsorbates in their case. The comparison with FILMS results at low coverage show that these become similar to ours (this behavior also remains for the other properties). Fairly good agreement is also found with MLEC results, the differences being smaller than 5%.

Concerning the equilibrium distances, all calculations give a very small value $(-0.5\ \text{a.u.} \leqslant R_e \leqslant 0.5\ \text{a.u.})$ which is indicative of the open crystalline structure of bcc Li. Better agreement is found with MLEC and FILMS values. The charge transfers calculated by either CP, BK, or HR are not strictly comparable with ours, since they employed a Mulliken population analysis in their calculations, although all agreed in predicting that hydrogen acts as a charge receptor $(\Delta n < 0)$. The same tendency emerges for MLEC and FILMS predictions. In Fig. 10, our results for the interaction energy vs distance are compared with those obtained by CP and GV.

IV. CONCLUSIONS

In this work we have proposed the use of a model Hamiltonian based on an AN picture solved in the HF approximation that allows one to include either extended and/or localized characters of surface states. The localized nature of the adsorption process is taken into account through an *ab initio* description of the interaction between the adsorbate and the substrate atoms. The resulting bond-pair Hamiltonian contains, in a natural and self-consistent way, the atomic nature of the interactions plus the extended features of the surface system, two main ingredients pursued by embedding cluster techniques. Orthogonalization contributions to the diagonal terms are included up to a second order in the overlaps, while three center integrals contributing to the hopping are approximated by a superposition of orthogonalized dimeric terms, selected consistently with the above-mentioned overlap expansion. On the other hand, the nonlocal exchange interaction contributes to renormalizing the hopping term parameters within a suitable HF self-consistent procedure. Our results for the interaction energy as well as for the adsorbate levels at large separation distances suggest the convenience of disregarding in this region, those contributions that are mainly responsible for the strong hybridization and mixing within the typical chemisorption distances. Well-behaved curves are obtained by joining the results from these two calculation prescriptions.

---

[1] B. I. Lunqvist, in *Theoretical Aspects of Adsorption in Interaction of Atoms and Molecules with Solid Surfaces*, edited by V. Bortolani, N. H. March, and M. P. Tosi (Plenum, New York, 1990).

[2] B. I. Lundqvist, O. Gunnarsson, H. Hjelmberg, and J. K. Nørskov, Surf. Sci. **68**, 158 (1979).

[3] H. Hjelmberg, Surf. Sci. **81**, 539 (1979).

[4] T. B. Grimley, J. Phys. C **3**, 1934 (1970); and in *The Nature of the Surface Chemical Bond*, edited by T. N. Rhodin and G. Ertl (North-Holland, Amsterdam, 1979).

[5] R. Hoffman, Rev. Mod. Phys. **60**, 601 (1988).

[6] M. Petersen, S. Wilke, P. Ruggerone, B. Kohler, and M. Scheffler, Phys. Rev. Lett. **76**, 995 (1996).

[7] E. Hult, Y. Andersson, and B. I. Lundqvist, Phys. Rev. Lett. **77**, 2029 (1996).

[8] S. Casassa and C. Pisani, Phys. Rev. B **51**, 7805 (1995).

[9] J. Merino, N. Lorente, P. Pou, and F. Flores, Phys. Rev. B **54**, 10 959 (1996).

[10] P. Nordlander and J. C. Tully, Phys. Rev. Lett. **61**, 990 (1988); Surf. Sci. **212**, 207 (1989); Phys. Rev. B **42**, 5564 (1990); **46**, 2584 (1992); P. Nordlander, Scanning Microsc. Suppl. **4**, 353 (1990).

[11] A. G. Borisov, D. Teillet-Billy, and J. P. Gauyacq, Nucl. Instrum. Methods Phys. Res. B **78**, 49 (1993); Phys. Rev. Lett. **68**, 2842 (1992); D. Tellet-Billy and J. P. Gauyacq, Surf. Sci. **269**, 162 (1992); **278**, 99 (1992).

[12] J. Merino, N. Lorente, W. More, F. Flores, and M. Yu. Gusev, Nucl. Instrum. Methods Phys. Res. B **125**, 250 (1997); J. Me-

rino, N. Lorente, F. Flores, and M. Yu. Gusev, *ibid.* **125**, 288 (1997).

[13] S. A. Deutscher, X. Yang, and J. Burgdörfer, Phys. Rev. A **55**, 466 (1997).

[14] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[15] O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

[16] G. S. Painter and F. W. Averill, Phys. Rev. B **26**, 1781 (1982).

[17] A.G. Eguiluz, M. Heinrichsmeier, A. Fleszar, and W. Hanke, Phys. Rev. Lett. **68**, 1359 (1992); A. G. Eguiluz, J. J. Deisz, M. Heinrichsmeier, A. Fleszar, and W. Hanke, Int. J. Quantum Chem. **26**, 837 (1992); M. Heinrichsmeier, A. Fleszar, and A. G. Eguiluz, Surf. Sci. **285**, 129 (1993).

[18] B. Hammer, M. Scheffler, K. W. Jacobsen, and J. K. Nørskov, Phys. Rev. Lett. **73**, 1400 (1994).

[19] J. A. White and D. M. Bird, Chem. Phys. Lett. **213**, 422 (1993); J. A. White, D. M. Bird, M. C. Payne, and I. Stich, Phys. Rev. Lett. **73**, 1404 (1994).

[20] B. Hammer and J. K. Nørskov, Surf. Sci. **343**, 211 (1994); B. Hammer, K. W. Jacobsen, and J. K. Nørskov, Phys. Rev. Lett. **69**, 1971 (1992); **70**, 3971 (1993).

[21] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. P. Pederson, D. J. Singh, and C. Fiolhais, Phys. Rev. B **46**, 6671 (1992); J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[22] H. O. Beckman and J. Koutecky, Surf. Sci. **120**, 127 (1982); G. Pacchioni, J. Koutecky, and H. O. Beckmann, *ibid.* **144**, 602 (1984).

[23] A. K. Ray and A. S. Hira, Phys. Rev. B **37**, 9943 (1988); A. S. Hira and A. K. Ray, *ibid.* **40**, 3507 (1989); Surf. Sci. **234**, 397 (1990); **249**, 199 (1991).

[24] V. Bonacic-Koutecky, J. Gaus, M. F. Guest, L. Cespiva, and J. Koutecky, Chem. Phys. Lett. **206**, 528 (1993).

[25] S. Krüger and N. Rösch, J. Phys.: Condens. Matter **6**, 8149 (1994).

[26] P. W. Anderson, Phys. Rev. **124**, 41 (1961).

[27] D. M. Newns, Phys. Rev. **178**, 1123 (1969); J. P. Muscat and D. M. Newns, Prog. Solid State Chem. **9**, 1 (1978).

[28] W. Brenig and K. Schonhammer, Z. Phys. **267**, 201 (1974).

[29] R. Taranko, E. Taranko, and G. M. Gavrilenko, Surf. Sci. **231**, 113 (1990).

[30] E. C. Goldberg and M. C. G. Passeggi, J. Phys.: Condens. Matter **8**, 7637 (1996).

[31] V. K. Fedyanin, G. M. Gavrilenko, R. Taranko, and E. Taranko, Surf. Sci. **230**, 329 (1990); G. M. Gavrilenko, R. Taranko, E. Taranko, and V. K. Fedyanin, *ibid.* **203**, 212 (1988).

[32] G. Doyen, Surf. Sci. **59**, 461 (1976); G. Doyen and G. Ertl, *ibid.* **65**, 641 (1977); **69**, 157 (1977).

[33] E. Zaremba and W. Kohn, Phys. Rev. B **15**, 1769 (1977); **13**, 2270 (1976).

[34] P. Nordlander and J. Harris, J. Phys. C **17**, 1141 (1984); P. Nordlander, Surf. Sci. **126**, 675 (1983).

[35] J. Harris and A. Liebsch, J. Phys. C **15**, 2275 (1982); Phys. Rev. Lett. **49**, 341 (1982).

[36] K. Schönhamer, Phys. Rev. B **13**, 4336 (1976); Z. Phys. B **21**, 389 (1975).

[37] T. L. Einstein, Phys. Rev. B **11**, 577 (1975).

[38] P. G. Bolcatto, E. C. Goldberg, and M. C. G. Passeggi, Phys. Rev. A **50**, 4643 (1994).

[39] F. J. García-Vidal, A. Martín-Rodero, F. Flores, J. Ortega, and R. Pérez, Phys. Rev. B **44**, 11 412 (1991).

[40] Evelina A. García, P. G. Bolcatto, and E. C. Goldberg, Phys. Rev. B **52**, 16 924 (1995); in *Surfaces, Vacuum and Their Applications*, edited by I. Hernandez Calderón and R. Asomoza (AIP, New York, 1996), p. 612.

[41] The pure atomic functions used in this work are a self-consistent combination of Gaussian orbitals extracted by S. Huzinaga, J. Chem. Phys. **42**, 1293 (1965); and S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, and H. Tatewaki, in *Gaussian Basis Set for Molecular Calculations*, edited by S. Huzinaga (Elsevier, Amsterdam, 1984).

[42] P. O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

[43] J. A. Bearden and A. F. Burr, Rev. Mod. Phys. **39**, 125 (1967).

[44] P. G. Bolcatto, E. C. Goldberg, M. C. G. Passeggi, and F. Flores, Anales Asociación Física Argentina **6**, 4 (1994).

[45] E. N. Economou, in *Green's Functions in Quantum Physics*, edited by P. Fulde, Springer Series in Solid-State Sciences Vol. 7 (Springer-Verlag, Berlin, 1983).

[46] P. G. Bolcatto, E. C. Goldberg, and M. C. G. Passeggi (unpublished).

[47] N. D. Lang and A. R. Williams, Phys. Rev. Lett. **34**, 531 (1975); **37**, 212 (1976); Phys. Rev. B **18**, 616 (1978).

[48] O. Gunnarsson, H. Hjelmberg, and B. I. Lundqvist, Phys. Rev. Lett. **37**, 292 (1976); Surf. Sci. **63**, 348 (1977).

[49] J. K. Nørskov and N. D. Lang, Phys. Rev. B **21**, 2131 (1980); M. J. Stott and E. Zaremba, *ibid.* **22**, 1564 (1980); J. K. Nørskov, *ibid.* **26**, 2875 (1982); Phys. Rev. Lett. **48**, 1620 (1982).

[50] F. Flores, A. Martín-Rodero, E. C. Goldberg, and J. C. Durán, Nuovo Cimento **10D**, 303 (1988); E. C. Goldberg, A. Martín-Rodero, R. Monreal, and F. Flores, Phys. Rev. B **39**, 5684 (1989).

[51] R. Pérez, Ph.D. thesis, Universidad Autónoma de Madrid, 1992.

[52] R. Stumpf, Phys. Rev. Lett. **78**, 4454 (1997).

[53] J. Paul, Phys. Rev. B **37**, 6164 (1988).

[54] L. W. Bruch and Th. W. Ruijgrok, Surf. Sci. **79**, 509 (1979).

[55] J. Mundenar, R. Murphy, K. D. Tsuci, and E. W. Plummer, Chem. Phys. Lett. **143**, 593 (1988).

[56] U. Birkenheuer, J. C. Boettger, and N. Rösch, Surf. Sci. **341**, 103 (1995).

[57] U. Birkenheuer, J. C. Boettger, and N. Rösch, J. Chem. Phys. **100**, 6824 (1994).