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Molecular-orbital theory for chemisorption: The case of H on normal metals

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An *ab initio* linear combination of atomic orbitals (LCAO) method is presented to calculate the electronic properties of solids. This method is based on the following points: (i) The total solution of the electronic system is obtained using an expansion of various physical parameters up to second order in the overlap between the different atomic orbitals; extensions to large-overlap cases are also discussed. (ii) The total many-body Hamiltonian is reduced to a superposition of Hamiltonian bonds, defined for each pair of atomic orbitals. (iii) The parameters for hopping between two orbitals are related to the Bardeen tunneling currents between the same wave functions; these tunneling currents play, in our approach, the same role as pseudopotentials in the free-electron theory of solids. (iv) Many-body effects are treated using a Slater-like approximation for the exchange and correlation interaction. We show that a many-body Slater-like potential can be introduced within our LCAO approach. Our method has been demonstrated by considering the simple molecules H_2 and LiH. A further application has been made for the chemisorption problem of a hydrogen monolayer adsorbed on the Li(100) and Al(100) surfaces. Results are presented for the chemisorption energies, equilibrium distance of the adsorbed layer, and the density of states. Good agreement is found with other theoretical results and experiment. Our results indicate that the main mechanism for the hydrogen adsorption on simple metals is associated with the lowering of the hydrogen affinity level due to the electrostatic interaction with the metal atoms.

I. INTRODUCTION

The tight-binding (TB) or linear combination of atomic orbitals (LCAO) methods[1-3] are receiving increasing attention for the solution of various problems in solid-state physics. They are also used in the analysis of disordered solids, surfaces, or systems without three-dimensional translational symmetry: In these cases, extended wave functions can be described by a linear combination of the orbitals of constituent atoms. An obvious advantage of this approach is its computational simplicity that allows calculations to be performed that would otherwise be too time consuming when alternative methods are used. Recently, for example, TB molecular dynamics has been developed for different systems,[4,5] showing its applicability to complex situations with great accuracy.

Some theoretical effort has sought to put this localized picture on a fundamental basis.[6-8] In general, the TB description developed in these references is based on the stationary properties of the self-consistent solutions of the density-functional theory.

A more semiempirical approach has been used[9-11] to rationalize the TB method from the physical and the chemical trends of different materials. This approach is deeply related to the Hückel theory in molecular physics,[3] a method that has been extensively used in surface physics.[12] In this field, some people[13] have introduced model Hamiltonians improving over the Hückel approach in order to obtain a better description of the chemisorption problem.

As regards this last field of chemisorption, it is worth mentioning that a great deal of progress has been achieved in it by means of elaborate numerical calculations performed using the local-density approximation.[14,15] This approach has been successfully applied to simple atoms chemisorbed on metal and semiconductor surfaces, but only in very simple cases has it been possible to calculate the important physical properties of chemisorbed molecules. As in the case mentioned above of molecular dynamics, a TB method not relying on phenomenological parameters for the interface calculations would offer an alternative approach to the local-density-approximation (LDA) method in order to analyze complicated chemisorbed molecules.

In spite of all the work mentioned above, there is still a lack of a simple fundamental approach relating the TB Hamiltonians to the basic properties of the constituent atoms.

The aim of this work is, following Ref. 16 (hereafter I) to fill this gap, presenting an *ab initio* discussion of how to calculate the different parameters of a TB Hamiltonian using no adjustable parameter. This discussion includes one-electron and many-electron effects and is applied to the case of atomic hydrogen chemisorbed on normal-metal surfaces. The results obtained for this system give strong support to the method presented here.

In Sec. II we discuss the general approach we follow to obtain the TB Hamiltonian. Contact is made with molecular physics to check the method, and a discussion about how to calculate the many-body properties of a system described with a TB Hamiltonian is also presented. This is necessary in order to obtain reliable results for the electronic properties of any system. In Sec. III we discuss the case of H chemisorbed on normal metals. We have chosen to analyze two cases: hydrogen on Al and hydrogen on Li. For Al there are accurate LDA results,[14,22] and this system will allow us to make a reliable comparison between the results calculated with our approach and with LDA. The case of Li is also interesting because it is a metal of low density presenting a different behavior with respect to Al: as will be discussed in Sec. III, Al is a high density metal, as hydrogen chemisorbs on without penetrating the surface, contrary to the case for Li. Finally, in Sec. IV we present our conclusions and an evaluation of the method presented here.

II. GENERAL METHOD

The method we shall present in this paper is an extension of that initially developed in I. Our aim is to find a solution of the general Hamiltonian of a solid or an interface by using a linear combination of the orbitals associated with the atomic constituents[17] of the system. In I we introduced some of the main ingredients of this work.

(i) The total solution of the electronic system was obtained by expanding various physical parameters up to second order in the overlap S_{ij} between different orbitals, say ψ_i and ψ_j. Although this method was applied in I to a physisorption problem, we shall show below that it can also be adopted as well for other physical problems of interest in solids, where chemical bonds are important.

(ii) The crystal Hamiltonian was reduced in I to a superposition of bonds, defined by each pair of atomic orbitals. This will be shown below to be consistent with the expansion up to second order in the overlap coefficients.

(iii) The hopping parameters between two orbitals were related to the Bardeen tunneling current between the same wave functions. We shall extend this approach to a more general case below. The advantage of proceeding in this way is that the Bardeen tunneling current embodies all the information associated with the atomic core wave functions. Thus, we can say that the Bardeen tunneling currents play the same role as pseudopotentials in the free-electron theory of solids.

In this section we shall not only discuss these points in detail but also analyze how to include exchange and correlation in this LCAO method. As before, we will not use any adjustable parameter.

A. Overlap expansion and molecules

We shall discuss here the validity of the overlap expansion as used in our method to calculate the electronic properties of the system. The best way of analyzing this point is by considering simple systems for which exact solutions can be obtained. We have chosen for the sake of simplicity the molecules H_2 and LiH. The results obtained for these cases will illustrate clearly the points under discussion.

Let us start by considering two atoms 1 and 2, with one orbital per atom: for H_2, we choose the $1s$ levels, while for LiH we consider the $2s$ and the $1s$ wave functions, respectively (for the LiH case, the Li $1s$ wave function shall be introduced below but, for the time being, let us keep the dicussion to this simplified level). In our LCAO approach, those two wave functions are used to calculate the properties of our electronic system defined by the following Hamiltonian:

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_i \frac{Z_1}{\mid \mathbf{r}_i - \mathbf{R}_1 \mid} - \sum_i \frac{Z_2}{\mid \mathbf{r}_i - \mathbf{R}_2 \mid} + \frac{1}{2}\sum_{i,j\neq i} \frac{1}{\mid \mathbf{r}_i - \mathbf{r}_j \mid} + \frac{Z_1 Z_2}{d} \; , \qquad (1)$$

where $\mathbf{r}_i$ and $\mathbf{r}_j$ refer to the electron coordinates, and $\mathbf{R}_1$ and $\mathbf{R}_2$ are the coordinates of the nuclei having charges Z_1 and Z_2, respectively. Using the atomic orbitals, $\psi_1(\mathbf{r}-\mathbf{R}_1)$ and $\psi_2(\mathbf{r}-\mathbf{R}_2)$ in atoms 1 and 2, we introduce the orthogonal basis, ϕ_1 and ϕ_2, by means of the general equation

$$\phi_i = \sum_j (S^{-1/2})_{ij}\psi_j \; , \qquad (2)$$

where S_{ij} is the overlap between wave functions i and j. For a two-level system, $S^{-1/2}$ can be exactly calculated yielding the following equations:

$$\phi_1 = \lambda\psi_1 + \mu\psi_2 \; , \qquad (3a)$$

$$\phi_2 = \mu\psi_1 + \lambda\psi_2 \; , \qquad (3b)$$

where

$$\lambda = \frac{1}{2}\left(\frac{1}{(1+S)^{1/2}} + \frac{1}{(1-S)^{1/2}}\right)$$

and

$$\mu = \frac{1}{2}\left(\frac{1}{(1+S)^{1/2}} - \frac{1}{(1-S)^{1/2}}\right) \; ,$$

S being the overlap between orbitals ψ_1 and ψ_2, $S = <\psi_1 \mid \psi_2>$.

Wave functions ϕ_1 and ϕ_2 are used to write the many-body Hamiltonian in the following second-quantized form:

$$\hat{H} = \sum_\sigma (\varepsilon_1 \hat{n}_{1\sigma} + \varepsilon_2 \hat{n}_{2\sigma}) + \sum_\sigma (t + h_1 \hat{n}_{1-\sigma} + h_2 \hat{n}_{2-\sigma})(\hat{c}^\dagger_{1\sigma}\hat{c}_{2\sigma} + \hat{c}^\dagger_{2\sigma}\hat{c}_{1\sigma}) + U_1 \hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + U_2 \hat{n}_{2\uparrow}\hat{n}_{2\downarrow} + \sum_\sigma [J\hat{n}_{1\sigma}\hat{n}_{2-\sigma} + (J - J_x)\hat{n}_{1\sigma}\hat{n}_{2\sigma}] + \frac{Z_1 Z_2}{d} \; , \qquad (4)$$

where the usual creation and anihilation operators are introduced ($\hat{n}_{i\sigma} = \hat{c}^{\dagger}_{i\sigma}\hat{c}_{i\sigma}$).

In I it was noted that other terms, like $J_x\hat{c}^{\dagger}_{1\sigma}\hat{c}^{\dagger}_{2-\sigma}\hat{c}_{1-\sigma}\hat{c}_{2\sigma}$ or $J_x\hat{c}^{\dagger}_{1\sigma}\hat{c}^{\dagger}_{1-\sigma}\hat{c}_{2-\sigma}\hat{c}_{2\sigma}$ have been neglected in writing the Hamiltonian (4). It is worth realizing that the order of magnitude of the contribution of these terms to the total energy of the system is proportional to $J_x < \hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma} >< \hat{c}^{\dagger}_{2-\sigma}\hat{c}_{1-\sigma} >$, a term going like S^4, since $J_x \sim S^2$ and $< \hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma} >\sim< \hat{c}^{\dagger}_{2-\sigma}\hat{c}_{1-\sigma} >\sim S$. This means that the main terms kept in Eq. (4) are proportional to, or larger than, S^2: this is consistent with the overlap expansion that is going to be introduced presently. We should stress here that this argument is going to be used in the more general case, as a guide to select the main terms of the more general Hamiltonian for a solid.

The different terms of the Hamiltonian (4) are defined in the usual way; for instance:

$$\varepsilon_i = \int \phi_i(\mathbf{r}) \left(-\frac{\nabla^2}{2} - \frac{Z_1}{\mid \mathbf{r} - \mathbf{R}_1 \mid} - \frac{Z_2}{\mid \mathbf{r} - \mathbf{R}_2 \mid} \right) \phi_i(\mathbf{r}) d\mathbf{r} \ , \tag{5a}$$

$$U_i = \int \int \phi_i^2(\mathbf{r}) \frac{1}{\mid \mathbf{r} - \mathbf{r}' \mid} \phi_i^2(\mathbf{r}') d\mathbf{r}\, d\mathbf{r}' \ , \tag{5b}$$

$$J_x = \int \int \phi_1(\mathbf{r})\phi_2(\mathbf{r}) \frac{1}{\mid \mathbf{r} - \mathbf{r}' \mid} \phi_1(\mathbf{r}')\phi_2(\mathbf{r}') d\mathbf{r}\, d\mathbf{r}' \ . \tag{5c}$$

(See I for further details.)

The overlap expansion is introduced here by using Eqs. (3), and expanding the coefficients λ and μ up to second order in S. This yields the following equations:

$$\varepsilon_i = \varepsilon_i^{(0)} + \frac{S^2}{4}(\varepsilon_i^{(0)} - \varepsilon_j^{(0)}) - St \ , \tag{6a}$$

$$t = t^{(0)} - \frac{S}{2}(\varepsilon_1^{(0)} + \varepsilon_2^{(0)}) \ , \tag{6b}$$

$$h_i = h_i^{(0)} - \frac{S}{2}(U_i^{(0)} + J^{(0)}) \ , \tag{6c}$$

$$U_i = U_i^{(0)} + \frac{S^2}{2}(U_i^{(0)} - J^{(0)}) - 2Sh_i \ , \tag{6d}$$

$$\begin{aligned} J = {} & J^{(0)} + \frac{S^2}{2}(2J^{(0)} - U_1^{(0)} - U_2^{(0)}) \\ & -S(h_1 + h_2) \ , \end{aligned} \tag{6e}$$

$$J - J_x = J^{(0)} - J_x^{(0)} + J^{(0)}S^2 \ , \tag{6f}$$

where the superscript (0) means that Eqs. (5) have to be used to calculate the different terms replacing ϕ_i by ψ_i. This procedure yields the following approximate Hamiltonian (up to second order in S):

$$\begin{aligned} \hat{H} = {} & \sum_{\sigma} \left(\varepsilon_1^{(0)} + \frac{S^2}{4}[\varepsilon_1^{(0)} - \varepsilon_2^{(0)} + (U_1^{(0)} - J^{(0)})\hat{n}_{1-\sigma} - (U_2^{(0)} - J^{(0)})\hat{n}_{2-\sigma}] - S(t + h_1\hat{n}_{1-\sigma} + h_2\hat{n}_{2-\sigma}) \right) \hat{n}_{1\sigma} \\ & + \sum_{\sigma} \left(\varepsilon_2^{(0)} + \frac{S^2}{4}[\varepsilon_2^{(0)} - \varepsilon_1^{(0)} + (U_2^{(0)} - J^{(0)})\hat{n}_{2-\sigma} - (U_1^{(0)} - J^{(0)})\hat{n}_{1-\sigma}] - S(t + h_1\hat{n}_{1-\sigma} + h_2\hat{n}_{2-\sigma}) \right) \hat{n}_{2\sigma} \\ & + \sum_{\sigma} (t + h_1\hat{n}_{1-\sigma} + h_2\hat{n}_{2-\sigma})(\hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma} + \hat{c}^{\dagger}_{2\sigma}\hat{c}_{1\sigma}) + U_1^{(0)}\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + U_2^{(0)}\hat{n}_{2\uparrow}\hat{n}_{2\downarrow} \\ & + \sum_{\sigma} [J^{(0)}\hat{n}_{1\sigma}\hat{n}_{2-\sigma} + (J^{(0)} - J_x^{(0)} + J^{(0)}S^2)\hat{n}_{1\sigma}\hat{n}_{2\sigma}] + \frac{Z_1 Z_2}{d} \ . \end{aligned} \tag{7}$$

We should make clear that in these approximate equations, t and h_i are not the exact values but the ones given by Eqs. (6b) and (6c).

In our approach to chemisorption we propose to introduce a further simplification related to the many-body terms appearing in $\hat{n}_{1\sigma}$ and $\hat{n}_{2\sigma}$. In this step, the terms $(S^2/4)(U_1^{(0)} - J^{(0)})\hat{n}_{1-\sigma}\hat{n}_{1\sigma}$, $-Sh_1\hat{n}_{1-\sigma}\hat{n}_{2\sigma}$, or $h_1\hat{n}_{1-\sigma}\hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma}$ will be replaced in a Hartree approximation: we can expect this approximation to be a reasonable one, since the main many-body effects are associated with $U_1^{(0)}\hat{n}_{1\uparrow}\hat{n}_{1\downarrow}$ or $J^{(0)}\hat{n}_1\hat{n}_2$. Therefore, we make the following substitutions:

$$\begin{aligned} \frac{S^2}{4}(U_1^{(0)} - J^{(0)})\hat{n}_{1-\sigma}\hat{n}_{1\sigma} \longrightarrow {} & \frac{S^2}{4}(U_1^{(0)} - J^{(0)}) < \hat{n}_{1-\sigma} > \hat{n}_{1\sigma} + \frac{S^2}{4}(U_1^{(0)} - J^{(0)})\hat{n}_{1-\sigma} < \hat{n}_{1\sigma} > \\ & -\frac{S^2}{4}(U_1^{(0)} - J^{(0)}) < \hat{n}_{1-\sigma} >< \hat{n}_{1\sigma} >, \end{aligned} \tag{8a}$$

$$-Sh_1\hat{n}_{1-\sigma}\hat{n}_{2\sigma} \longrightarrow -Sh_1 < \hat{n}_{1-\sigma} > \hat{n}_{2\sigma} - Sh_1\hat{n}_{1-\sigma} < \hat{n}_{2\sigma} > +Sh_1 < \hat{n}_{1-\sigma} >< \hat{n}_{2\sigma} > \ , \tag{8b}$$

$$h_1\hat{n}_{1-\sigma}\hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma} \longrightarrow h_1 < \hat{n}_{1-\sigma} > \hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma} + h_1\hat{n}_{1-\sigma} < \hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma} > -h_1 < \hat{n}_{1-\sigma} >< \hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma} > \ . \tag{8c}$$

The last term of each of these equations has to be introduced in order not to change the total energy in performing the Hartree approximation. Moreover, we have also found that, with a good approximation in the total energy, we can neglect these contributions if, at the same time, we neglect the second term of each equation. This amounts to making the following replacements:

$$\frac{S^2}{4}(U_1^{(0)} - J^{(0)})\hat{n}_{1-\sigma}\hat{n}_{1\sigma} \longrightarrow \frac{S^2}{4}(U_1^{(0)} - J^{(0)}) < \hat{n}_{1-\sigma} > \hat{n}_{1\sigma} \ , \tag{9a}$$

$$-Sh_1\hat{n}_{1-\sigma}\hat{n}_{2\sigma} \longrightarrow -Sh_1 < \hat{n}_{1-\sigma} > \hat{n}_{2\sigma} \ , \tag{9b}$$

$$h_1\hat{n}_{1-\sigma}\hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma} \longrightarrow h_1 < \hat{n}_{1-\sigma} > \hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma} \ . \tag{9c}$$

We should remark that in going from Eqs. (8) to Eqs. (9) we still retain good accuracy in the calculation of the total energy of the system. This approximation implies, however, neglecting some terms [like $(S^2/4)(U_1^{(0)} - J^{(0)})\hat{n}_{1-\sigma} < \hat{n}_{1\sigma} >$, $-Sh_1\hat{n}_{1-\sigma} < \hat{n}_{2\sigma} >$, and $h_1\hat{n}_{1-\sigma} \times < \hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma} >$] that must be included if one is interested in calculating with high accuracy the electrostatic potential acting upon each orbital. For example, the term $h_1\hat{n}_{1-\sigma} < \hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma} >$ is associated with the electrostatic potential created by the 1-2 bond charge upon the $1-\sigma$ orbital; the other two terms, $(S^2/4)(U_1^{(0)} - J^{(0)})\hat{n}_{1-\sigma} \times < \hat{n}_{1\sigma} >$ and $-Sh_1\hat{n}_{1-\sigma} < \hat{n}_{2\sigma} >$ are related to the electrostatic potential created by the 1σ and 2σ charges upon the $1-\sigma$ orbital, due to the renormalization in the 2σ and 1σ wave-function weights due to the creation of a 1-2 bond. In this paper, we shall study the total energy of some chemisorption problems without analyzing the induced interface dipole and the changes in work function and stick therefore to the approximation given by Eqs. (9).

Then, Hamiltonian (7) can be written as follows:

$$\begin{aligned}\hat{H} = {} & \sum_{\sigma} E_1^{\sigma}\hat{n}_{1\sigma} + \sum_{\sigma} E_2^{\sigma}\hat{n}_{2\sigma} + \sum_{\sigma} T^{\sigma}(\hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma} + \hat{c}^{\dagger}_{2\sigma}\hat{c}_{1\sigma}) \\ & + U_1^{(0)}\hat{n}_{1\uparrow}\hat{n}_{1\downarrow} + U_2^{(0)}\hat{n}_{2\uparrow}\hat{n}_{2\downarrow} \\ & + \sum_{\sigma}[J^{(0)}\hat{n}_{1\sigma}\hat{n}_{2-\sigma} + (J^{(0)} - J_x^{(0)} + J^{(0)}S^2)\hat{n}_{1\sigma}\hat{n}_{2\sigma}] \\ & + \frac{Z_1Z_2}{d} \ ,\end{aligned} \tag{10}$$

where

$$\begin{aligned}E_i^{\sigma} = {} & \varepsilon_i^{(0)} + \frac{S^2}{4}[\ \varepsilon_i^{(0)} - \varepsilon_j^{(0)} + (U_i^{(0)} - J^{(0)}) < \hat{n}_{i-\sigma} > \\ & -(U_j^{(0)} - J^{(0)}) < \hat{n}_{j-\sigma} >] - ST^{\sigma} \ ,\end{aligned} \tag{11a}$$

$$T^{\sigma} = t + h_1 < \hat{n}_{1-\sigma} > + h_2 < \hat{n}_{2-\sigma} > \ . \tag{11b}$$

Equations (10) and (11) are the basis of our method for calculating the total energy of molecules with only two atomic orbitals.

For more orbitals and two atoms, Eqs. (10) and (11) can be generalized as follows:

$$\begin{aligned}\hat{H} = {} & \sum_{i,\sigma} E_i^{\sigma}\hat{n}_{i\sigma} + \sum_{\sigma,(i,j)} T_{ij}^{\sigma}(\hat{c}^{\dagger}_{i\sigma}\hat{c}_{j\sigma} + \hat{c}^{\dagger}_{j\sigma}\hat{c}_{i\sigma}) + \sum_{i} U_i^{(0)}\hat{n}_{i\uparrow}\hat{n}_{i\downarrow} \\ & + \tfrac{1}{2}\sum_{i,j\neq i,\sigma}[J_{ij}^{(0)}\hat{n}_{i\sigma}\hat{n}_{j-\sigma} + (J_{ij}^{(0)} - J_{x,ij}^{(0)} + J_{ij}^{(0)}S_{ij}^2)\hat{n}_{i\sigma}\hat{n}_{j\sigma}] + \frac{Z_1Z_2}{d} \ .\end{aligned} \tag{12}$$

In this equation:

$$\begin{aligned}E_i^{\sigma} = {} & \varepsilon_i^{(0)} + \sum_{j\neq i}\frac{S_{ij}^2}{4}\left[\left(\varepsilon_i^{(0)} + U_i^{(0)} < \hat{n}_{i-\sigma} > + J_{ij}^{(0)} < \hat{n}_{j-\sigma} > + \sum_{\sigma',l\neq i,j} J_{il}^{(0)} < \hat{n}_{l\sigma'} > - \sum_{l\neq i,j} J_{il}^{x,(0)} < \hat{n}_{l\sigma} >\right)\right. \\ & \left. - \left(\varepsilon_j^{(0)} + U_j^{(0)} < \hat{n}_{j-\sigma} > + J_{ij}^{(0)} < \hat{n}_{i-\sigma} > + \sum_{\sigma',l\neq i,j} J_{jl}^{(0)} < \hat{n}_{l\sigma'} > - \sum_{l\neq i,j} J_{jl}^{x,(0)} < \hat{n}_{l\sigma} >\right)\right] \\ & - \sum_{j\neq i} S_{ij}T_{ij}^{\sigma} \ ,\end{aligned} \tag{13a}$$

$$T_{ij}^{\sigma} = t_{ij} + h_i < \hat{n}_{i-\sigma} > + h_j < \hat{n}_{j-\sigma} > + \sum_{\sigma' l\neq i,j} h_{l,ij} < \hat{n}_{l\sigma'} > - \sum_{l\neq i,j} h_{l,ij}^{x} < \hat{n}_{l\sigma} > \ , \tag{13b}$$

$$h_{l,ij} = \int\int \phi_l^2(\mathbf{r})\frac{1}{|\,\mathbf{r} - \mathbf{r}'\,|}\phi_i(\mathbf{r}')\phi_j(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' \ , \tag{13c}$$

$$h_{l,ij}^{x} = \int\int \phi_l(\mathbf{r})\phi_l(\mathbf{r}')\frac{1}{|\,\mathbf{r} - \mathbf{r}'\,|}\phi_i(\mathbf{r})\phi_j(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' \tag{13d}$$

(remember that in these equations, t and h should be calculated up to second order in the corresponding overlaps).

The additional terms appearing in these equations with respect to Eqs. (10) and (11) are contributions due to other orbitals. Thus, $\sum_{\sigma' l \neq i,j} J_{il}^{(0)} < \hat{n}_{l\sigma'} >$ yields the Hartree contribution of the l orbital to the i level, while $\sum_{\sigma' l \neq i,j} h_{l,ij} < \hat{n}_{l\sigma'} >$ yields also the Hartree contribution of the l orbital to the ij hopping. We shall show presently that the more general Hamiltonian (12) follows from the total Hamiltonian by expanding the different interactions in the overlap coefficients.

We apply now Eqs. (12) and (13) to the calculation of the binding energies of the H_2 and LiH molecules. Figures 1 and 2 show the results of a standard Hartree-Fock calculation using for H_2 a $1s$ level per atom, and for LiH a $1s,2s$ configuration for Li and $1s$ level for H. In the same figures we also show the results obtained with our method for the same configurations. In the case of H_2, we find that our method (S^2 expansion) underestimates grossly the binding energies (by $\sim$ 2 eV), although it yields a good equilibrium distance. For LiH, the results of our S^2-expansion method yield a much better agreement with a Hartree-Fock (HF) calculation: the difference in the binding energy is around 0.2 eV, and in the equilibrium distance less than 0.2 a.u. These results can be understood because for H_2, S can be as large as 0.7 at the equilibrium distance (see Fig. 1), while for LiH the $2s$(Li)-$1s$(H) overlap is only 0.43 at the equilibrium distance (see Fig. 3). Notice that even for H_2, our S^2 expansion starts diverging from the HF results for $S \geq 0.4$. These results show that our Hamiltonian (12) is a good approximation to the actual problem if $S \leq 0.4$.

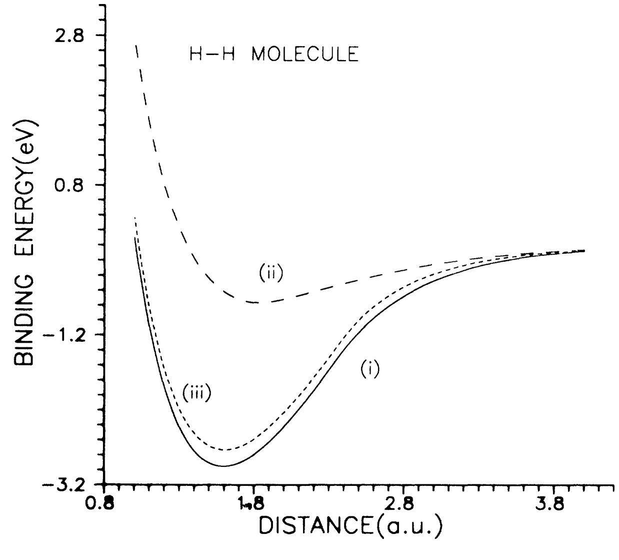

FIG. 1. Binding energy for H_2 calculated using (i) a standard HF approximation, (ii) our S^2 expansion in all the terms of the Hamiltonian, (iii) as in (ii) except for the hopping term that is calculated exactly. We also show the $1s$-$1s$ overlap (iv) as a function of the H-H distance.

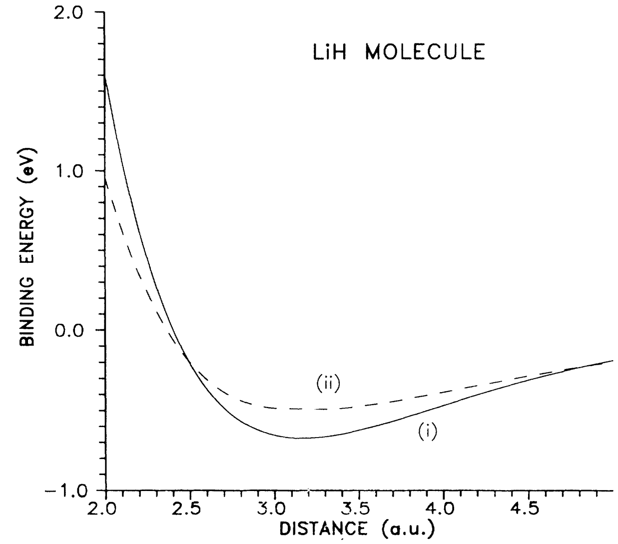

FIG. 2. Binding energy for LiH calculated using (i) a standard HF calculation, (ii) our S^2 expansion in all the terms of the Hamiltonian.

We have investigated further which is the main reason for the inaccuracies in our S^2-expansion approach. To this end, it is convenient to consider the one-electron Hamiltonian of two levels, as obtained from Eq. (4) by neglecting many-body effects. Then, we get the reduced Hamiltonian ($Z_1 = Z_2 = 1$)

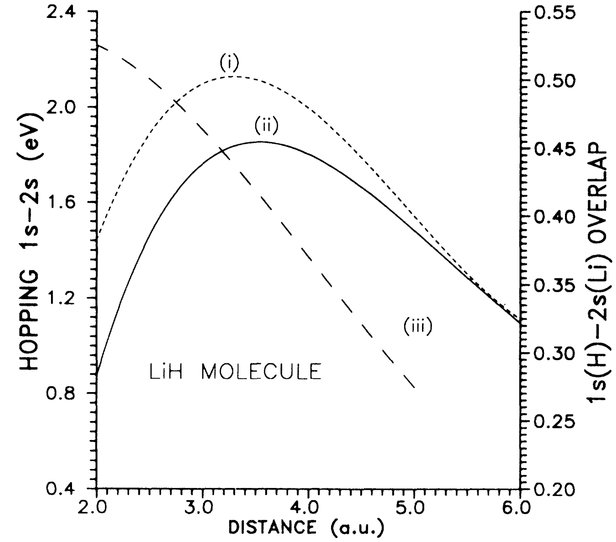

FIG. 3. Hopping interaction between the H $1s$ and the Li $2s$ orbitals as calculated; with the exact Hamiltonian; (ii) using our S^2 expansion. We also show (iii) the overlap between these two orbitals as a function of the Li-H distance.

$$\hat{H} = \sum_{\sigma}(\varepsilon_1\hat{n}_{1\sigma} + \varepsilon_2\hat{n}_{2\sigma}) + \sum_{\sigma} t(\hat{c}^{\dagger}_{1\sigma}\hat{c}_{2\sigma} + \hat{c}^{\dagger}_{2\sigma}\hat{c}_{1\sigma}) + \frac{1}{d} , \tag{14}$$

where

$$\varepsilon_i = \varepsilon_i^{(0)} + \tfrac{1}{2}[1 - (1 - S^2)^{-1/2}](\varepsilon_j^{(0)} - \varepsilon_i^{(0)}) - St , \tag{15a}$$

$$t = \frac{1}{(1 - S^2)}\left(t^{(0)} - \frac{S}{2}(\varepsilon_1^{(0)} + \varepsilon_2^{(0)})\right) \tag{15b}$$

(see I for further details). The main point to notice here is that the exact value for t is given by $t^{(0)} - \frac{S}{2}(\varepsilon_1^{(0)} + \varepsilon_2^{(0)})$, the hopping as calculated in a S^2-expansion approach, times $(1 - S^2)^{-1}$. This last factor, $(1 - S^2)^{-1}$, yields the correction introduced upon the lowest approximation to t by the wave-function overlap. It is easy to check that this factor is very large for $S \sim 0.7$, the overlap appearing at the equilibrium distance of H_2.

In order to check that the hopping is the main factor introducing the inaccuracies in our S^2-expansion approach, we have calculated the total energy of H_2 using Hamiltonian (10) and Eqs. (11) with t, h_i, and h_i^x calculated exactly to all orders of S. In Fig. 1, we have also included the H_2 binding energy as calculated with this approximation: these results show a very good agreement with the HF calculations and confirm our comments about the inaccuracies introduced by our S^2-expansion method. Similar results have been obtained for LiH; in Fig. 3 we only show the $2s$(Li)-$1s$(H) hopping; as in the case of H_2, we also find that our approximate calculation yields smaller values for this hopping integral than the HF results.

To conclude this section, we should say that our results show that our S^2-expansion method is a very accurate approximation to the bond problem for not very large overlaps, say, $S \leq 0.4$. For higher overlaps Eqs. (12) and (13) are, however, a good approximation if T, t, and h are calculated exactly up to all orders of S.

B. The total Hamiltonian as the superposition of bonds

Let us now discuss how the total crystal Hamiltonian can be written as a superposition of the bonds defined for each pair of atomic orbitals, as in Eqs. (10) and (11).

Our starting point is the general many-body Hamiltonian:

$$\hat{H} = -\frac{1}{2}\sum_i \nabla_i^2 - \sum_{i,k}\frac{Z_k}{|\,\mathbf{r}_i - \mathbf{R}_k\,|} + \frac{1}{2}\sum_{i,j\neq i}\frac{1}{|\,\mathbf{r}_i - \mathbf{r}_j\,|} + \frac{1}{2}\sum_{l,k\neq l}\frac{Z_k Z_l}{|\,\mathbf{R}_k - \mathbf{R}_l\,|} . \tag{16}$$

We propose to solve the electronic part of this Hamiltonian by means of an electron basis defined by the atomic orbitals $\psi_\alpha(\mathbf{r} - \mathbf{R}_i)$ where α refers to the atomic orbital. For the sake of simplicity, we shall write from now on $(i, \alpha) \equiv \nu$, and introduce the Löwdin orthogonal basis:

$$\phi_\mu = \sum_\nu (S^{-1/2})_{\mu\nu}\psi_\nu , \tag{17}$$

where $S_{\mu\nu} =< \psi_\mu \mid \psi_\nu >$. Using this new basis, the electronic part of Hamiltonian (14) can be written in a second quantization language as follows:

$$\hat{H} = \sum_{\nu,\sigma}\varepsilon_\nu\hat{n}_{\nu,\sigma} + \sum_{\sigma,(\mu,\nu)} t_{\mu\nu}(\hat{c}^{\dagger}_{\nu\sigma}\hat{c}_{\mu\sigma} + \hat{c}^{\dagger}_{\mu\sigma}\hat{c}_{\nu\sigma}) + \sum_{\nu\omega\sigma\mu\lambda\sigma'} O^{\nu\mu}_{\omega\lambda}\hat{c}^{\dagger}_{\nu\sigma}\hat{c}^{\dagger}_{\mu\sigma'}\hat{c}_{\lambda\sigma'}\hat{c}_{\omega\sigma} , \tag{18}$$

where

$$\varepsilon_\nu = \int \phi_\nu(\mathbf{r})\left(-\frac{\nabla^2}{2} - \sum_k \frac{Z_k}{|\,\mathbf{r} - \mathbf{R}_k\,|}\right)\phi_\nu(\mathbf{r})d\mathbf{r} , \tag{19a}$$

$$t_{\nu\mu} = \int \phi_\nu(\mathbf{r})\left(-\frac{\nabla^2}{2} - \sum_k \frac{Z_k}{|\,\mathbf{r} - \mathbf{R}_k\,|}\right)\phi_\mu(\mathbf{r})d\mathbf{r} , \tag{19b}$$

$$O^{\nu\mu}_{\omega\lambda} = \frac{1}{2}\int\int \phi_\nu(\mathbf{r})\phi_\omega(\mathbf{r})\frac{1}{|\,\mathbf{r} - \mathbf{r}'\,|}\phi_\mu(\mathbf{r}')\phi_\lambda(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' . \tag{19c}$$

The first step to simplify Hamiltonian (18) is to neglect terms contributing to the total energy that are proportional to S^4, where S is a parameter measuring the overlap between different orbitals. This implies neglecting all terms in the many-body part of the Hamiltonian that have four different orbitals. In general, these terms contribute in S^4, as

$$O^{\nu\mu}_{\omega\lambda} < \hat{c}^{\dagger}_{\nu\sigma}\hat{c}_{\omega\sigma} >< \hat{c}^{\dagger}_{\mu\sigma'}\hat{c}_{\lambda\sigma'} >\sim S^4 \tag{20a}$$

since

$$O^{\nu\mu}_{\omega\lambda} \sim S^2 \tag{20b}$$

and

$$< \hat{c}^{\dagger}_{\nu\sigma}\hat{c}_{\omega\sigma} >\sim< \hat{c}^{\dagger}_{\mu\sigma'}\hat{c}_{\lambda\sigma'} >\sim S . \tag{20c}$$

Then, Hamiltonian (18) can be written as follows:

$$\hat{H} = \sum_{\nu\sigma}\varepsilon_\nu\hat{n}_{\nu\sigma} + \sum_{(\nu,\mu),\sigma}\left(t_{\nu\mu} + \sum_{\lambda,\sigma'} h^{\sigma\sigma'}_{\lambda,\nu\mu}\hat{n}_{\lambda\sigma'} - \sum_\lambda h^x_{\lambda,\nu\mu}\hat{n}_{\lambda\sigma}\right)(\hat{c}^{\dagger}_{\nu\sigma}\hat{c}_{\mu\sigma} + \hat{c}^{\dagger}_{\mu\sigma}\hat{c}_{\nu\sigma}) + \sum_\nu U_\nu\hat{n}_{\nu\uparrow}\hat{n}_{\nu\downarrow} + \tfrac{1}{2}\sum_{\nu,\mu\neq\nu,\sigma}[J_{\nu\mu}\hat{n}_{\nu\sigma}\hat{n}_{\mu-\sigma} + (J_{\nu\mu} - J_{x,\nu\mu})\hat{n}_{\nu\sigma}\hat{n}_{\mu\sigma}] , \tag{21}$$

where

$$h^{\sigma\sigma'}_{\lambda,\nu\mu} = \int\int \phi^2_\lambda(\mathbf{r})\phi_\nu(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_\mu(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' \quad \text{for } \lambda \neq \nu \text{ and } \mu \text{ or } \sigma \neq \sigma' , \tag{22a}$$

$$h^{\sigma\sigma'}_{\lambda,\nu\mu} = 0 \quad \text{for } \lambda = \nu \text{ or } \mu \text{ and } \sigma = \sigma', \tag{22b}$$

$$h^{x}_{\lambda,\nu\mu} = \int\int \phi_\lambda(\mathbf{r})\phi_\lambda(\mathbf{r}')\phi_\nu(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_\mu(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' , \tag{22c}$$

$$U_\nu = \int \phi^2_\nu(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi^2_\nu(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' , \tag{22d}$$

$$J_{\nu\mu} = \int\int \phi^2_\nu(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi^2_\mu(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' , \tag{22e}$$

and

$$J_{x,\nu\mu} = \int\int \phi_\nu(\mathbf{r})\phi_\mu(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_\nu(\mathbf{r}')\phi_\mu(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}'. \tag{22f}$$

In Eq. (21) the many-body terms depending on three orbitals have been written like $h_{\lambda,\nu\mu}\hat{n}_{\lambda\sigma'}\hat{c}^\dagger_{\nu\sigma}\hat{c}_{\mu\sigma}$ or $h^x_{\lambda,\nu\mu}\hat{n}_{\lambda\sigma}\hat{c}^\dagger_{\nu\sigma}\hat{c}_{\mu\sigma}$, while the terms depending only on two orbitals go like $U_\nu\hat{n}_{\nu\uparrow}\hat{n}_{\nu\downarrow}$, $J_{\nu\mu}\hat{n}_{\nu\sigma}\hat{n}_{\mu-\sigma}$ or $(J_{\nu\mu} - J_{x,\nu\mu})\hat{n}_{\nu\sigma}\hat{n}_{\mu\sigma}$.

Apparently, the terms proportional to $h^x_{\lambda,\nu\mu}$ go like S^2, and their contribution to the total energy like S^3; however, we shall show later that $h^x_{\lambda,\nu\mu}$ contributes to the total energy with a term proportional to S^2, if λ and μ or ν belong to the same atom.

Hamiltonian (21) can be further simplified if we use Eq. (17) and expand the matrix $(S^{-1/2})_{\mu\nu}$ up to second order in the overlap as follows:

$$\phi_\mu = \psi_\mu - \tfrac{1}{2}\sum_\nu S_{\mu\nu}\psi_\nu + \tfrac{3}{8}\sum_{\lambda,\nu} S_{\mu\lambda}S_{\lambda\nu}\psi_\nu . \tag{23}$$

Introducing this expresion in Eqs. (22) yields the following equations:

$$\varepsilon_\nu = \varepsilon^{(0)}_\nu + \tfrac{1}{4}\sum_\mu S^2_{\nu\mu}(\varepsilon^{(0)}_\nu - \varepsilon^{(0)}_\mu) - \sum_\mu S_{\nu\mu}t_{\mu\nu} , \tag{24a}$$

$$t_{\nu\mu} = t^{(0)}_{\nu\mu} - \tfrac{1}{2}S_{\nu\mu}(\varepsilon^{(0)}_\nu + \varepsilon^{(0)}_\mu) , \tag{24b}$$

$$h^{\sigma\sigma'}_{\lambda,\nu\mu} = h^{(0)}_{\lambda,\nu\mu} - \tfrac{1}{2}(J^{(0)}_{\lambda\nu} + J^{(0)}_{\lambda\mu}) \quad S_{\nu\mu} \text{ for } \lambda \neq \nu \text{ and } \mu, \text{ or } \sigma \neq \sigma' , \tag{24c}$$

$$h^{\sigma\sigma'}_{\lambda,\nu\mu} = 0 \quad \text{for } \lambda = \nu \text{ and } \mu, \text{ or } \sigma = \sigma' , \tag{24d}$$

$$h^{x}_{\lambda,\nu\mu} = h^{x(0)}_{\lambda,\nu\mu} - \tfrac{1}{2}S_{\mu\nu}(J^{x(0)}_{\lambda\nu} + J^{x(0)}_{\lambda\mu}) , \tag{24e}$$

$$U_\nu = U^{(0)}_\nu + \tfrac{1}{2}\sum_{\nu\neq\mu} S^2_{\nu\mu}(U^{(0)}_\nu - J^{(0)}_{\nu\mu}) - 2\sum_\mu S_{\nu\mu}h^{\uparrow\downarrow}_{\nu,\nu\mu} , \tag{24f}$$

$$\begin{aligned} J_{\nu\mu} = {} & J^{(0)}_{\nu\mu} + \tfrac{1}{4}S^2_{\nu\mu}(2J^{(0)}_{\nu\mu} - U^{(0)}_\nu - U^{(0)}_\mu) \\ & - S_{\nu\mu}(h^{\uparrow\downarrow}_{\nu,\nu\mu} + h^{\uparrow\downarrow}_{\mu,\mu\nu}) \\ & - \sum_{\lambda\neq\mu\nu}(S_{\nu\lambda}h^{\uparrow\downarrow}_{\mu,\nu\lambda} + S_{\mu\lambda}h^{\uparrow\downarrow}_{\nu,\mu\lambda}) \\ & + \tfrac{1}{4}\sum_\lambda S^2_{\nu\lambda}(J^{(0)}_{\mu\nu} - J^{(0)}_{\mu\lambda}) + \tfrac{1}{4}\sum_\lambda S^2_{\mu\lambda}(J^{(0)}_{\mu\nu} - J^{(0)}_{\lambda\nu}) , \end{aligned} \tag{24g}$$

$$\begin{aligned} J_{\nu\mu} - J_{x,\nu\mu} = {} & J^{(0)}_{\nu\mu} - J^{(0)}_{x,\nu\mu} + J^{(0)}_{\nu\mu}S^2_{\nu\mu} \\ & + \tfrac{3}{4}\sum_{\lambda\neq\mu\nu} J^{(0)}_{\nu\mu}(S^2_{\nu\lambda} + S^2_{\mu\lambda}) \\ & + \tfrac{1}{4}\sum_{\lambda\neq\nu\mu}(S^2_{\nu\lambda}J^{(0)}_{\lambda\mu} + S^2_{\mu\lambda}J^{(0)}_{\lambda\mu}) , \end{aligned} \tag{24h}$$

where the superscript (0) means that Eqs. (22) have to be used to calculate the different terms replacing ϕ_ν by ψ_ν. In Eqs. (24), $J^{(0)}_{\lambda\lambda}$ is equal to $U^{(0)}_\lambda$. Notice that $h^x_{\lambda,\nu\mu}$, if λ and ν or μ belongs to the same atom, is of order S, and therefore this term contributes to the total energy of order S^2 as commented above.

When Eqs. (24) are introduced in Hamiltonian (21) and different terms are rearranged, the following result is obtained:

$$\begin{aligned} \hat{H} = \sum_{\nu\sigma}\Bigg[& \varepsilon^{(0)}_\nu + \frac{1}{4}\sum_{\mu\neq\nu} S^2_{\nu\mu}\Bigg(\varepsilon^{(0)}_\nu + U^{(0)}_\nu\hat{n}_{\nu-\sigma} + J^{(0)}_{\nu\mu}\hat{n}_{\mu-\sigma} + \sum_{\sigma'\lambda\neq\mu\nu} J^{(0)}_{\nu\lambda}\hat{n}_{\lambda\sigma'} - \sum_{\lambda\neq\mu\nu} J^{x(0)}_{\nu\lambda}\hat{n}_{\lambda\sigma}\Bigg) \\ & - \Bigg(\varepsilon^{(0)}_\mu + U^{(0)}_\mu\hat{n}_{\mu-\sigma} + J^{(0)}_{\mu\nu}\hat{n}_{\nu-\sigma} + \sum_{\sigma'\lambda\neq\mu\nu} J^{(0)}_{\mu\lambda}\hat{n}_{\lambda\sigma'} - \sum_{\lambda\neq\mu\nu} J^{x(0)}_{\mu\lambda}\hat{n}_{\lambda\sigma}\Bigg) \\ & - \sum_{\mu\neq\nu} S_{\nu\mu}\Bigg(t_{\nu\mu} + \sum_{\lambda\sigma'} h^{\sigma\sigma'}_{\lambda,\nu\mu}\hat{n}_{\lambda\sigma'} - \sum_\lambda h^x_{\lambda,\nu\mu}\hat{n}_{\lambda\sigma}\Bigg)\Bigg]\hat{n}_{\nu\sigma} \\ & + \sum_{\sigma,(\nu,\mu)}\Bigg(t_{\nu\mu} + \sum_{\lambda\sigma'} h^{\sigma\sigma'}_{\lambda,\nu\mu}\hat{n}_{\lambda\sigma'} - \sum_\lambda h^x_{\lambda,\nu\mu}\hat{n}_{\lambda\sigma}\Bigg)(\hat{c}^\dagger_{\nu\sigma}\hat{c}_{\mu\sigma} + \hat{c}^\dagger_{\mu\sigma}\hat{c}_{\nu\sigma}) + \sum_\nu U^{(0)}_\nu\hat{n}_{\nu\uparrow}\hat{n}_{\nu\downarrow} \\ & + \tfrac{1}{2}\sum_{\nu,\mu\neq\nu\;\sigma}[J^{(0)}_{\nu\mu}\hat{n}_{\nu\sigma}\hat{n}_{\mu-\sigma} + (J^{(0)}_{\nu\mu} - J^{(0)}_{x,\nu\mu} + J^{(0)}_{\nu\mu}S^2_{\nu\mu})\hat{n}_{\nu\sigma}\hat{n}_{\mu\sigma}] . \end{aligned} \tag{25}$$

The next approximation follows the line of the discussion given above in II A, and replace the terms multiplying $\hat{n}_\nu$ and $(\hat{c}^\dagger_{\nu\sigma}\hat{c}_{\mu\sigma} + \hat{c}^\dagger_{\mu\sigma}\hat{c}_{\nu\sigma})$ by their mean values. This yields the following equations:

$$\begin{aligned}\hat{H} = {} & \sum_{\nu,\sigma} E^\sigma_\nu \hat{n}_{\nu\sigma} + \sum_{\sigma,\nu\neq\mu} T^\sigma_{\nu\mu}(\hat{c}^\dagger_{\nu\sigma}\hat{c}_{\mu\sigma} + \hat{c}^\dagger_{\mu\sigma}\hat{c}_{\nu\sigma}) \\ & + \sum_\nu U^{(0)}_\nu \hat{n}_{\nu\uparrow}\hat{n}_{\nu\downarrow} + \tfrac{1}{2}\sum_{\nu,\mu\neq\nu,\sigma}[J^{(0)}_{\nu\mu}\hat{n}_{\nu\sigma}\hat{n}_{\mu-\sigma} + (J^{(0)}_{\nu\mu} - J^{(0)}_{x,\nu\mu} + J^{(0)}_{\nu\mu}S^2_{\nu\mu})\hat{n}_{\nu\sigma}\hat{n}_{\mu\sigma}]\ ,\end{aligned} \tag{26}$$

where

$$\begin{aligned}E^\sigma_\nu = {} & \varepsilon^{(0)}_\nu + \sum_{\mu\neq\nu}\frac{S^2_{\nu\mu}}{4}\Bigg[\Bigg(\varepsilon^{(0)}_\nu + U^{(0)}_\nu < \hat{n}_{\nu-\sigma} > + J^{(0)}_{\nu\mu} < \hat{n}_{\mu-\sigma} > + \sum_{\sigma',\lambda\neq\nu,\mu} J^{(0)}_{\nu\lambda} < \hat{n}_{\lambda\sigma'} > - \sum_{\lambda\neq\nu,\mu} J^{x,(0)}_{\nu\lambda} < \hat{n}_{\lambda\sigma} >\Bigg) \\ & - \Bigg(\varepsilon^{(0)}_\mu + U^{(0)}_\mu < \hat{n}_{\mu-\sigma} > + J^{(0)}_{\mu\nu} < \hat{n}_{\nu-\sigma} > + \sum_{\sigma',\lambda\neq\nu,\mu} J^{(0)}_{\mu\lambda} < \hat{n}_{\lambda\sigma'} > - \sum_{\lambda\neq\mu,\nu} J^{x,(0)}_{\mu\lambda} < \hat{n}_{\lambda\sigma} >\Bigg)\Bigg] \\ & - \sum_{\mu\neq\nu} S_{\nu\mu}T_{\nu\mu}\end{aligned} \tag{27a}$$

and

$$T^\sigma_{\nu\mu} = t_{\nu\mu} + \sum_{\sigma'\lambda} h^{\sigma\sigma'}_{\lambda,\nu\mu} < \hat{n}_{\lambda\sigma'} > - \sum_\lambda h^x_{\lambda,\nu,\mu} < \hat{n}_{\lambda\sigma} >\ . \tag{27b}$$

This is the same Hamiltonian given for molecules in Eqs. (12) and (13) above. These results show that our basic Hamiltonian is given by the superposition of the different Hamiltonians defined for each pair of atomic orbitals. One word of caution should be said here: strictly, other orbitals modify a single bond Hamiltonian through the new terms appearing in E_ν and $T_{\nu\mu}$. As it will be discussed below for some specific cases, these three orbital interactions can play significant effects in the final solution of our problem. Let us stress, however, that formally, the total Hamiltonian in our S^2-expansion approach can be viewed as the superposition of the Hamiltonians for all the independent pairs, whether they are chemically bonded or not.

Equations (26) and (27) define the electronic properties of a given system as a function of the properties of their atomic constituents. For the case of hydrogen or any other adsorbate interacting with a metal surface, this approach implies solving in a previous step the electronic properties of the metal surface from the characteristics of the metal atoms. Here we have followed a simpler approach, assuming that the metal surface properties are known from independent calculations; in other words, the aim of this analysis is to apply our *ab initio* LCAO approach to calculate the electronic properties and adsorption energies of some adsorbates on metal surfaces, which we assume to be well described by **k** eigenfunctions, $\psi_{\mathbf{k}}$, and the corresponding eigenvectors, $\varepsilon(\mathbf{k})$. In practice, these eigenfunctions are obtained by using an appropriate tight-binding description of the metal band: we have followed Papaconstantopoulos[18] and used for the calculation of the metal structure the parameters given in Ref. 18. Thus, we introduce the metal Hamiltonian

$$\hat{H}_M = \sum_{\mathbf{k},\sigma} \varepsilon(\mathbf{k})\hat{c}^\dagger_{\mathbf{k}\sigma}\hat{c}_{\mathbf{k}\sigma} \tag{28}$$

and consider the metal as a single system with many different levels, interacting with the adsorbate. Notice that before, we assumed each atom to be well characterized and the total system to be built up as the superposition of all the atoms; in the present case, we assume the metal and the adsorbed atoms to be well characterized, and the total system as the superposition of the metal and the adsorbate. We apply the approach developed previously to this system, and define the Hamiltonian as in Eqs. (26) and (27). We shall only consider the one-electron terms as they are the only ones having some slight differences with respect to the previous approach.

The important result we obtain in this one-electron approach is that, due to the overlap with the **k** states, the α level is shifted by the following energy (see I):

$$\delta\varepsilon_\alpha = \tfrac{1}{4}\sum_{\mathbf{k}} S^2_{\mathbf{k},\alpha}[E_\alpha - \varepsilon(\mathbf{k})] - \sum_{\mathbf{k}} S_{\mathbf{k},\alpha}T_{\mathbf{k},\alpha}\ , \tag{29}$$

where $S_{\mathbf{k},\alpha} =< \psi_{\mathbf{k}} \mid \psi_\alpha >$ is the overlap between $\psi_{\mathbf{k}}$ and the atomic wave function ψ_α of an adatom, E_α the corresponding atomic level, and $T_{\mathbf{k},\alpha}$ the hopping element. Comparing Eqs. (27a) and (29), we see that both equations yield similar results showing how overlaps modify the effective one-electron level. Equation (29) can be written in a local basis defining

$$\psi_{\mathbf{k}} = \sum_i C^i_{\mathbf{k}}\psi^M_i\ , \tag{30}$$

where ψ^M_i is an atomic metal orbital. Introducing this equation in $S_{\mathbf{k},\alpha}$ of Eq. (29), integrating in **k**, and neglecting interferences between different metal atoms, one gets the following result:

$$\delta\varepsilon_\alpha = \tfrac{1}{4}\sum_i S^2_{i\alpha}\int_{-\infty}^{\infty}(E_\alpha - \varepsilon)n^M_i(\varepsilon)d\varepsilon - \sum_i S_{i\alpha}T_{i\alpha}\ . \tag{31}$$

This equation yields the main difference between the actual approach and the one giving Eq. (27a): instead of the term $\frac{1}{4}S^2_{i\alpha}(E^M_i - E_\alpha)$, E^M_i being the metal atomic level, one finds E^M_i replaced by $\int_{-\infty}^{\infty}\varepsilon n^M_i(\varepsilon)d\varepsilon$, $n^M_i(\varepsilon)$ being the local density of states on the metal atom.

The result obtained in Eq. (31) suggests a further generalization of Eq. (27a), replacing

$$\left(\varepsilon_\nu^{(0)} + U_\nu^{(0)}\hat n_{\nu-\sigma} + J_{\nu\mu}^{(0)}\hat n_{\mu-\sigma} + \sum_{\sigma'\lambda\neq\mu\nu} J_{\nu\lambda}^{(0)}\hat n_{\lambda\sigma'} - \sum_{\lambda\neq\mu\nu} J_{\nu\lambda}^{x(0)}\hat n_{\lambda\sigma}\right)$$

$$- \left(\varepsilon_\mu^{(0)} + U_\mu^{(0)}\hat n_{\mu-\sigma} + J_{\mu\nu}^{(0)}\hat n_{\nu-\sigma} + \sum_{\sigma'\lambda\neq\mu\nu} J_{\mu\lambda}^{(0)}\hat n_{\lambda\sigma'} - \sum_{\lambda\neq\mu\nu} J_{\mu\lambda}^{x(0)}\hat n_{\lambda\sigma}\right)$$

by

$$\delta\varepsilon_{\nu\mu} = \int_{-\infty}^{\infty} d\varepsilon\, n_\nu(\varepsilon) \int_{-\infty}^{\infty} d\varepsilon' n_\mu(\varepsilon')[(\varepsilon - J_{\nu\mu}^{(0)} < n_{\mu\sigma} >) - (\varepsilon' - J_{\mu\nu}^{(0)} < n_{\nu\sigma} >)] \tag{32}$$

where $n_\nu(\varepsilon)$ and $n_\mu(\varepsilon')$ are the local densities of states associated with the ν and μ levels, respectively. In this equation, we have eliminated the contributions $J_{\nu\mu}^{(0)} < n_{\mu\sigma} >$ and $J_{\nu\mu}^{(0)} < n_{\nu\sigma} >$ to the ε and ε' levels, respectively, because the electron hopping between the ν and μ levels does not see those mean potentials (see I). Using Eq. (30) we can replace (27a) by

$$E_\nu = \varepsilon_\nu^{(0)} + \tfrac{1}{4}\sum_{\mu\neq\nu} S_{\nu\mu}^2 \delta\varepsilon_{\nu\mu} - \sum_{\mu\neq\nu} S_{\nu\mu} T_{\nu\mu}^\sigma \tag{33}$$

which will be used below instead of Eq. (27a) given above.

In our approach to the chemisorption problem, $\varepsilon_\nu^{(0)}$ can represent the metal level as given by the tight-binding parameters, and the correction terms $\frac{1}{4}\sum_{\mu\neq\nu} S_{\nu\mu}^2\delta\varepsilon_{\nu\mu}$ and $-\sum_{\mu\neq\nu} S_{\mu\nu}T_{\mu\nu}^\sigma$ are calculated for the metal adsorbate coupling, with μ referring to the different adatoms. Alternatively, $\varepsilon_\nu^{(0)}$ can represent the bare adatom level; then, the correction terms are calculated for the metal-adsorbate coupling, or the adatom-adatom interaction if more than one atom is adsorbed on the metal surface.

C. Exchange and correlation

Hamiltonian (26) and Eqs. (27b), (32), and (33) define our model for the chemisorption problem. This Hamiltonian is a many-body one, and many different approximations are possible to obtain the total energy and the electronic properties of the system. First of all, we discuss the Hartree-Fock approximation and, later on, we show a better kind of approach which we have used to introduce many-body effects: this approach is equivalent, within a LCAO method, to the $X\alpha$ method proposed by Slater for a free-electron-like system.[19]

The many-body terms appearing in Hamiltonian (26) are

$$\hat H^{\mathrm{mb}} = \sum_\nu U_\nu^{(0)}\hat n_{\nu\uparrow}\hat n_{\nu\downarrow} + \tfrac{1}{2}\sum_{\nu,\mu\neq\nu,\sigma}(J_{\nu\mu}^{(0)}\hat n_{\nu\sigma}\hat n_{\mu-\sigma} + \tilde J_{\nu\mu}^{(0)}\hat n_{\nu\sigma}\hat n_{\mu\sigma}) , \tag{34}$$

where

$$\tilde J_{\nu\mu}^{(0)} = J_{\nu\mu}^{(0)} - J_{x,\nu\mu}^{(0)} + J_{\nu\mu}^{(0)} S_{\nu\mu}^2 . \tag{34a}$$

In a Hartree-Fock approximation, the different terms of Eqs. (34) are decoupled in the following way:

$$U_\nu^{(0)}\hat n_{\nu\uparrow}\hat n_{\nu\downarrow} \longrightarrow U_\nu^{(0)}\hat n_{\nu\uparrow} < \hat n_{\nu\downarrow} > + U_\nu^{(0)} < \hat n_{\nu\uparrow} > \hat n_{\nu\downarrow} - U_\nu^{(0)} < \hat n_{\nu\uparrow} >< \hat n_{\nu\downarrow} > , \tag{35a}$$

$$J_{\nu\mu}^{(0)}\hat n_{\nu\sigma}\hat n_{\mu-\sigma} \longrightarrow J_{\nu\mu}^{(0)}\hat n_{\nu\sigma} < \hat n_{\mu-\sigma} > + J_{\nu\mu}^{(0)} < \hat n_{\nu\sigma} > \hat n_{\mu-\sigma} - J_{\nu\mu}^{(0)} < \hat n_{\nu\sigma} >< \hat n_{\mu-\sigma} > , \tag{35b}$$

$$\begin{aligned}\tilde J_{\nu\mu}^{(0)}\hat n_{\nu\sigma}\hat n_{\mu\sigma} \longrightarrow{}& \tilde J_{\nu\mu}^{(0)}\hat n_{\nu\sigma} < \hat n_{\mu\sigma} > + \tilde J_{\nu\mu}^{(0)} < \hat n_{\nu\sigma} > \hat n_{\mu\sigma} - \tilde J_{\nu\mu}^{(0)} < \hat n_{\nu\sigma} >< \hat n_{\mu\sigma} > \\ & - \tilde J_{\nu\mu}^{(0)}(< \hat c_{\nu\sigma}^\dagger \hat c_{\mu\sigma} > \hat c_{\mu\sigma}^\dagger \hat c_{\nu\sigma} + \hat c_{\nu\sigma}^\dagger \hat c_{\mu\sigma} < \hat c_{\mu\sigma}^\dagger \hat c_{\nu\sigma} > - < \hat c_{\nu\sigma}^\dagger \hat c_{\mu\sigma} >< \hat c_{\mu\sigma}^\dagger \hat c_{\nu\sigma} >) ,\end{aligned} \tag{35c}$$

where < > means the mean value in the ground state. The terms introduced in (35a) and (35b) and the first three terms of (35c) correspond to the typical Hartree approximation, while the last three terms of Eq. (35c) correspond to the exchange contribution associated with $\tilde J_{\nu\mu}^{(0)}$. From the point of view of the total energy, the many-body terms yield the following HF contributions:

$$U_\nu^{(0)}\hat n_{\nu\uparrow}\hat n_{\nu\downarrow} \rightarrow U_\nu^{(0)} < \hat n_{\nu\uparrow} >< \hat n_{\nu\downarrow} > , \tag{36a}$$

$$J_{\nu\mu}^{(0)}\hat n_{\nu\sigma}\hat n_{\mu-\sigma} \rightarrow J_{\nu\mu}^{(0)} < \hat n_{\nu\sigma} >< \hat n_{\mu-\sigma} > , \tag{36b}$$

$$\begin{aligned}\tilde J_{\nu\mu}^{(0)}\hat n_{\nu\sigma}\hat n_{\mu\sigma} \rightarrow{}& \tilde J_{\nu\mu}^{(0)} < \hat n_{\nu\sigma} >< \hat n_{\mu\sigma} > \\ & - \tilde J_{\nu\mu}^{(0)} < \hat c_{\nu\sigma}^\dagger \hat c_{\mu\sigma} >< \hat c_{\mu\sigma}^\dagger \hat c_{\nu\sigma} > .\end{aligned} \tag{36c}$$

Hamiltonian (26) can be solved in a HF approximation by using Eqs. (35), and the total energy can be calculated by means of Eqs. (36). It is of interest for the discussion presented below to reconsider the simple case of two levels, φ_1 and φ_2 (Sec. II A). In a HF approximation, the restricted one-electron solutions of the HF Hamiltonian take the following general form:

$$\begin{aligned}\chi_1 &= \alpha\mid 1\uparrow> +\beta\mid 2\uparrow>\ ,\\ \chi_2 &= \alpha\mid 1\downarrow> +\beta\mid 2\downarrow>\ ,\\ \chi_3 &= -\beta\mid 1\uparrow> +\alpha\mid 2\uparrow>\ ,\\ \chi_4 &= -\beta\mid 1\downarrow> +\beta\mid 2\downarrow>\ ,\end{aligned} \tag{37}$$

with eigenvalues E_1, $E_2 = E_1$, E_3, and $E_4 = E_3$.

For this simple case, if we have only two electrons filling the lowest level, say $E_1 < E_3$:

$$\begin{aligned}&< \hat{n}_{1\sigma} >= \alpha^2\ ,\\ &< \hat{n}_{2\sigma} >= \beta^2\ ,\\ &< \hat{c}^\dagger_{1\sigma}\hat{c}_{2\sigma} >= \alpha\beta\ .\end{aligned} \tag{38}$$

Then, the many-body terms can be calculated straightforwardly using Eqs. (35) and (36). Notice that α and β should be calculated self-consistently, since the Hamiltonian depends on the wave-function ground state.

What is of interest to comment here is that the term $\tilde{J}^{(0)}_{\mu\nu}$ in (35c) yields the following contributions:

$$\tilde{J}^{(0)}_{12}\beta^2\hat{n}_{1\sigma} + \tilde{J}^{(0)}_{12}\alpha^2\hat{n}_{2\sigma} - \tilde{J}^{(0)}_{12}\alpha^2\beta^2 - \tilde{J}^{(0)}_{12}\alpha\beta\hat{c}^\dagger_{1\sigma}\hat{c}_{2\sigma} - \tilde{J}^{(0)}_{12}\alpha\beta\hat{c}^\dagger_{2\sigma}\hat{c}_{1\sigma} + \tilde{J}^{(0)}_{12}\alpha^2\beta^2 \tag{39a}$$

to the total Hamiltonian, and the following contribution:

$$\tilde{J}^{(0)}_{12}\alpha^2\beta^2 - \tilde{J}^{(0)}_{12}\alpha^2\beta^2 = 0 \tag{39b}$$

to the total energy. Equation (39b) shows that no contribution to the total energy comes from the $\tilde{J}^{(0)}_{\nu\mu}\hat{n}_{\nu\sigma}\hat{n}_{\mu\sigma}$ term, the reason being that one electron cannot interact with itself. If we look at Eq. (39a) we find, however, that the $\tilde{J}^{(0)}_{\nu\mu}\hat{n}_{\nu\sigma}\hat{n}_{\mu\sigma}$ term yields a nonzero contribution to the HF Hamiltonian.

In the following we propose to introduce an alternative to the HF approximation, similar to the Slater $X\alpha$ method, in order to avoid the problems associated with the previous discussion [basically, Eq. (39a) yields very large negative values for the 1-2 hopping and too large positive shifts in the energy levels].

Our basic idea in this point is to replace the off-diagonal contribution

$$-\tilde{J}^{(0)}_{\nu\mu}(< \hat{c}^\dagger_{\nu\sigma}\hat{c}_{\mu\sigma} > \hat{c}^\dagger_{\mu\sigma}\hat{c}_{\nu\sigma} + \hat{c}^\dagger_{\nu\sigma}\hat{c}_{\mu\sigma} < \hat{c}^\dagger_{\mu\sigma}\hat{c}_{\nu\sigma} > - < \hat{c}^\dagger_{\nu\sigma}\hat{c}_{\mu\sigma} >< \hat{c}^\dagger_{\mu\sigma}\hat{c}_{\nu\sigma} >) \tag{40a}$$

by a diagonal one of the form

$$-J^{\rm eff}_{\mu\nu} < \hat{n}_{\nu\sigma} > \hat{n}_{\mu\sigma} - J^{\rm eff}_{\mu\nu}\hat{n}_{\nu\sigma} < \hat{n}_{\mu\sigma} > + J^{\rm eff}_{\mu\nu} < \hat{n}_{\nu\sigma} >< \hat{n}_{\mu\sigma} >\ , \tag{40b}$$

where $J^{\rm eff}_{\mu\nu}$ is defined by

$$\tilde{J}^{(0)}_{\mu\nu} < \hat{c}^\dagger_{\nu\sigma}\hat{c}_{\mu\sigma} >< \hat{c}^\dagger_{\mu\sigma}\hat{c}_{\nu\sigma} >= J^{\rm eff}_{\mu\nu} < \hat{n}_{\nu\sigma} >< \hat{n}_{\mu\sigma} >\ . \tag{40c}$$

Equation (40c) guarantees that our ansatz [Eq. (40b)] yields the same energy as the exchange contribution for a given ground state. Moreover, for a two-level case it is easy to find from Eq. (40b) that $J^{\rm eff}_{\mu\nu} = \tilde{J}^{(0)}_{\mu\nu}$; then, the exchange term cancels out exactly the Hartree-term appearing in (35c), as it should, because the single electron cannot influence itself.

Equation (40c) is the basic equation replacing the exchange off-diagonal contribution by a diagonal one. This substitution will be used in our approximated Hamiltonian for calculating all the electronic properties. The adequacy of this ansatz can be further explored by analyzing the exchange pair correlation function associated with Eq. (40c). To this end, let us notice that

$$\sum_\mu < \hat{c}^\dagger_{\nu\sigma}\hat{c}_{\mu\sigma} >< \hat{c}^\dagger_{\mu\sigma}\hat{c}_{\nu\sigma} >=< \hat{c}^\dagger_{\nu\sigma}\hat{c}_{\nu\sigma} >=< \hat{n}_{\nu\sigma} >\ . \tag{41}$$

This equation suggests the introduction of the pair correlation function $g_\sigma(\nu,\mu)$, by means of the equation

$$< \hat{c}^\dagger_{\nu\sigma}\hat{c}_{\mu\sigma} >< \hat{c}^\dagger_{\mu\sigma}\hat{c}_{\nu\sigma} >=< \hat{n}_{\nu\sigma} > g_\sigma(\nu,\mu) \tag{42}$$

because Eqs. (41) and (42) show that

$$\sum_\mu g_\sigma(\nu,\mu) = 1 \tag{43}$$

as corresponds to the exchange hole appearing around an electron. Now, it is convenient to rewrite the total exchange energy in the following way:

$$\begin{aligned}E_x &= -\tfrac{1}{2}\sum_{\nu,\mu\neq\nu,\sigma}\tilde{J}^{(0)}_{\nu\mu} < \hat{c}^\dagger_{\nu\sigma}\hat{c}_{\mu\sigma} >< \hat{c}^\dagger_{\mu\sigma}\hat{c}_{\nu\sigma} >\\ &= -\tfrac{1}{2}\sum_{\nu,\mu\neq\nu,\sigma}\tilde{J}^{(0)}_{\nu\mu} < \hat{n}_{\nu\sigma} > g_\sigma(\nu,\mu)\end{aligned} \tag{44}$$

with g_σ given by Eq. (42). Equation (44) defines E_x as a function of $g_\sigma(\nu,\mu)$ in the appropriate way. We can also define the exchange energy $E^{\nu\sigma}_x$, for a level $\nu\sigma$, by

$$E^{\nu\sigma}_x = -\sum_{\mu\neq\nu}\tilde{J}^{(0)}_{\nu\mu} < \hat{n}_{\nu\sigma} > g_\sigma(\nu,\mu)\ ; \tag{45}$$

the factor $\frac{1}{2}$ appearing in (44) accounts for double counting of the electron-electron interaction. Thus

$$E_x = \tfrac{1}{2}\sum_{\nu\sigma} E^{\nu\sigma}_x\ . \tag{46}$$

It is instructive to consider a simple case: assume that the exchange hole around an electron in the ν level is localized in the first-nearest neighbors. Then

$$E^{\nu\sigma}_x = -\sum_{\mu\neq\nu}\tilde{J}^{(0)}_{\nu\mu} < \hat{n}_{\nu\sigma} > g_\sigma(\nu,\mu)\ , \tag{47}$$

where μ and ν are nearest neighbors. A further step can be given using the sum rule,

$$g_\sigma(\nu,\nu) + \sum_{\mu\neq\nu} g_\sigma(\nu,\mu) = 1 \tag{48a}$$

and

$$g_\sigma(\nu,\nu) =< \hat{n}_{\nu\sigma} >\ . \tag{48b}$$

Equations (47) and (48) yield

$$E_x^{\nu\sigma} = -\tilde{J}_{\mu\nu}^{(0)} < \hat{n}_{\nu\sigma} > (1 - < \hat{n}_{\nu\sigma} >) \ , \tag{49}$$

where $J_{\mu\nu}^{(0)}$ is the bare Coulomb interaction between electrons in nearest-neighbor orbitals, μ and ν. Equation (49) will be shown below to be related to the correlation energy $E_c^{\nu\sigma}$ associated with the electrons filling the ν level.

Having discussed the exchange energy, let us turn our attention to correlation. In a first step, we consider the case of H approaching a metal surface. Figure 4(a) shows a typical energy diagram for this case. It is well known that correlation effects between the metal and the adatom are treated in a simple way introducing the image potential $e^2/4d$: the affinity and ionization levels are changed to $A - e^2/4d$ and $I + e^2/4d$, respectively, with an effective intrasite Coulomb repulsion of $U - e^2/2d$.

In our approach, we consider metal-adatom correlation effects in a similar way. When an electron jumps from the metal to the adatom [see Fig. 4(b)], creating a negative ion on the surface, the metal screens the extra charge and a hole is created around the adatom. If we assume this hole to be localized in the adatom nearest neighbors, the intra-atomic Coulomb interaction U is reduced to $U - J^{(0)}$ [see Fig. 4(b)]. At the same time, the ionization level should be shifted by some amount as in the case shown in Fig. 4(a). The point to be noticed here is that the new ionization level I^{eff} should be taken in such a way that the Hartree solution of the new effective Hamiltonian is not modified by the new levels. This means that we should take

$$\begin{aligned} I^{\text{eff}} &= I + J^{(0)} < \hat{n}_{-\sigma} > \ , \\ U^{\text{eff}} &= U - J^{(0)} \end{aligned} \tag{50}$$

with these definitions:

$$I^{\text{eff}} + U^{\text{eff}} < \hat{n}_{-\sigma} > = I + U < \hat{n}_{-\sigma} > \tag{51}$$

as it should be.

Equations (50) include metal correlation effects on the adatom. In order to calculate the modification that these new levels introduce in the total energy,[20] we assume $(U - J^{(0)})$ small enough for a Hartree approximation to be appropriate. Equation (51) shows that, in this limit, the electronic spectrum obtained from the total Hamiltonian [Eq. (27)] is the same as the one calculated with the initial ionization level I and the intrasite Coulomb interaction U. The total energy is not, however, the same, the reason being that the "initial" ionization level I has been shifted by $J^{(0)} < \hat{n}_{-\sigma} >$, and that the intrasite Coulomb interaction has been reduced to $U - J^{(0)}$. The ionization shift reduces the total energy by $J^{(0)} < \hat{n}_{-\sigma} >$, due to the change in the initial level which has to be used as a reference to calculate the total energy;[20] moreover, the reduction of U modifies the intrasite repulsion and changes the total energy by $J^{(0)} < \hat{n}_{\uparrow} > < \hat{n}_{\downarrow} >$ (this value accounts for double counting of the intrasite Coulomb interaction). Both contributions yield the following adatom correlation energy:

$$E_{\text{correl}}^{\text{adatom}} = -J^{(0)} < \hat{n}_{\sigma} > (1 - < \hat{n}_{\sigma} >) \ , \tag{52}$$

where we have assumed $< \hat{n}_{\sigma} > = < \hat{n}_{-\sigma} >$.

Equation (52) has been obtained for an adatom chemisorbed on a metal surface, but the same argument can be applied to any other physical case, say, with an atom located inside the solid. The only important conditions that have been introduced to obtain Eq. (52) are the following: (i) the screening hole has been assumed to be located in the nearest neighbors; (ii) $(U - J^{(0)})$ has been assumed to be small enough for a Hartree solution of the adatom effective Hamiltonian to be accurate. This would not be the case for the adatom far from the surface when intrasite correlation effects are important.

It is of interest to compare Eqs. (52) and (49). For the restricted case we are considering here,

$$E_x^{\nu} = \sum_{\sigma} E_x^{\nu\sigma} = -2J^{(0)} < \hat{n}_{\nu\sigma} > (1 - < \hat{n}_{\nu\sigma} >) \ . \tag{53}$$

If we take ν as the adatom, Eqs. (52) and (53) show that

$$E_{\text{correl}}^{\text{adatom}} = \tfrac{1}{2} E_x^{\text{adatom}} \ . \tag{54}$$

This is an important result that has been obtained by assuming the correlation and the exchange hole are localized on the nearest-neighbor sites. We will assume that the same equation holds for a more general hole (or correlation) pair distribution function. This allows us to write, for the more general case,

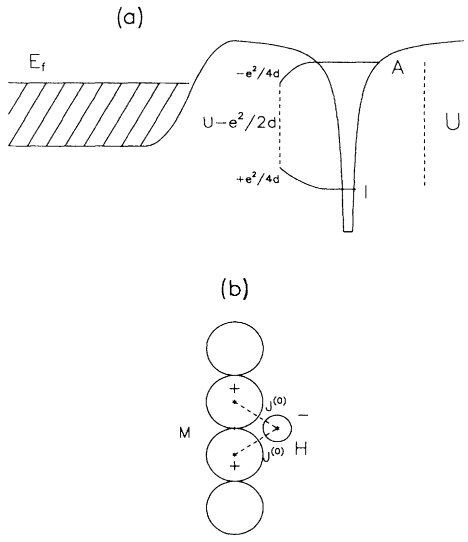

FIG. 4. (a) Energy diagram for a hydrogen-atom chemisorbed on a metal surface. The affinity (A) and the ionization (I) levels are corrected by the image potential: $e^2/4d$. The effective intrasite Coulomb interaction is reduced by $e^2/2d$. (b) When an electron (−) fills the affinity level, the metal screens this extra charge and a hole (+) is created around hydrogen. This effect reduces U to $U - J^{(0)}$, $-J^{(0)}$ being the interaction between the extra electron and its hole which is assumed localized in the adatom nearest neighbors.

$$E^{\nu}_{\mathrm{correl}} = \tfrac{1}{2}E^{\nu}_{x} = -\sum_{\mu\neq\nu} J^{(0)}_{\mu\nu} < \hat{n}_{\nu\sigma} > g_{\sigma}(\nu,\mu) \ . \tag{55}$$

In general, we shall take

$$E^{\nu}_{\mathrm{exchange}} + E^{\nu}_{\mathrm{correl}} = \tfrac{3}{2}E^{\nu}_{\mathrm{exchange}} \ . \tag{56}$$

Equation (56) yields the total exchange and correlation energy per orbital, and allows us to introduce many-body effects in our LCAO approach following a method closely related to the Slater $X\alpha$ approach [in our case, no parameter appears; the equivalent of the parameter α for the Slater approach is fixed by the argument yielding Eq. (56)].

D. Hopping integrals. Bardeen tunneling currents

Sections II A–II C give our formal procedure to calculate the electronic properties of any system. In particular, the hopping integrals $T_{\mu\nu}$ between two orbitals are given by Eqs. (27b), (22a), (22b), and (22c). In this section we discuss how to obtain these hopping terms by means of the Bardeen tunneling currents between the atomic orbitals ψ_{ν} and ψ_{μ}. The advantage of this procedure is that one can reduce the calculation of $T_{\mu\nu}$ to expressions involving only valence orbitals: in other words, in the final equations, the atomic core orbitals do not appear. This means that, from the point of view of the LCAO method presented here, the tunneling currents play the same role as pseudopotentials in the free-electron calculations.

Our starting point, as mentioned above, is afforded by Eqs. (27b), (22a), (22b), and (22c). Notice that, in principle, $T_{\mu\nu}$ is given exactly by these equations if the different terms, $t_{\mu\nu}$, $h^{\sigma\sigma'}_{\lambda,\nu\mu}$, and $h^{x}_{\lambda,\nu\mu}$ are calculated to all orders of the overlap. As discussed in Sec. II A, $T_{\mu\nu}$ should be calculated in this way if the (ν,μ) overlap, $S_{\mu\nu}$, is very large. For most purposes, $S_{\mu\nu}$ is small, and we can obtain $T_{\mu\nu}$ up to second order in the overlap coefficients. Then, $t_{\mu\nu}$, $h^{\sigma\sigma'}_{\lambda,\nu\mu}$, and $h^{x}_{\lambda,\nu\mu}$ should be replaced by the values given by Eqs. (24b), (24c), (24d), and (24e). This yields the following equation:

$$\begin{aligned} T^{\sigma}_{\nu\mu} = {} & t^{(0)}_{\nu\mu} + h^{(0)}_{\nu,\nu\mu} < \hat{n}_{\nu-\sigma} > + h^{(0)}_{\mu,\nu\mu} < \hat{n}_{\mu-\sigma} > + \sum_{\sigma'\lambda} h^{(0)}_{\lambda,\nu\mu} < \hat{n}_{\lambda\sigma'} > - \sum_{\lambda} h^{x(0)}_{\lambda,\nu\mu} < \hat{n}_{\lambda\sigma} > \\ & -\frac{S_{\nu\mu}}{2}\Bigg[\Bigg(\varepsilon^{(0)}_{\nu} + U^{(0)}_{\nu} < \hat{n}_{\nu-\sigma} > + J^{(0)}_{\nu\mu} < \hat{n}_{\mu-\sigma} > + \sum_{\sigma',\lambda\neq\nu,\mu} J^{(0)}_{\nu\lambda} < \hat{n}_{\lambda\sigma'} > - \sum_{\lambda\neq\nu,\mu} J^{x,(0)}_{\nu\lambda} < \hat{n}_{\lambda\sigma} >\Bigg) \\ & + \Bigg(\varepsilon^{(0)}_{\mu} + U^{(0)}_{\mu} < \hat{n}_{\mu-\sigma} > + J^{(0)}_{\mu\nu} < \hat{n}_{\nu-\sigma} > + \sum_{\sigma',\lambda\neq\nu,\mu} J^{(0)}_{\mu\lambda} < \hat{n}_{\lambda\sigma'} > - \sum_{\lambda\neq\mu,\nu} J^{x,(0)}_{\mu\lambda} < \hat{n}_{\lambda\sigma} >\Bigg)\Bigg] \ . \end{aligned} \tag{57}$$

This equation can be rewritten in a more transparent way as follows:

$$T^{\sigma}_{\nu\mu} = < \psi_{\nu} \mid \hat{H}^{\sigma}_{(0)} \mid \psi_{\mu} > - \frac{S_{\nu\mu}}{2}(< \psi_{\nu} \mid \hat{H}^{\sigma}_{(0)} \mid \psi_{\nu} > + < \psi_{\mu} \mid \hat{H}^{\sigma}_{(0)} \mid \psi_{\mu} >) \ , \tag{58}$$

where

$$\begin{aligned} \hat{H}^{\sigma}_{(0)} = {} & -\tfrac{1}{2}\nabla^{2} + V_{\nu}(\mathbf{r}-\mathbf{R}_{\nu}) + V_{\mu}(\mathbf{r}-\mathbf{R}_{\mu}) + \sum_{\omega\neq\mu\nu} V_{\omega}(\mathbf{r}-\mathbf{R}_{\omega}) + \left(\int \frac{\psi^{2}_{\nu}(\mathbf{r}')}{\mid \mathbf{r}-\mathbf{r}' \mid} d\mathbf{r}'\right) < \hat{n}_{\nu-\sigma} > \\ & + \left(\int \frac{\psi^{2}_{\mu}(\mathbf{r}')}{\mid \mathbf{r}-\mathbf{r}' \mid} d\mathbf{r}'\right) < \hat{n}_{\mu-\sigma} > + \sum_{\lambda,\sigma'} \left(\int \frac{\psi^{2}_{\lambda}(\mathbf{r}')}{\mid \mathbf{r}-\mathbf{r}' \mid} d\mathbf{r}'\right) < n_{\lambda\sigma'} > - \sum_{\lambda} \left(\int \frac{\psi_{\lambda}(\mathbf{r}')\psi_{\lambda}(\mathbf{r})}{\mid \mathbf{r}-\mathbf{r}' \mid} d\mathbf{r}'\right) < \hat{n}_{\lambda\sigma} > \ . \end{aligned} \tag{59}$$

In this equation V_{ν} and V_{μ} are the potentials created by the nuclei of the atoms where the orbitals ν and μ are located, respectively, V_{ω} the potential created by the other nuclei; the next three terms represent the Hartree potentials created by the electrons located in orbitals ν, μ, and λ, while the last term represents the exchange interaction associated with the λ orbitals. One has to notice that the last term of $\hat{H}^{\sigma}_{(0)}$ operates on ψ_{ν} and ψ_{μ} as follows:

$$\left\langle \psi_{\nu} \middle| \left(\int \frac{\psi_{\lambda}(\mathbf{r}')\psi_{\lambda}(\mathbf{r})}{\mid \mathbf{r}-\mathbf{r}' \mid} d\mathbf{r}'\right) \middle| \psi_{\mu} \right\rangle = \int\!\!\int \frac{\psi_{\lambda}(\mathbf{r}')\psi_{\lambda}(\mathbf{r})\psi_{\nu}(\mathbf{r}')\psi_{\mu}(\mathbf{r})}{\mid \mathbf{r}-\mathbf{r}' \mid} d\mathbf{r}'d\mathbf{r} \ . \tag{60}$$

Equation (58) has the same form as Eq. (10b) of I, where a one-electron local potential was introduced; in our actual case, $H^{\sigma}_{(0)}$ yields the Hartree-Fock nonlocal potential that depends on the different ocupation numbers, $< \hat{n}_{\lambda\sigma} >$. We should stress that $H^{\sigma}_{(0)}$ is an approximate Hartree-Fock potential, since terms yielding contributions proportional to, or larger than, S^{2} have been neglected (if $H^{\sigma}_{(0)}$ is proportional to S, $< \psi_{\nu} \mid \hat{H}^{\sigma}_{(0)} \mid \psi_{\mu} >$ is proportional to S^{2}). The exchange term [last term in Eq. (59)] yields only a non-negligible contribution if ψ_{λ} belongs to one of the atoms associated with the orbitals ψ_{ν} or ψ_{μ}.

The Hamiltonian (59) includes the Hartree-Fock contribution associated with atoms ν and μ, and the Hartree potential created by the nuclei, and mean charges of the other atoms. We rewrite $H^\sigma_{(0)}$ in the following way:

$$H^\sigma_{(0)} = H^\sigma_\alpha + H^\sigma_\beta + H^\sigma_\omega \ , \tag{61}$$

where H^σ_α and H^σ_β represent the Hartree-Fock potential of the atoms associated with orbitals ν and μ, respectively, while H^σ_ω refers to the other atoms. Thus,

$$\begin{aligned}\hat{H}^\sigma_\alpha = -\frac{1}{2}\nabla^2 - \frac{Z_\alpha}{\mathbf{r}-\mathbf{R}_\alpha} + \left(\int \frac{\psi_\nu^2(\mathbf{r}')}{\mid \mathbf{r}-\mathbf{r}' \mid} d\mathbf{r}'\right) < \hat{n}_{\nu-\sigma} > \\ + \sum_{\alpha\neq\nu,\sigma'} \left(\int \frac{\psi_\alpha^2(\mathbf{r}')}{\mid \mathbf{r}-\mathbf{r}' \mid} d\mathbf{r}'\right) < \hat{n}_{\alpha\sigma'} > \\ - \sum_{\alpha\neq\nu} \left(\int \frac{\psi_\alpha(\mathbf{r}')\psi_\alpha(\mathbf{r})}{\mid \mathbf{r}-\mathbf{r}' \mid} d\mathbf{r}'\right) < \hat{n}_{\alpha\sigma} > \ ,\end{aligned} \tag{62}$$

where Z_α is the nuclear charge, and the other terms yield the Hartree potential and the exchange contribution associated with the orbitals ψ_α of the α atom. The nonlocal term of Eq. (62) operates on the wave functions as explained in Eq. (60). A similar equation can be written for H^σ_β replacing α by β and ν by μ. As regards H^σ_ω we use a Hartree approximation:

$$\hat{H}^\sigma_\omega = -\sum_{\omega\neq\alpha\beta} \frac{Z_\alpha}{\mathbf{r}-\mathbf{R}_\alpha} + \sum_{\lambda,\sigma'} \left(\int \frac{\psi_\lambda^2(\mathbf{r}')}{\mid \mathbf{r}-\mathbf{r}' \mid} d\mathbf{r}'\right) < \hat{n}_{\lambda\sigma'} > \ . \tag{63}$$

In order to calculate $T^\sigma_{\nu\mu}$ we use Eqs. (58) and (60) and write:

$$\begin{aligned}T^\sigma_{\nu\mu} = < \psi_\nu \mid (\hat{H}^\sigma_\alpha + \hat{H}^\sigma_\beta) \mid \psi_\mu > - \frac{S_{\nu\mu}}{2}[< \psi_\nu \mid (\hat{H}^\sigma_\alpha + \hat{H}^\sigma_\beta) \mid \psi_\nu > + < \psi_\mu \mid (\hat{H}^\sigma_\alpha + \hat{H}^\sigma_\beta) \mid \psi_\mu >] \\ + < \psi_\nu \mid \hat{H}^\sigma_\omega \mid \psi_\mu > - \frac{S_{\nu\mu}}{2}(< \psi_\nu \mid \hat{H}^\sigma_\omega \mid \psi_\nu > + < \psi_\mu \mid \hat{H}^\sigma_\omega \mid \psi_\mu >) \ .\end{aligned} \tag{64}$$

We proceed to discuss the contribution to $T^\sigma_{\nu\mu}$ coming from the α and β atoms. Notice that Hamiltonians $\hat{H}^\sigma_\alpha$ and $\hat{H}^\sigma_\beta$ include all the electrons of both atoms, and their contribution to $T^\sigma_{\nu\mu}$ has to be worked out in detail. We shall show that all these details can be embodied in the Bardeen tunneling current plus some correction terms to be discussed below.

In a first step, assume that ψ_ν and ψ_μ are chosen such that

$$\hat{H}^\sigma_\alpha \psi_\nu = E^{at}_\nu \psi_\nu \ , \quad \hat{H}^\sigma_\beta \psi_\mu = E^{at}_\mu \psi_\mu \ . \tag{65}$$

Then, using the same argument given in I, it can be shown that

$$\begin{aligned}< \psi_\nu \mid (\hat{H}^\sigma_\alpha + \hat{H}^\sigma_\beta) \mid \psi_\mu > - \frac{S_{\nu\mu}}{2}[< \psi_\nu \mid (\hat{H}^\sigma_\alpha + \hat{H}^\sigma_\beta) \mid \psi_\nu > + < \psi_\mu \mid (\hat{H}^\sigma_\alpha + \hat{H}^\sigma_\beta) \mid \psi_\mu >] \\ = T^B_{\nu\mu} + \int_{\Omega_\alpha} \psi_\nu \hat{V}_\beta \psi_\mu d\mathbf{r} + \int_{\Omega_\beta} \psi_\nu \hat{V}_\alpha \psi_\mu d\mathbf{r} - \frac{S_{\nu\mu}}{2}\left(\int_\Omega \psi_\nu \hat{V}_\beta \psi_\nu d\mathbf{r} + \int_\Omega \psi_\mu \hat{V}_\alpha \psi_\mu d\mathbf{r}\right) \ ,\end{aligned} \tag{66}$$

where the whole space, Ω, is split into the subspaces Ω_ν and Ω_μ, associated with orbitals ν and μ, respectively.

In Eq. (66),

$$T^B_{\nu\mu} = -\tfrac{1}{2}\int_{\sigma_{\nu\mu}} (\psi_\nu \nabla \psi_\mu - \psi_\mu \nabla \psi_\nu) d\mathbf{S} \ , \tag{67}$$

$\sigma_{\nu\mu}$ being the surface limiting the subspaces Ω_ν and Ω_μ and satisfying the condition

$$\int_{\Omega_\nu} \psi_\nu \psi_\mu d\mathbf{r} = \int_{\Omega_\mu} \psi_\nu \psi_\mu d\mathbf{r} = \tfrac{1}{2}\int_\Omega \psi_\nu \psi_\mu d\mathbf{r} \ . \tag{68}$$

Moreover, $\hat{V}_\alpha$ and $\hat{V}_\beta$ are defined by the following equations:

$$\hat{H}_\alpha = -\tfrac{1}{2}\nabla^2 + \hat{V}_\alpha \ , \quad \hat{H}_\beta = -\tfrac{1}{2}\nabla^2 + \hat{V}_\beta \ . \tag{69}$$

Equation (66) includes the long-range effects associated with the atomic potentials $\hat{V}_\alpha$ and $\hat{V}_\beta$. If we assume these effects to be small, Eq. (66) reduces to

$$\begin{aligned}T^B_{\nu\mu} = < \psi_\nu \mid (\hat{H}^\sigma_\alpha + \hat{H}^\sigma_\beta) \mid \psi_\mu > \\ - \frac{S_{\nu\mu}}{2}[< \psi_\nu \mid (\hat{H}^\sigma_\alpha + \hat{H}^\sigma_\beta) \mid \psi_\nu > \\ + < \psi_\mu \mid (\hat{H}^\sigma_\alpha + \hat{H}^\sigma_\beta) \mid \psi_\mu >] \ ,\end{aligned} \tag{70}$$

the same equation as obtained in I [see here Eq. (19)].

In obtaining Eq. (66) we have assumed Eqs. (65) to hold. In general, this assumption is not appropriate due to change in the orbital occupancies, $< \hat{n}_{\nu-\sigma} >$, $< \hat{n}_{\mu-\sigma} >$, and $< \hat{n}_{\lambda\sigma'} >$ when going from the atom to the more general system. Then, it is convenient to introduce the atomic potentials, $\hat{V}^{\text{at}}_\alpha$ and $\hat{V}^{\text{at}}_\beta$, such that

$$\hat{H}^{\text{at}}_\alpha = -\tfrac{1}{2}\nabla^2 + \hat{V}^{\text{at}}_\alpha, \quad \hat{H}^{\text{at}}_\beta = -\tfrac{1}{2}\nabla^2 + \hat{V}^{\text{at}}_\beta \ . \tag{71}$$

The atomic orbitals ψ_ν and ψ_μ are chosen to satisfy the following equations:

$$\hat{H}_\alpha^{\text{at}}\psi_\nu = E_\nu^{\text{at}}\psi_\nu, \quad \hat{H}_\beta^{\text{at}}\psi_\mu = E_\mu^{\text{at}}\psi_\mu \ . \tag{72}$$

Here $\hat{V}_\alpha^{\text{at}}$ and $\hat{V}_\beta^{\text{at}}$ are as $\hat{V}_\alpha$ and $\hat{V}_\beta$ replacing the level occupancies by their atomic values.

In the next step, we write

$$\hat{H}_{(0)}^\sigma = \hat{H}_\alpha^{\text{at},\sigma} + \hat{H}_\beta^{\text{at},\sigma} + (\hat{H}_\alpha^\sigma - \hat{H}_\alpha^{\text{at},\sigma}) + (\hat{H}_\beta^\sigma - \hat{H}_\beta^{\text{at},\sigma}) + \hat{H}_\omega^\sigma \tag{73}$$

and calculate, independently, the contributions coming from $(\hat{H}_\alpha^{\text{at},\sigma} + \hat{H}_\beta^{\text{at},\sigma})$.

Using the previous argument for the new Hamiltonian $(\hat{H}_\alpha^{\text{at},\sigma} + \hat{H}_\beta^{\text{at},\sigma})$, we obtain the following equation:

$$\begin{aligned} T_{\nu\mu}^{\text{at}} &= < \psi_\nu \mid (\hat{H}_\alpha^{\sigma,\text{at}} + \hat{H}_\beta^{\sigma,\text{at}}) \mid \psi_\mu > - \frac{S_{\nu\mu}}{2}[< \psi_\nu \mid (\hat{H}_\alpha^{\sigma,\text{at}} + \hat{H}_\beta^{\sigma,\text{at}}) \mid \psi_\nu >< \psi_\mu \mid (\hat{H}_\alpha^{\sigma,\text{at}} + \hat{H}_\beta^{\sigma,\text{at}}) \mid \psi_\mu >] \\ &= T_{\nu\mu}^B + \int_{\Omega_\alpha} \psi_\nu \hat{V}_\beta^{\text{at}} \psi_\mu d\mathbf{r} + \int_{\Omega_\beta} \psi_\nu \hat{V}_\alpha^{\text{at}} \psi_\mu d\mathbf{r} - \frac{S_{\nu\mu}}{2} \left(\int_\Omega \psi_\nu \hat{V}_\beta^{\text{at}} \psi_\nu d\mathbf{r} + \int_\Omega \psi_\mu \hat{V}_\alpha^{\text{at}} \psi_\mu d\mathbf{r} \right) \ . \end{aligned} \tag{74}$$

The total hopping element, $T_{\nu\mu}^\sigma$, is given by

$$\begin{aligned} T_{\nu\mu}^\sigma = T_{\nu\mu}^{\text{at}} &+ < \psi_\nu \mid \delta(\hat{H}_\alpha^\sigma + \hat{H}_\beta^\sigma) \mid \psi_\mu > - \frac{S_{\nu\mu}}{2}[< \psi_\nu \mid \delta(\hat{H}_\alpha^\sigma + \hat{H}_\beta^\sigma) \mid \psi_\nu > + < \psi_\mu \mid \delta(\hat{H}_\alpha^\sigma + \hat{H}_\beta^\sigma) \mid \psi_\mu >] \\ &+ < \psi_\nu \mid \hat{H}_\omega^\sigma \mid \psi_\mu > - \frac{S_{\nu\mu}}{2}(< \psi_\nu \mid \hat{H}_\omega^\sigma \mid \psi_\nu > + < \psi_\mu \mid \hat{H}_\omega^\sigma \mid \psi_\mu >) \ , \end{aligned} \tag{75}$$

where

$$\delta(\hat{H}_\alpha^\sigma + \hat{H}_\beta^\sigma) = (\hat{H}_\alpha^\sigma + \hat{H}_\beta^\sigma) - (\hat{H}_\alpha^{\sigma,\text{at}} + \hat{H}_\beta^{\sigma,\text{at}}) \ . \tag{76}$$

Equations (74) and (75) yield our results for $T_{\nu\mu}^\sigma$, the hopping between orbitals ν and μ, belonging to the atoms α and β, respectively. Equation (74) yields the hopping for two isolated atoms, and this equation shows that, basically, this contribution is given by the Bardeen tunneling current $T_{\nu\mu}^B$. Other contributions in Eq. (74) are long-range effects of the atomic potentials $\hat{V}_\alpha^{\text{at}}$ and $\hat{V}_\beta^{\text{at}}$, and it should be stressed that they can be calculated assuming all the orbital charge concentrated in the respective nucleus except for the valence electrons.

Equation (75) yields two other contributions. The first one comes from the change in the orbital charge for the atom in the system; its contribution is controlled by $\delta(\hat{H}_\alpha^\sigma + \hat{H}_\beta^\sigma)$. In this case, only the valence orbitals present changes in their occupancies and yield non-negligible contributions to $T_{\nu\mu}^\sigma$. On the other hand, Eq. (75) also yields contributions associated with the Hartree potential created by other atoms: these are given by the terms associated with $\hat{H}_\omega^\sigma$ in Eq. (75). In general these last contributions are not important, the reason being the cancellation between $< \psi_\nu \mid \hat{H}_\omega^\sigma \mid \psi_\mu >$ and the next term $-(S_{\nu\mu}/2)[< \psi_\nu \mid \hat{H}_\omega^\sigma \mid \psi_\nu > + < \psi_\mu \mid \hat{H}_\omega^\sigma \mid \psi_\mu >]$.

To complete the discussion of this section, we comment that the contributions associated with $\hat{H}_\alpha$ and $\hat{H}_\beta$ can be calculated using only two-center integrals, while the ones coming from $\hat{H}_\omega$ need three-center integrals that can be calculated expanding the Slater atomic wave functions in Gaussian orbitals.

E. Surface calculations

Hamiltonian (26) and Eqs. (27) yield our basic approach to the chemisorption problem. Many-body effects are reduced to a one-electron Hamiltonian using the Slater-like approach developed in Sec. II C, while the hopping interactions are calculated in the way discussed in Sec. II D. This defines a one-electron Hamiltonian for the whole system: the metal surface and the adsorbate. We have solved this Hamiltonian in a self-consistent way as follows: (i) The one-electron Hamiltonian is projected onto the last few layers of the surface metal and the adsorbate by means of a decimation technique.[21] Thus, the interface properties are calculated by solving a reduced effective matrix that includes all the bulk metal effects. (ii) The projected one-electron Hamiltonian is solved using a Green-function method; this yields the one-electron occupancies

$$< \hat{n}_i > = -\frac{1}{\pi}\int_{-\infty}^{E_F} \text{Im}G_{ii}(w)dw \ , \tag{77a}$$

$$< \hat{c}_i^\dagger \hat{c}_j > = -\frac{1}{\pi}\int_{-\infty}^{E_F} \text{Im}G_{ij}(w)dw \ , \tag{77b}$$

needed for defining the complete Hamiltonian, since the many-body effects and the hopping interactions depend on $< \hat{n}_i >$ and the $< \hat{c}_i^\dagger \hat{c}_j >$. (iii) The one-electron Hamiltonian is solved self-consistently in the electron occupancies, $< \hat{n}_i >$ and $< \hat{c}_i^\dagger \hat{c}_j >$, by means of the electrostatic potential created by all the charges of the system and the Slater-like potential associated with the exchange and correlation effects.

III. RESULTS AND DISCUSSION

In this paper we present detailed results for the adsorption of a monolayer of H on the Li(100) and Al(100) surfaces. We have chosen these cases because there are a lot of theoretical[22–28] and experimental results[29,30] for these systems. The purpose of our calculation is to check the validity of our *ab initio* approach and, at the same time, to analyze the main physical factors controlling the chemisorption of H on simple metals.

We start considering the H/Al(100) system for which there are some accurate LDA calculations.[22–24] Figure 5 shows the surface geometry: we have analyzed the chemisorption energy for a hydrogen monolayer relaxing perpendicular to the surface, with the hydrogen atoms moving along the (a) center and (b) bridge metal surface sites. In our calculations we have used the $1s, 2s, 2p, 3s, 3p$ orbitals for Al, and the $1s$ H level; the different atomic wave functions have been taken directly from Ref. 17, without allowing any changes in the parameters defined in the orbitals. We have checked by introducing a relaxed orbital for H, that a wave-function expansion introduces a decrease in the total energy of the system smaller than 0.1 eV per surface atom.

Figure 5 gives the total chemisorption energy per unit cell for the hydrogen monolayer on Al(100) on the center and bridge sites of the surface. The origin of distances is the last metal layer. In our results, the H monolayer always finds its equilibrium position above the last metal layer: the distance between the H monolayer and the last metal layer is 2.0 and 2.4 a.u. for the center and bridge sites, respectively. This result shows that the high metal electron density of Al prevents the hydrogen atoms from penetrating the crystal. At the equilibrium distances, the chemisorption energies are 0.80 and 2.07 eV for the center and bridge sites, respectively. These results should be compared with the LDA figures as calculated for a single hydrogen atom chemisorbed on the same Al surface.[22] The results of Ref. 22 give the following chemisorption energies: 1.4 eV (center) and 2.3 eV (bridge). Our results are a little smaller [0.6 eV (center) and 0.22 (bridge)] than the LDA results: this reflects the fact that for a monolayer there is some repulsion between the hydrogen atoms that reduces the chemisorption energy per unit cell. It is interesting to mention that in some recent LDA calculations, Mallo[31] has shown that for a monolayer of H on the Mg(1000) surface the chemisorption energy per atom is reduced by a few tenths of eV with respect to the single atom case, in good agreement with the results obtained here. Similar results for the Be(1000) have been obtained by Yu and Lam.[32] In general, the results of Fig. 5 show a good agreement with the LDA results: the small differences between both calculations can be traced back to the effect of having in our actual case a hydrogen monolayer instead of a single atom.

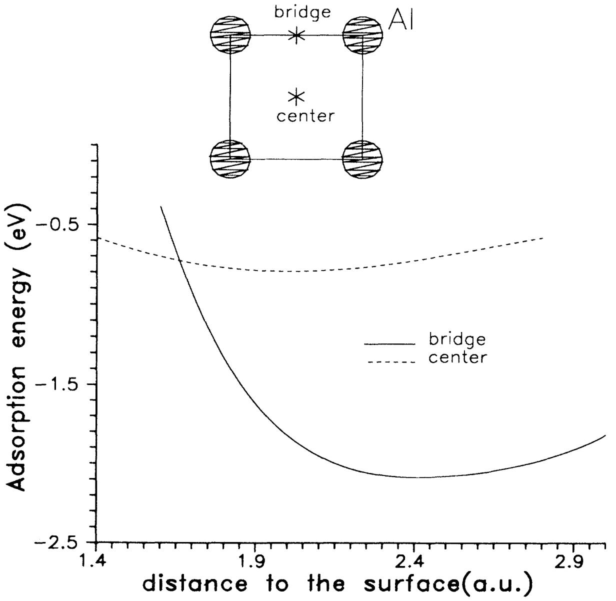

FIG. 5. Chemisorption energy per unit cell for a hydrogen monolayer on Al(100). Bridge and center sites are shown. The distance refers the hydrogen monolayer to the last metal layer.

In order to have a better understanding of the different effects controlling the adsorption process, we show in Fig. 6 the different contributions we have obtained in our calculation to the chemisorption energy of H on Al(100). This is split into the following terms: (i) electrostatic energy; (ii) valence kinetic repulsion; (iii) core kinetic repulsion; (iv) hybridization; and (v) exchange and correlation energies. The electrostatic energy includes all the contribution from the different charges, nuclei, and core and valence electrons. The kinetic repulsion yields the energy associated with the terms going like $-S_{ij}T_{ij}$ and $\frac{1}{4}S_{ij}^2(E_i - E_j)$ [see Eqs. (27) and (33)]; we have split this energy for the valence electrons and the core electrons interacting with the hydrogen level. The hybridization term yields the energy associated with all the hopping interactions and with the transfer of charge between different levels: thus, it includes the changes of energy due to the transfer of electronic charge between hydrogen and the substrate. Finally, the many-body terms associated with the exchange and correlation effects are also shown.

The first thing to notice is the large contribution that

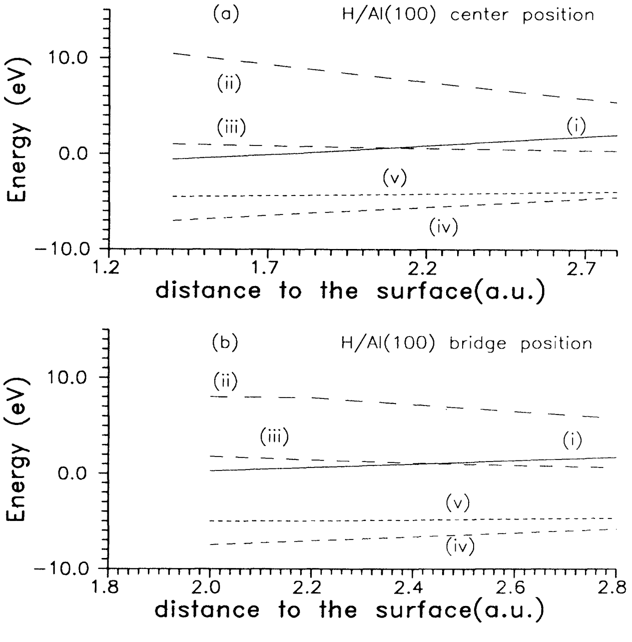

FIG. 6. Different contributions to the chemisorption energy of H on Al(100). (a) Center. (b) Bridge. (i) Electrostatic energy. (ii) Valence kinetic repulsion. (iii) Core kinetic repulsion. (iv) Hybridization. (v) Exchange and correlation.

most of the different terms have to the total energy that appears as the result of a delicate balance among all the terms. It is also important to realize that the core and valence kinetic repulsion are the main factor controlling the equilibrium distance between hydrogen and the metal; in the particular case of Al, the valence kinetic energy gives enough repulsion to prevent the hydrogen from penetrating the metal: this is mainly due to the high electron density in the metal. The main atractive energy is due to the hybridization term, although the exchange and correlation energy also plays an important role. In general, the hybridization energy is controlled by the shift of the mean hydrogen level with respect to the metal: when the ad-atom penetrates the metal, its mean level is lowered by the electrostatic potential created by the atoms and some electron charge is transferred from the metal to the hydrogen atom, this transfer of charge increasing the chemisorption energy. In Fig. 7 we show the local density of states on the hydrogen monolayer for the equilibrium distance at the center and bridge positions: it is interesting to realize that for the bridge site, this density of states is a little larger due to the shift of the H mean level to lower energies. This explains that the hybridization and the chemisorption energies are larger for the bridge site, and that the electron transfer of charge is also larger for this case: we have found that 0.05 electron are transferred from the metal to the hydrogen atom at the bridge equilibrium distance.

We should also mention that for this H/Al(100) case, the hydrogen atom is kept so far away from the metal surface that the overlap between the different atomic wave functions is always smaller than 0.4. This can be checked in Fig. 8, where the overlap between the 1s H level and the other Al orbitals is shown as a function of the hydrogen distance to the metal surface. These results validate the S^2 expansion used to calculate the H/Al(100) interaction.

Let us now discuss the results we have obtained for the H/Li(100) interface. For this case, we only present detailed calculations for the center position. The main reason is that, as discussed below, the Li electron density is rather low and the hydrogen atom can penetrate the metal: this behavior favors the center position where hydrogen penetrates the metal more easily and finds an equilibrium position between the first and second metal layers.

Figure 9 shows the total chemisorption energy per unit cell for the hydrogen monolayer on Li(100) (center position). The equilibrium distance is found 0.4 a.u. underneath the last metal layer, and the chemisorption energy 2.1 eV.

We should mention that the overlap between the wave functions of hydrogen and the nearest neighbor of the metal second layer can be larger than in the Al case (see Fig. 10). In this case, we have followed the prescription given in Sec. II A, and have calculated the hopping integrals between the hydrogen and the metal atom to all orders in the overlap coefficient. Otherwise, we follow the method discussed above.

In Fig. 11 we show the different contributions to the chemisorption energy. For the H/Li(100) system we find that the core kinetic repulsion between the H 1s level and the Li 1s level is the main term controlling the H-Li equilibrium distance. The main attractive term is afforded by the hybridization term and the transfer of charge between the metal and the H atom. In our calculations this transfer of charge introduces three-center contribu-

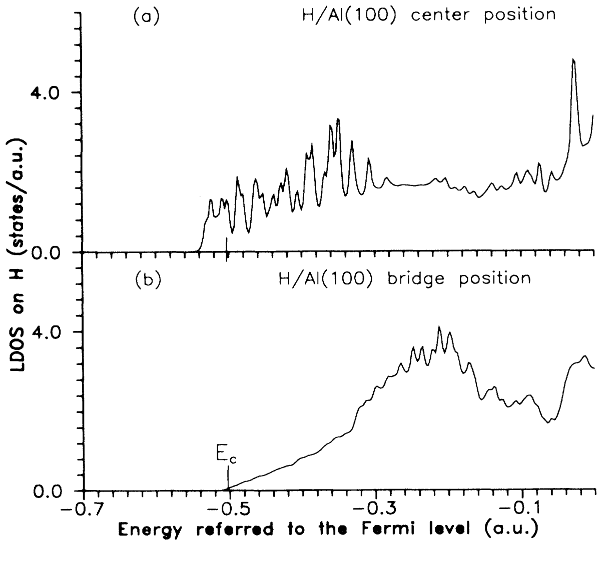

FIG. 7. Local density of states on the hydrogen monolayer at the chemisorption energy minimum for the H/Al(100) case. (a) Center. (b) Bridge. E_c is the conduction-band bottom of the metal.

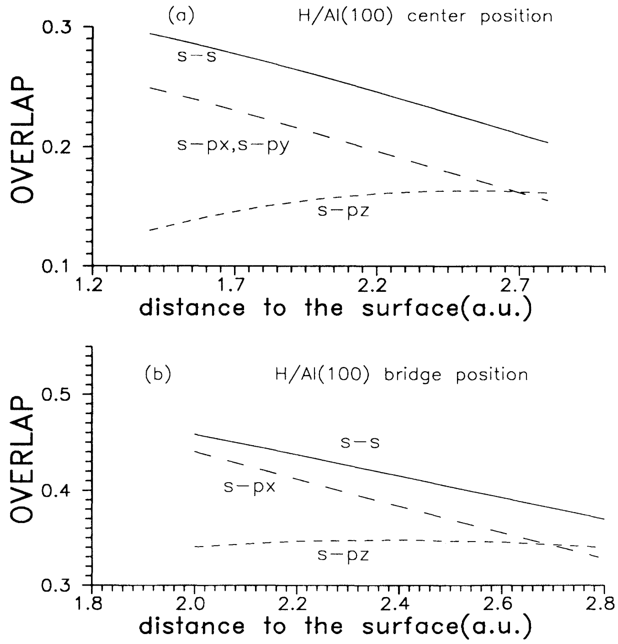

FIG. 8. Overlap between the 1s H level and the Al orbitals of the last metal layer. (a) Center. (b) Bridge.

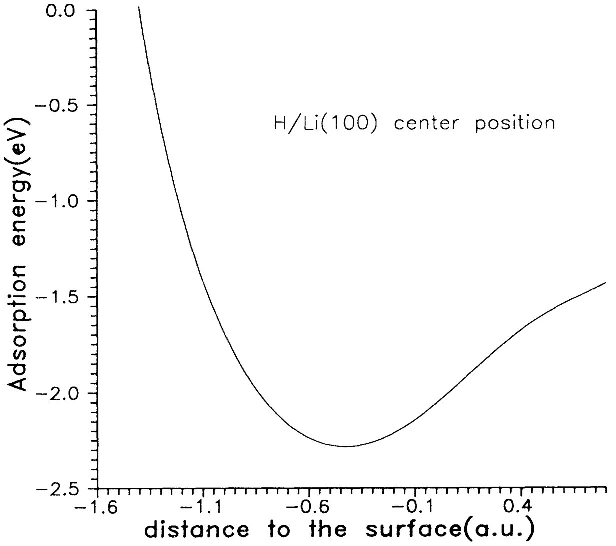

FIG. 9. Chemisorption energy per unit cell for a hydrogen monolayer on Li(100). Center site. The distance refers the hydrogen monolayer to the last metal layer.

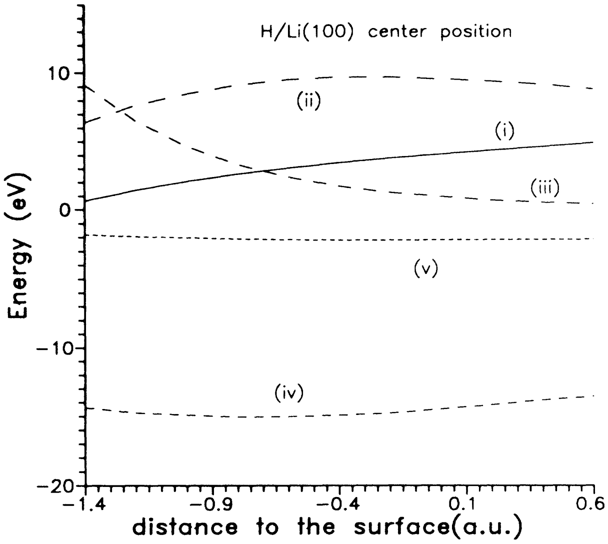

FIG. 11. As in Fig. 6 for a hydrogen monolayer on Li(100).

tions yielding important effects on the hopping between hydrogen and the metal. For the H/Li(100) system, the hydrogen affinity level is strongly decreased by the electrostatic potential created by the metal atoms below the metal Fermi energy. Due to this effect, at the equilibrium distance, 0.61 electron are transferred from the metal to the adsorbed atom, this mechanism tending to increase substantially the chemisorption energy. In Fig. 12 we show the local density of states on the hydrogen layer at the equilibrium distance: it is clearly seen in this figure that the hydrogen level is just below the conduction-band bottom, and that a high density of states associated with the formation of a 1*s* H level band appears below that conduction-band bottom.

It is worth comparing our results for the H/Li(100) with other independent approaches. We mention[26–28] the theoretical work of Beckman and Koutecky,[26] and Ray and Hira:[27,28] these authors have investigated the interaction of a single H atom with Li clusters using a full configuration interaction method. The chemisorption energies calculated in these references are a little

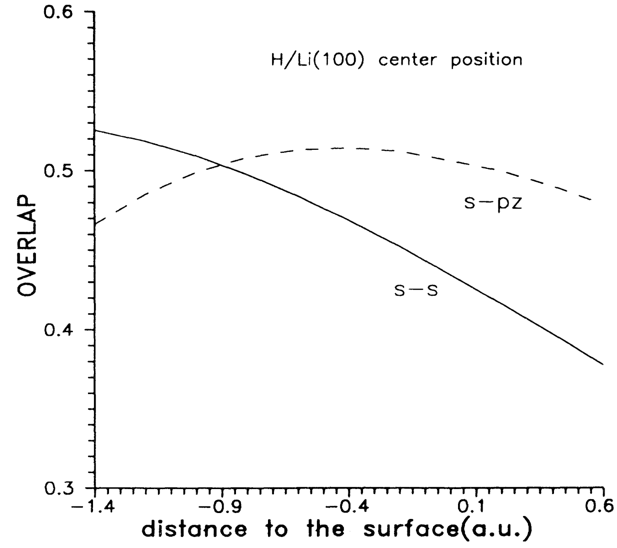

FIG. 10. Overlap between the 1*s* H level and the Li orbitals of the metal second layer.

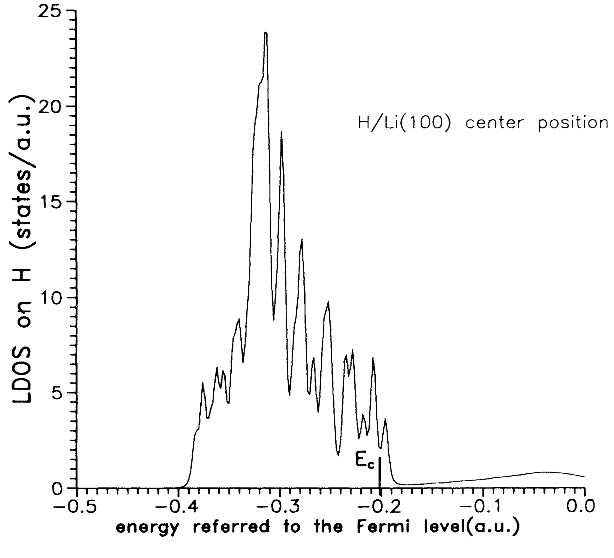

FIG. 12. Local density of states on the hydrogen layer at the chemisorption energy minimum for the H/Li(100) case. E_c is the conduction-band bottom of the metal.

larger than 2 eV, in good agreement with our results. As regards the equilibrium distance for the H/Li(100) interface, the cluster calculations[26–28] show a large dispersion in the H-site position. Some information can be surmised, however, by considering the similar system of H on Na(100) [this is an open bcc structure like Li(100), having also a low electron density]: experimental[29] and theoretical results[22,23] suggest that hydrogen is located below the last Na layer, as our results show for the Li case.

We should finally comment that the main mechanism associated with the hydrogen chemisorption of H on simple metals depends on the lowering of the hydrogen affinity level below the Fermi level by the electrostatic potential created by the metal atoms. This mechanism is fully developed for the H/Li(100) case, where the hydrogen can penetrate the metal, the hydrogen mean level being located just below the bottom of the metal conduction band. For the H/Al(100) case, the high electron density in Al prevents the hydrogen atom penetrating the metal: due to this reason, the hydrogen mean level is not lowered as much as in the Li(100) case, although the most favorable hydrogen adsorption site is determined at the bridge site by maximizing the transfer of charge from the metal to the adsorbate. These results are similar to the ones found in the LDA method,[22–24] or within the framework of the overcomplete Anderson model.[25] As shown in the LDA calculations,[23] when hydrogen penetrates the metal surface, its affinity level crosses the Fermi energy, moving down in energy, until the hydrogen is located inside the solid: then, the mean hydrogen level is located just below the bottom of the metal conduction band.

IV. CONCLUSIONS

In this paper we have presented an *ab initio* LCAO method devised to calculate the electronic properties of solids, in general, and surfaces and interfaces, in particular. The case of a H monolayer adsorbed on normal metals (Li and Al) has been analyzed following the discussion of the method presented here.

The essential idea of this paper is to introduce a total Hamiltonian which is expressed as the superposition of Hamiltonians defined for each pair of atomic orbitals. The terms appearing in this simplified Hamiltonian have been obtained from the most general Hamiltonian by using a well-defined prescription: first, we introduce S, the overlap between different orbitals; then, we only keep in the most general initial Hamiltonian those terms contributing to the total energy up to second order, S^2, in this overlap. The total Hamiltonian obtained with this procedure is similar to the one proposed by Harrison;[9] the main advantage of the discussion presented here is, however, that we have given a clear prescription to calculate all the different terms appearing in the Hamiltonian, many-body terms included, using the atomic wave functions of the constituents. In particular, the hopping integrals between two orbitals have been related to the Bardeen tunneling currents between those orbitals, these currents playing in our approach the same role as pseudopotentials in the free-electron methods.

It should also be commented that for the cases of large orbital overlaps, we have found that the total Hamiltonian introduced in this paper still represents a good approximation to the most complete initial Hamiltonian of the problem if the hopping integrals are calculated up to infinite order in the overlap.[33]

We have found that this prescription should be applied for $S > 0.4$; for smaller overlaps, the up-to-second-order expansion in S yields very accurate results. We should mention that, in practice, only the overlap between nearest neighbors can be large (with $S > 0.4$); for this case, only the hopping integrals between nearest neighbors should be calculated using the full Löwdin wave functions [Eq. (17)] instead of the approximate ones [Eq. (23)].

Another important point of the discussion presented in this paper is the treatment of the many-body effects. Our total Hamiltonian is a many-body one, with electron-electron interactions that have been analyzed within our LCAO method using an approach similar, but not identical, to the $X\alpha$ method proposed by Slater for a free-electron-like system. We should stress that the main point of our procedure to analyze many-body effects is the introduction of the pair correlation function associated with the exchange hole created around an electron; the total exchange-correlation energy is also related, like in the Slater method, to the energy associated with this pair correlation function. It should be noticed, however, that in our treatment, this pair correlation function is calculated specifically for each orbital, its value depending on the electronic properties of the actual environment.

The method has been checked by calculating the electronic properties of the simple molecules H_2 and LiH, and analyzing the interface properties of a hydrogen monolayer adsorbed on the Li(100) and Al(100) surfaces. We have chosen to present the case of H on the Li and Al surfaces, because we have found these cases to present the strongest test on the method discussed here. We have been currently calculating the cases of alkali-metal atoms on semiconductor and metal surfaces, as well as the case of oxygen on metal surfaces with our method (details of these calculations will be published elsewhere) and we have found these chemisorption systems not to be so critically dependent on the correct treatment of all the terms contributing to the total energy. In particular, we have found that for H on metal surfaces either the overlap between H and the metal atoms can be large (the case of Li) or the many-body interactions very important (the case of Al). The results for H on metals allow us also to compare our method with other independent theoretical approaches and the experimental evidence. The agreement with these cases is very satisfactory, in particular with the LDA results. This comparison suggests that the chemisorption energy, as calculated within our approach, has an accuracy better than 0.2 eV.

The main advantages of the method presented here are as follows: (i) Its relatively easy implementation to more complicated problems of molecules chemisorbed on surfaces. As mentioned in the Introduction, it is not easy to obtain the properties of chemisorbed molecules using the LDA method; the simplicity of the LCAO method presented here in comparison with the LDA approach offers the possibility of treating those more complicated chemisorbed systems, while retaining good accuracy in the result. (ii) Second, the method presents the advantage of all the LCAO approaches: a careful description of the chemical bond properties associated with the system under consideration. One example is the problem of the charge transfer between an adsorbate and the substrate: in the LDA methods, it is not well defined as to how one can obtain this charge transfer, while in the LCAO approach discussed here this can be easily extracted from the atomic basis used in the calculation. This problem is closely related to the H-Li(100) system discussed above: our calculation yields an important charge transfer from Li to H; this is not surprising since it is well known that for the Li-H molecule an important charge transfer from Li to H is found.[34] This is mainly due to the electrostatic potential created by the Li atom on the hydrogen level that is strongly lowered in energy. Some people have argued that this charge transfer, as calculated in the LDA approaches for H on low density metals, is fictitious because the extra charge on H is compensated by an extra positive charge tightly localized around the atom. Our approach shows that this is not the case: the charge transfer is indeed localized on H and the few metal atoms surrounding the adatom, but its appearance is due to the same chemical effects one finds for the LiH molecule, which are clearly incorporated in our approach.

We should finally discuss a little further our approximation for calculating many-body effects in our system. Our approach is only valid if the effective intrasite Coulomb interaction, $U - J^{(0)}$ [see Eq. (50)], can be treated in a mean-field approximation. There appear cases where this approximation is not valid anymore: a typical case is the adsorption of alkali-metal atoms on semiconductors, when metal-induced levels appear in the semiconductor gap. Then, our approximation for this effective intrasite Coulomb interaction [going as $(U - J^{(0)})\hat{n}_{i\uparrow}\hat{n}_{i\downarrow}$] should be improved by introducing intrasite correlation effects. We only mention here that this can be implemented in our method by introducing an appropriate self-energy associated with the Hubbard-like term of the Hamiltonian.[35]

Finally, we conclude that the *ab initio* LCAO method presented here is very reliable for calculating the chemisorption properties of interface problems. In general, the method offers a simple and reliable way of calculating more complex systems that cannot be easily solved by an LDA approach. Moreover, it provides a natural way of extending our calculations to systems having important many-body effects, by treating the intrasite Coulomb interaction by means of conventional many-body techniques (details will be published elsewhere).

The application of the present method to the calculation of bulk materials is under current research in our laboratory.

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