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Molecular orbital theory for chemisorption and physisorption: The case of He on metals

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A first-principles tight-binding method is presented, with the basic Hamiltonian parameters related to the properties of the constituent atoms of the solid. In a one-electron approach we find the off-diagonal terms of the Hamiltonian related to the Bardeen tunneling current between the wave functions of the atoms, and the diagonal energies related to this current and the corresponding overlap. Many-body effects are also analyzed within a bond theory, and corrections to the intra-atomic, interatomic, and exchange interactions are discussed. We apply this approach to the analysis of the interaction between a He atom and a metal surface. We find that our calculations reproduce most of the results obtained using a local-density approach and yield a good description of the metal surface roughness as seen by a thermal He atom.

I. INTRODUCTION

Main theoretical approaches to solid-state problems are based on the use of either extended wave functions or localized orbitals.[1] A point of view based on the use of localized orbitals can be more convenient for the analysis of disordered solids, surfaces, molecules, etc., i.e., systems having lost a translational symmetry. The localized picture is intimately related to the molecular-orbital theory,[2] whereby the orbitals of the constituent atoms are assumed to interact in order to form extended wave functions. The simplest related approach is the Hückel theory in molecular physics.[3] As regards solid-state physics, it is common practice to use an empirical or semiempirical tight-binding method[4] in order to analyze the electronic properties of solids. In this last case, a lot of work has been done to parametrize[5,6] the basic Hamiltonians of different crystals. On the other hand, some theoretical effort has been done recently to put that approach in a fundamental basis; in this respect, we mention the work of Harris[7] and Sutton *et al.*[8] who have developed a tight-binding model based on the results of the variational principle of the density-functional theory. Related to this approach, we also mention different calculations of the electronic structure of solids,[9] from which the different parameters of a tight-binding model can be surmized. There also exists a semiempirical tight-binding model[10,11] which predicts the chemical trends in the structural properties of a wide range of nonmetals; this approach includes charge-transfer and nonorthogonality effects, and requires properties of the isolated atoms as empirical input. In spite of these approaches and of other more semiempirical methods,[12] there is a lack of a simple fundamental approach relating straightforwardly the tight-binding Hamiltonians to the basic properties of the constituent atoms, in particular for the case of atoms interacting with a solid surface.

The aim of this work is to fill this gap, presenting a discussion of how to calculate the different tight-binding parameters from a first-principles approach using no adjustable parameter (a preliminary report of this work was published in Ref. 13). We discuss our model and our methods in Sec. II, showing also how total energies can be calculated with our approach; this discussion is kept at a very general level, in such a way that applications are contemplated in Sec. III. In our work, we are mostly concerned about surface problems but in this paper we only discuss in detail the case of He physisorbed on metal surfaces. This will show for a simple and well-known physical case[14–19] how our tight-binding approach can be applied to the calculation of the total energy and the electronic properties of a surface case.

Let us mention that our approach is related to the theory of the scanning tunneling microscope.[20] In this case, tunneling current, image effects,[21] and repulsive forces between surfaces[22] are important, and an appropriate discussion of those effects within a simplified tight-binding approach would be very convenient. In the discussion presented in Sec. II, the relationship between the method presented there and the theory of both the scanning tunneling microscope[20] and the atomic force microscope[22] will be apparent.

II. BASIC THEORY

We present our analysis in two steps. First of all, we discuss a one-electron model neglecting many-body effects associated with the electron-electron interaction. These effects will be discussed later on, in this same section.

A. One-electron approach

We start by considering the one-electron Hamiltonian (atomic units are used):

$$\hat{H} = -\tfrac{1}{2}\nabla_r^2 + \sum_i V_i(\mathbf{r}-\mathbf{R}_i) \ , \tag{1}$$

where V_i is the potential created by an atom i, placed at site $\mathbf{R}_i$. Following the standard linear-combination-of-atomic-orbitals (LCAO) solution to Hamiltonian (1), we define Hamiltonian $\hat{H}_i$

$$\hat{H}_i=-\tfrac{1}{2}\nabla_{\mathbf{r}}^2+V_i(\mathbf{r}-\mathbf{R}_i) \tag{2}$$

and assume that the eigenvalues and eigenfunctions of $\hat{H}_i$ are known:

$$\hat{H}_i\psi_i=E_i\psi_i \ . \tag{3}$$

Then, eigenfunctions of $\hat{H}$ are sought within the linear combination of atomic orbitals, ψ_i:

$$\psi=\sum_i C_i\psi_i \ . \tag{4}$$

Eigenvalues of Hamiltonian $\hat{H}$ are given by the secular equation

$$\det|\langle\psi_j|-E+\hat{H}|\psi_i\rangle|=0 \ . \tag{5}$$

Thus, the matrix defining the eigenstates of $\hat{H}$ can be written as follows:

$$(-ES_{ji}+H_{ji}) \ , \tag{6}$$

where S_{ji} is the overlap between wave functions j and i, and $H_{ji}=\langle\psi_j|\hat{H}|\psi_i\rangle$.

Now, it is convenient to introduce the Löwdin's orthogonalized wave functions:[23]

$$\phi_i=\sum_{i'}(S^{-1/2})_{ii'}\psi_{i'} \tag{7}$$

using the overlap matrix S_{ij}. Then, using this new orthogonalized basis, the matrix defining eigenstates reads as follows:

$$-EI_{ji}+(S^{-1/2})_{jj'}H_{j'i'}(S^{-1/2})_{i'i} \ , \tag{8}$$

where I_{ji} is the unit matrix. Equation (8) shows that we can introduce an effective Hamiltonian:

$$\mathbf{H}_{\rm eff}=\mathbf{S}^{-1/2}\cdot\mathbf{H}\cdot\mathbf{S}^{-1/2} \tag{9}$$

for our one-electron problem. This effective Hamiltonian can be calculated up to second order in the overlap coefficients S_{ij} by assuming $S_{ij}(i\neq j)$ to be small. A straightforward calculation yields the following results:

$$(H_{\rm eff})_{ii}=H_{ii}+\tfrac{1}{4}\sum_j(S_{ij})^2(H_{ii}-H_{jj})-\sum_j S_{ij}T_{ij} \ , \tag{10a}$$

$$(H_{\rm eff})_{ij}=T_{ij}=H_{ij}-\tfrac{1}{2}S_{ij}(H_{ii}+H_{jj}), \quad i\neq j \ . \tag{10b}$$

These equations show how the diagonal elements of the effective one-electron Hamiltonian are related to the off-diagonal terms, T_{ij}, and the overlap matrix, S_{ij}. We should mention that an important effect of the overlap coefficients in the effective Hamiltonian is to renormalize the diagonal elements: physically, this renormalization reflects the repulsion between nonorthogonal orbitals due to their overlap. In particular, the term $-S_{ij}T_{ij}$ gives a net repulsive energy appearing in both orbitals i and j.

As regards the off-diagonal terms, let us show that, under given condition the matrix element T_{ij} coincides with the Bardeen tunneling current, T_{ij}^B:

$$T_{ij}^B=-\tfrac{1}{2}\int_{\sigma_{ij}}(\psi_i\nabla\psi_j-\psi_j\nabla\psi_i)\cdot d\mathbf{s} \ , \tag{11}$$

σ_{ij} being a particular surface between atoms i and j to be specified below. For this purpose, we calculate the matrix elements, H_{ij}, by assuming that the atomic potentials are short-ranged around the corresponding position $\mathbf{R}i$, and that they do not overlap. Then, we calculate H_{ij} in the following way. First, we notice that

$$\int_\Omega\psi_j\hat{H}\psi_i d\mathbf{r}=\int_{\Omega_j}\psi_j\hat{H}\psi_i d\mathbf{r}+\int_{\Omega_i}\psi_j\hat{H}\psi_i d\mathbf{r} \ , \tag{12}$$

where the whole space Ω is split into subspaces Ω_i and Ω_j (see Fig. 1). We also assume the wave functions ψ_i and ψ_j to be real eigenfunctions of Hamiltonians $\hat{H}_i$ and $\hat{H}_j$. Notice that $\hat{H}\psi_i=E_i\psi_i$ in subspace Ω_i if we neglect any other center different from i and j. Then, Eq. (12) yields

$$\begin{aligned}\int_\Omega\psi_j\hat{H}\psi_i d\mathbf{r}=&E_i\int_{\Omega_i}\psi_j\psi_i d\mathbf{r}\\&+\int_{\Omega_j}(\psi_j\hat{H}\psi_i-\psi_i\hat{H}\psi_j)d\mathbf{r}\\&+E_j\int_{\Omega_j}\psi_j\psi_i d\mathbf{r} \ ,\end{aligned} \tag{13}$$

where we have added and subtracted

$$\int_{\Omega_j}\psi_i\hat{H}\psi_j d\mathbf{r}=E_j\int_{\Omega_j}\psi_i\psi_j d\mathbf{r} \ .$$

On the other hand,

$$\begin{aligned}\int_{\Omega_j}(\psi_j\hat{H}\psi_i-\psi_i\hat{H}\psi_j)d\mathbf{r}&=-\tfrac{1}{2}\int_{\Omega_j}(\psi_j\nabla^2\psi_i-\psi_i\nabla^2\psi_j)d\mathbf{r}\\&=-\tfrac{1}{2}\int_{\sigma_{ij}}(\psi_j\nabla\psi_i-\psi_i\nabla\psi_j)\cdot d\mathbf{s} \ ,\end{aligned} \tag{14}$$

where σ_{ij} is the surface limiting the volume Ω_j. Combining Eqs. (13) and (14), we obtain the following equation:

$$\begin{aligned}\int_\Omega\psi_j H\psi_i d\mathbf{r}=&-\tfrac{1}{2}\int_{\sigma_{ij}}(\psi_j\nabla\psi_i-\psi_i\nabla\psi_j)\cdot d\mathbf{s}\\&+E_j\int_{\Omega_j}\psi_j\psi_i d\mathbf{r}+E_i\int_{\Omega_j}\psi_j\psi_i d\mathbf{r} \ .\end{aligned} \tag{15}$$

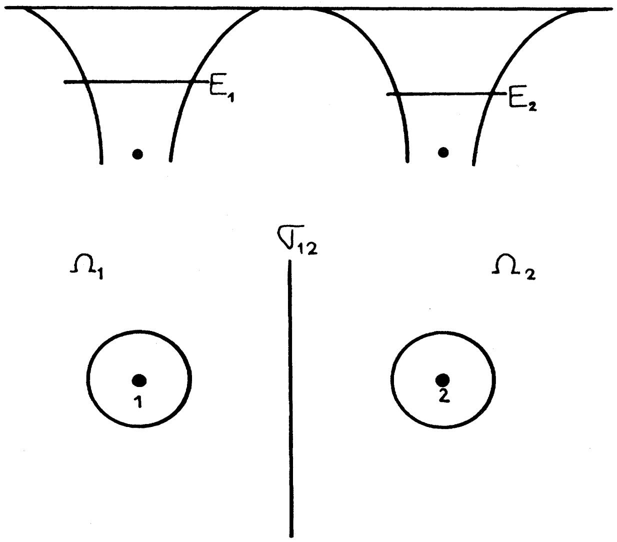

FIG. 1. Muffin-tin model used for Hamiltonian (1). Surface σ_{12} divides the whole space into two subspaces Ω_1 and Ω_2. (σ_{12} is assumed not to go across the muffin-tin potentials of either atom.)

Let us remark that in obtaining Eq. (15), we have assumed any three-center integrals to be negligible. This is equivalent to using a kind of bond approach, in such a way that the results presented in this paper can be related to a tight-binding bond theory.[8]

Equation (15) can be written in a more convenient way, if we choose the surface σ_{ij} (see Fig. 1) with the condition

$$\int_{\Omega_i} \psi_i \psi_j d\mathbf{r} = \int_{\Omega_j} \psi_i \psi_j d\mathbf{r} = \tfrac{1}{2} \int_{\Omega} \psi_i \psi_j d\mathbf{r} = \tfrac{1}{2} S_{ij} \ . \tag{16}$$

Then Eq. (15) yields the following result:

$$\int_{\Omega} \psi_j \hat{H} \psi_i d\mathbf{r} = -\tfrac{1}{2} \int_{\sigma_{ij}} (\psi_j \nabla \psi_i - \psi_i \nabla \psi_j) \cdot d\mathbf{s} + \tfrac{1}{2} S_{ij} (E_i + E_j) \ . \tag{17}$$

With an accuracy of second order in the overlap coefficients we can replace $(E_i + E_j)$ by $(H_{ii} + H_{jj})$ in Eq. (17). This yields the equation we are looking for:

$$\int_{\Omega} \psi_j \hat{H} \psi_i d\mathbf{r} = -\tfrac{1}{2} \int_{\sigma_{ij}} (\psi_j \nabla \psi_i - \psi_i \nabla \psi_j) \cdot d\mathbf{s} + \tfrac{1}{2} S_{ij} (H_{ii} + H_{jj}) \ . \tag{18}$$

Equations (10b) and (18) show that

$$T_{ij} = -\tfrac{1}{2} \int_{\sigma_{ij}} (\psi_j \nabla \psi_i - \psi_i \nabla \psi_j) \cdot d\mathbf{s} \tag{19}$$

this being the Bardeen's tunneling current defined in Eq. (11). Thus, the off-diagonal elements of the effective Hamiltonian coincide with the tunneling current calculated using the initial nonorthogonal atomic basis. This result is only valid if we calculate T_{ij} using a surface σ_{ij} satisfying condition (16). Equation (19) has been obtained using three assumptions: (i) first, we have considered short-range atomic potentials; (ii) second, we have neglected three-centers integrals this being equivalent to using a kind of bond theory; (iii) finally we have assumed $E_i \sim H_{ii}$. This last assumption implies that Eq. (19) is valid up to third order in the overlapping coefficients, this conditions being consistent with the degree of accuracy used to calculate $\hat{H}_{\text{eff}}$ in Eqs. (10). The second assumption, associated with the three-center integrals, does not affect the accuracy of our result for T_{ij} either.

The first condition about the short-range potential is, however an oversimplification since, in most cases, atoms and ions create long-range potentials having a non-negligible overlap (in a local-density theory, potentials are short-range; we consider, however, an atomic-orbital approach and, in this case, electrons see long-range potentials). We have analyzed the case of long-range potentials by considering diatomic molecules; to be specific we shall discuss presently the case of $H_2{}^+$ molecule. Let us now comment that for the case of a long-range potential, we expect T_{ij} to be well approximated by the Bardeen's tunneling current T_{ij}^B corrected by a constant factor γ:

$$T_{ij} = \gamma T_{ij}^B \ . \tag{20}$$

This guess is supported by the following one-dimensional argument: consider the tunneling across a one-dimensional barrier. Simple arguments show that the tunneling current is proportional to $\exp(-2d\sqrt{2W})$ where d is the width of the barrier, W. We introduce long-range effects in the barrier, W, by assuming that

$$W = W_0 - \alpha / d \ .$$

Then, the tunneling current is proportional to

$$\exp\{-2d[2(W_0 - \alpha/d)]^{1/2}\} \approx \exp[-2d(2W_0)^{1/2}] \exp[\alpha(2/W_0)^{1/2}] \ . \tag{21}$$

This equation suggests that the long-range tail of the barrier affects the tunneling current by a constant factor

$$\gamma = \exp[\alpha(2/W_0)^{1/2}] \ .$$

Coming back to the case of a $H_2{}^+$ molecule, we consider the Hamiltonian:

$$\hat{H} = -\tfrac{1}{2}\nabla^2 - \frac{1}{|\mathbf{r} - \mathbf{R}_1|} - \frac{1}{|\mathbf{r} - \mathbf{R}_2|} + \frac{1}{d} \ , \tag{22}$$

where R_1 and R_2 are the coordinates of the two ions, respectively, and $d = |\mathbf{R}_1 - \mathbf{R}_2|$.

We discuss this problem by using atomic orbitals ψ_1 and ψ_2, such that

$$\psi_1(\mathbf{r}) = (\alpha^3/\pi)^{1/2} e^{-\alpha|\mathbf{r} - \mathbf{R}_1|} \ , \tag{23a}$$

$$\psi_2(\mathbf{r}) = (\beta^3/\pi)^{1/2} e^{-\beta|\mathbf{r} - \mathbf{R}_2|} \ . \tag{23b}$$

Introducing the orthogonalized basis, ϕ_1 and ϕ_2

$$\phi_1(\mathbf{r}) = \lambda \psi_1 + \mu \psi_2 \ , \tag{24a}$$

$$\phi_2(\mathbf{r}) = \mu \psi_1 + \lambda \psi_2 \ , \tag{24b}$$

where $\lambda = (1/\sqrt{1+S} + 1/\sqrt{1-S})/2$ and $\mu = (1/\sqrt{1+S} - 1/\sqrt{1-S})/2$, S being the overlap between orbitals ψ_1 and ψ_2, we define the corresponding operators $C_{i\sigma}^\dagger$ and $C_{i\sigma}$ associated with the new orbitals ϕ_i. Then Hamiltonian (22) can be written as follows, using a second quantization language:

$$H = \sum_{\sigma} (\varepsilon_1 n_{1\sigma} + \varepsilon_2 n_{2\sigma}) + t \sum_{\sigma} (C_{1\sigma}^\dagger C_{2\sigma} + C_{2\sigma}^\dagger C_{1\sigma}) + 1/d \ , \tag{25}$$

where

$$\varepsilon_i = \int \phi_i \left[-\tfrac{1}{2}\nabla^2 - \frac{1}{|\mathbf{r} - \mathbf{R}_1|} - \frac{1}{|\mathbf{r} - \mathbf{R}_2|} \right] \phi_i d\mathbf{r} \tag{26a}$$

and

$$t = \int \phi_1 \left[-\tfrac{1}{2}\nabla^2 - \frac{1}{|\mathbf{r} - \mathbf{R}_1|} - \frac{1}{|\mathbf{r} - \mathbf{R}_2|} \right] \phi_2 d\mathbf{r} \ . \tag{26b}$$

Parameters ε_i and t are defined as a function of the orthogonalized wave functions ϕ_i; we can obtain their expressions as a function of the atomic orbitals ψ_i, replacing Eqs. (24) in (26). This yields the following equations:

$$\varepsilon_i = \varepsilon_i^0 - \tfrac{1}{2}[1 - (1 - S^2)^{1/2}](\varepsilon_j^0 - \varepsilon_i^0) - St \ , \tag{27a}$$

$$t = -\frac{1}{1 - S^2} \frac{S}{2} (\varepsilon_1^0 + \varepsilon_2^0) + \frac{1}{1 - S^2} t^0 \ , \tag{27b}$$

where

$$\varepsilon_i^0=\int \psi_i \left[-\tfrac{1}{2}\nabla^2-\frac{1}{|\mathbf{r}-\mathbf{R}_1|}-\frac{1}{|\mathbf{r}-\mathbf{R}_2|}\right]\psi_i d\mathbf{r}\ , \tag{28a}$$

$$t^0=\int \psi_1 \left[-\tfrac{1}{2}\nabla^2-\frac{1}{|\mathbf{r}-\mathbf{R}_1|}-\frac{1}{|\mathbf{r}-\mathbf{R}_2|}\right]\psi_2 d\mathbf{r}\ . \tag{28b}$$

Equations (27) are equivalent to Eqs. (10) if we expand the different terms up to a second order in S. In other words, if we replace

$$1-(1-S^2)^{1/2} \text{ by } S^2/2$$

and

$$1/(1-S^2) \text{ by } 1$$

in Eqs. (27) we recover Eqs. (10). Notice that this simple case shows that the different terms calculated in (10) have an accuracy of S^2 in 1; accordingly, the expansion used to get Eqs. (10) has a large validity: as discussed below, we find that Eqs. (10) yield good results for H_{eff} even for values of S as high as 0.6 or 0.7.

For the case of $H_2{}^+$, taking $\varepsilon_1^0=\varepsilon_2^0=\frac{1}{2}$, we find

$$t=\left[-\frac{S}{2}+t^0\right]\Big/(1-S^2)\ . \tag{29}$$

We have compared this exact value for t with the Bardeen tunneling current t^B calculated using Eq. (11) and wave functions (23) with $\alpha=\beta=1$. In Fig. 2, we show d^2t and $\gamma d^2 t^B$ as a function of d; $\gamma=\frac{4}{3}$ has been chosen such that $\gamma t^B \to t$ for $d\to\infty$.

The results of Fig. 2 show that γt^B is a fair approximation to t for all values of d larger than 1.5 a.u.; even for $d=1$ a.u., with $S=0.7$, γt^B is smaller than t by 30%. Thus, we conclude that γt^B is a good approximation to t for all the distances of physical interest. Let us also comment that d^2t has a broad maximum near the point for which the equilibrium distance of this molecule is found (this is 2.50 a.u. in a LCAO calculation); this relates the results found here to the well-known d^{-2} law, proposed by Harrison[12] and often used to scale the different off-diagonal interactions in solids.[10,11] We claim that a more appropriate behavior could be found using the Bardeen tunneling current as proposed in this paper.[13]

Similar results have been found for other hydrogenic levels. Without going into details, let us only mention that we have found the hopping elements between orbitals $2s$-$2s$, $2p$-$2p$, and $3s$-$3s$ to be well approximated by γt^B for $d>2.50$ a.u., γ being a constant depending only on the orbital energy. In Fig. 3 we show our results for γ as a function of the orbital energy, including the case of He-He, which is fully discussed below. The curve shown in this figure is a smooth line obtained by interpolating along the different points calculated as discussed above. The results of Fig. 3 can be applied to calculate $t=\gamma t^B$, for any two orbitals of two different atoms having the same energy. Indeed, at very large distances the wave functions of both atoms have the same asymptotic behavior: then, we apply to them the same argument as for the hydrogenic levels, the conclusion being that the factor γ only depends on the orbital energy.

The case of orbitals having different energy levels has to be analyzed in a different way. In this case, we proceed in the following way, starting from Eq. (10b). Assume we consider levels 1 and 2, having $E_1>E_2$; at very large distances, $d\to\infty$, we write

$$H_{12}=\int \psi_1(-\tfrac{1}{2}\nabla^2+V_1+V_2)\psi_2 d\mathbf{r}=\int \psi_1 V_1 \psi_2 d\mathbf{r}+E_2 S_{12} \tag{30}$$

making use of Eq. (3). If $E_1>E_2$, wave function ψ_2 is more localized than ψ_1 and for $d\to\infty$, we can replace approximately $\int \psi_1 V_1 \psi_2 d\mathbf{r}$ by $-S_{12}/d$, $(-1/d)$ being the potential electron 1 sees as created by its own atom at large distances from the nucleus. Then, according with Eq. (10b) we can write

$$\begin{aligned} T_{12} &\cong -S_{12}/d+E_2S_{12}-S_{12}(E_1+E_2-2/d)/2 \\ &=S_{12}(E_2-E_1)/2\ . \end{aligned} \tag{31}$$

This equation is only valid if $E_1>E_2$ and for large distances. Now, this limit can be used to calculate the coefficient γ such that $T_{12}=\gamma T_{12}^B$; this can be easily performed calculating T_{12}^B at large distances and comparing with Eqs. (31). In practice, we use tabulated wave functions from Herman-Skillman[25] or Clementi-Roetti[26] tables. In any case, d has to be large enough for the atomic wave functions to have a small overlap and the potential of atom 1, as seen by electron 1, at the atomic position 2 to be well approximated by $(-1/d)$.

It is of interest to comment here that in the Hückel theory[3] it is common practice to approximate H_{ij} by $\frac{1}{2}KS_{ij}(H_{ij}+H_{jj})$, which is equivalent to approximating

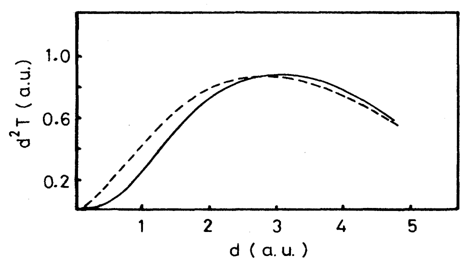

FIG. 2. $\gamma d^2 T_{12}^B$ (solid curve) and $d^2 T_{12}$ (dashed curve) as a function of d for the $H_2{}^+$ case ($\gamma=\frac{4}{3}$).

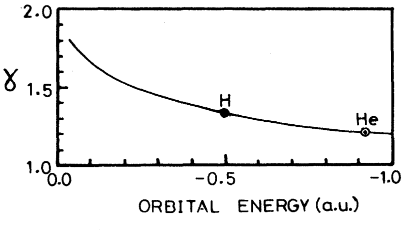

FIG. 3. $\gamma T_{12}/T_{12}^B$ as a function of the orbital energy for $d\to\infty$. The particular cases of the $1s$ levels of H and He are shown.

T_{ij} by $\frac{1}{2}(K-1)S_{ij}(H_{ii}+H_{jj})$. Our discussion shows that it is a better approximation to replace T_{ij} by γT_{ij}^B with γ calculated as discussed above.

B. Many-electron effects and bonds

In the preceding section we have presented the one-electron version of our approach to tight binding. This is basically a bond theory as can be easily checked by comparing the general results of Eqs. (10) with the results of Eq. (17) calculated for a single bond. Equation (10) appears, in the limit of small S, as the superposition of the different bond contributions obtained as in Eqs. (17). In this section we discuss many electron effects, but keeping us at the same level of approximation as in the preceding section, we only consider those effects in local bonds.

Accordingly we start with the case of two atoms 1 and 2 having electrons which only fill one orbital per atom. Our starting point is the following Hamiltonian:

$$\hat{H}=-\frac{1}{2}\sum_i \nabla_i^2-\sum_i \frac{Z_1}{|\mathbf{r}_i-\mathbf{R}_1|}-\sum_i \frac{Z_2}{|\mathbf{r}_i-\mathbf{R}_2|} +\frac{1}{2}\sum_{i\neq j}\frac{1}{|\mathbf{r}_i-\mathbf{r}_j|}+\frac{Z_1Z_2}{d} , \tag{32}$$

where i refers to the electrons of the system and $\mathbf{R}_1,\mathbf{R}_2$ are the coordinates of the nuclei having charges Z_1,Z_2, respectively. We assume that electrons fill states $\psi_1(\mathbf{r}-\mathbf{R}_1)$ and $\psi_2(\mathbf{r}-\mathbf{R}_2)$ in atoms 1 and 2, respectively and, now we use these nonorthogonal wave functions to introduce, as in Eq. (24), the orthogonal basis ϕ_1,ϕ_2. Using these wave functions ϕ_1 and ϕ_2, we can write many-body Hamiltonian (32) in the following second quantization form:

$$\begin{aligned}\hat{H}=&\sum_\sigma(\varepsilon_1 n_{1\sigma}+\varepsilon_2 n_{2\sigma})\\&+\sum_\sigma(t+h_1n_{1-\sigma}+h_2n_{2-\sigma})(C_{1\sigma}^\dagger C_{2\sigma}+C_{2\sigma}^\dagger C_{1\sigma})\\&+U_1n_{1\uparrow}n_{1\downarrow}+U_2n_{2\uparrow}n_{2\downarrow}\\&+\sum_\sigma[Jn_{1\sigma}n_{2-\sigma}+(J-J_c)n_{1\sigma}n_{2\sigma}]+\frac{Z_1Z_2}{d} ,\end{aligned} \tag{33}$$

where as usual $n_{i\sigma}=C_{i\sigma}^\dagger C_{i\sigma}$ is the number of particles operator associated with the state ψ_i and the spin σ.

In Eq. (33), we have neglected other terms going like $C_{1\sigma}^\dagger C_{2-\sigma}^\dagger C_{1-\sigma}C_{2\sigma}$ or $C_{1\sigma}^\dagger C_{1-\sigma}^\dagger C_{2-\sigma}C_{2\sigma}$ which give a small contribution to the total energy. Hamiltonian (33) includes different Coulomb interactions between charges at atoms 1 and 2, the usual hopping terms and the many-body terms like $h_1n_{1-\sigma}(C_{1\sigma}^\dagger C_{2\sigma}+C_{2\sigma}^\dagger C_{1\sigma})$ or $h_2n_{2-\sigma}(C_{1\sigma}^\dagger C_{2\sigma}+C_{2\sigma}^\dagger C_{1\sigma})$, which change the hopping interaction as a function of the particle numbers $n_{1-\sigma}$ and $n_{2-\sigma}$. On the other hand, the usual exchange interaction appears as $J_cn_{1\sigma}n_{2\sigma}$ in the last term of Eq. (33).

Different terms of Hamiltonian (33) are defined in the following way:

$$\varepsilon_i=\int\phi_i\left[-\frac{1}{2}\nabla^2-\frac{Z_1}{|\mathbf{r}-\mathbf{R}_1|}-\frac{Z_2}{|\mathbf{r}-\mathbf{R}_2|}\right]\phi_i d\mathbf{r} , \tag{34a}$$

$$t=\int\phi_1\left[-\frac{1}{2}\nabla^2-\frac{Z_1}{|\mathbf{r}-\mathbf{R}_1|}-\frac{Z_2}{|\mathbf{r}-\mathbf{R}_2|}\right]\phi_2 d\mathbf{r} , \tag{34b}$$

$$h_i=\int\phi_i^2(\mathbf{r})\phi_1(\mathbf{r}')\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_2(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' , \tag{34c}$$

$$U_i=\int\phi_i^2(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_i^2(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' , \tag{34d}$$

$$J=\int\phi_1^2(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_2^2(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' , \tag{34e}$$

$$J_c=\int\phi_1(\mathbf{r})\phi_2(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}\phi_1(\mathbf{r}')\phi_2(\mathbf{r}')d\mathbf{r}\,d\mathbf{r}' . \tag{34f}$$

As we have explained in Sec. II A, we introduce Eqs. (24) into Eqs. (34) and calculate the parameters of Hamiltonian (33) as a function of the wave functions for the independent atoms, ψ_i. This yields the following equation (up to second order in the overlap, S):

$$\varepsilon^0=\varepsilon_i^0+\frac{1}{4}S^2(\varepsilon_i^0-\varepsilon_j^0)-St , \tag{35a}$$

$$t=t^0-\frac{S}{2}(\varepsilon_1^0+\varepsilon_2^0) , \tag{35b}$$

$$h_i=h_i^0-\frac{S}{2}(U_i^0+J^0) , \tag{35c}$$

$$U_i=U_i^0+\frac{S^2}{2}(U_i^0-J^0)-2Sh_i , \tag{35d}$$

$$J=J^0+\frac{S^2}{4}(2J^0-U_1^0-U_2^0)-S(h_1+h_2) , \tag{35e}$$

$$J-J_c=J^0-J_c^0+J^0S^2 , \tag{35f}$$

where the superscript (0) means that Eqs. (34) have to be used to calculate the different terms replacing ϕ_i by ψ_i. When Eqs. (35) are introduced in Hamiltonian (33) and different terms are rearranged, the following result is obtained:

$$\begin{aligned}\hat{H}=&\sum_\sigma\{\varepsilon_1^0+\frac{1}{4}S^2[\varepsilon_1^0-\varepsilon_2^0+(U_1^0-J^0)n_{1-\sigma}-(U_2^0-J^0)n_{2-\sigma}]-S(t+h_1n_{1-\sigma}+h_2n_{2-\sigma})\}n_{1\sigma}\\&+\sum_\sigma\{\varepsilon_2^0+\frac{1}{4}S^2[\varepsilon_2^0-\varepsilon_1^0+(U_2^0-J^0)n_{2-\sigma}-(U_1^0-J^0)n_{1-\sigma}]-S(t+h_1n_{1-\sigma}+h_2n_{2-\sigma})\}n_{2\sigma}\\&+\sum_\sigma(t+h_1n_{1-\sigma}+h_2n_{2-\sigma})(C_{1\sigma}^\dagger C_{2\sigma}+C_{2\sigma}^\dagger C_{1\sigma})+U_1^0n_{1\uparrow}n_{1\downarrow}+U_2^0n_{2\uparrow}n_{2\downarrow}\\&+\sum_\sigma[J^0n_{1\sigma}n_{2-\sigma}+(J^0-J_c^0+J^0S^2)n_{1\sigma}n_{2\sigma}]+\frac{Z_1Z_2}{d} .\end{aligned} \tag{36}$$

This is the main result of our many-electron case: comparing with the one-electron approach [Eqs. (10) or Eqs. (27)] we find the following results.

(i) The hopping term, t, appearing in the one-electron case is now replaced by $t+h_1n_{1-\sigma}+h_2n_{2-\sigma}$, where the last two terms correspond to the hopping interaction due to electrons of opposite spin.

(ii) In the effective energy level for $n_{i\sigma}$ we find the repulsive term $-S(t+h_1n_{1-\sigma}+h_2n_{2-\sigma})$, in agreement with (i). Moreover, the effective energy level for $n_{i\sigma}$ is also changed by the contribution:

$$\frac{S^2}{4}[(\varepsilon_1^0+U_1n_{1-\sigma}+J^0n_{2-\sigma})-(\varepsilon_2^0+U_2n_{2-\sigma}+J^0n_{1-\sigma})]\ .$$

This is similar to the one-electron case; there is, however, a subtle difference; instead of the total-energy level $\varepsilon_1^0+U_1^0n_{1-\sigma}+J^0n_{2-\sigma}+(J^0-J_c^0)n_{2\sigma}$, we only find $\varepsilon_1^0+U_1^0n_{1-\sigma}+J^0n_{2-\sigma}$, term $(J^0-J_c^0)n_{2\sigma}$ is missing. The physical meaning of this result is clear: the correction term $(S^2/4)[\cdots]$ is associated with the hopping of one electron from state ψ_1 to state ψ_2; then, there must be one state filled, the other empty, and no interaction $(J^0-J_c^0)n_{1\sigma}n_{2\sigma}$ contributes to the energy levels of particles $n_{1\sigma}$ and $n_{2\sigma}$.

(iii) As regards the Coulomb interaction between different electrons, we find that in Hamiltonian (36), the Hubbard terms $U_i^0n_{i\uparrow}n_{i\downarrow}$ are defined by the Coulomb interactions U_i^0 of the localized atomic wave functions. The same result holds for $J^0n_{1-\sigma}n_{2-\sigma}$, but we find a correction term to the exchange contribution:

$$-J_c^0+J^0S^2\ .$$

This is the only new effect appearing in Hamiltonian (36), associated with the orthogonalization of the atomic wave functions.

In our approach to physisorption and chemisorption we propose to use the following approximate Hamiltonian:

$$\begin{aligned}H={}&\sum_\sigma E_1n_{1\sigma}+\sum_\sigma E_2n_{2\sigma}+\sum_\sigma T(C_{1\sigma}^\dagger C_{2\sigma}+C_{2\sigma}^\dagger C_{1\sigma})\\&+U_1^0n_{1\uparrow}n_{1\downarrow}+U_2^0n_{2\uparrow}n_{2\downarrow}\\&+\sum_\sigma[J^0n_{1\sigma}n_{2-\sigma}+(J^0-J_c^0+J^0S^2)n_{1\sigma}n_{2\sigma}]\\&+\frac{Z_1Z_2}{d}\ ,\end{aligned}\tag{37}$$

where we have introduced mean values for the effective energies E_1 and E_2, of particles $n_{1\sigma}$ and $n_{2\sigma}$, and for the hopping interaction T:

$$\begin{aligned}E_i=\varepsilon_i^0+\tfrac{1}{4}S^2[&(\varepsilon_i^0+U_i^0\langle n_{i-\sigma}\rangle+J^0\langle n_{j-\sigma}\rangle)\\&-(\varepsilon_j^0+U_j^0\langle n_{j-\sigma}\rangle+J^0\langle n_{i-\sigma}\rangle)]\ ,\end{aligned}\tag{38a}$$

$$T=t+h_1\langle n_{1-\sigma}\rangle+h_2\langle n_{2-\sigma}\rangle\ .\tag{38b}$$

Following the discussion of Sec. II A, in these equations, T, the hopping parameter, will be approximated by γT^B, using in Eq. (11) the atomic wave function ψ_1 and ψ_2. Notice that this approximation implies that we expect the atomic orbitals not to change much in the molecular state: this is an accurate result for many physical systems.[7,8]

III. PHYSISORPTION OF He ON METALS

In this section we apply previous results to the case of He physisorbed on metals. As an introduction to the problem it is convenient to start discussing the problem of two He atoms interacting at large distances. This is done in Sec. III A, while in Sec. III B we discuss the case we are interested in, using a simplified approach. Finally, in Sec. III C we present our full analysis.

A. He-He interaction

This case can be analyzed using the effective Hamiltonian (36) or (37). For the He-He case we find

$$\begin{aligned}H={}&\sum_\sigma(\varepsilon_0^0-ST)(n_{1\sigma}+n_{2\sigma})+\sum_\sigma T(C_{1\sigma}^\dagger C_{2\sigma}+C_{2\sigma}^\dagger C_{1\sigma})\\&+U_0^0n_{1\uparrow}n_{1\downarrow}+U_0^0n_{2\uparrow}n_{2\downarrow}\\&+\sum_\sigma[J^0n_{1\sigma}n_{2-\sigma}+(J^0-J_c^0+S^2J)n_{1\sigma}n_{2\sigma}]+\frac{Z_1Z_2}{d}\ ,\end{aligned}\tag{39}$$

where only the 1s orbitals for both atoms have been included.

In this approach, we neglect contributions from higher orbitals: this implies that the van der Waals interaction has to be added to the repulsive term given by Hamiltonian (39).

The repulsive energy can be straightforwardly calculated from Hamiltonian (39), taking $\langle n_{1\sigma}\rangle=\langle n_{2\sigma}\rangle=1$. This yields the following total energy:

$$E=4(\varepsilon_0^0-ST)+2U_0^0+4J^0+2(-J_c^0+J^0S^2)+\frac{Z_1Z_2}{d}\ ,\tag{40}$$

where $2\varepsilon_0^0+U_0^0$ is the total energy of an atom plus the interaction energy of the electrons of atom 1 (or 2) with the ion 2 (or 1) [see Eq. (28a) for ε_1^0]. Then, the repulsive energy is given by

$$V_{\text{rep}}=-4ST+2(-J_c^0+J^0S^2)+V_{\text{elect}}\ .\tag{41}$$

In obtaining Eq. (41), we have defined the electrostatic interaction as follows:

$$V_{\text{elect}}=Z_1Z_2/d+4J^0+2I_{12}+2I_{21}\ ,\tag{42}$$

where I_{12} (I_{21}) is the electrostatic interaction between an electron of atom 1 (2) with the nucleus of atom 2 (1).

Equation (41) has a simple interpretation: the term $(-4ST)$ represents the repulsion between orbitals of different atoms due to their overlap; the term $2(-J_c^0+J^0S^2)$ is the exchange interaction between electrons having the same spin: notice the overlap correction appearing as J^0S^2; finally, V_{elect} is the classical interaction between the charges of both atoms.

Equation (41) reproduces the well-known repulsive interaction between two He atoms[27] if we write $T=\gamma T^B$ and take $\gamma=1.20$: this value has been included in Fig. 3 where γ is shown as function of the orbital energy level contributing to the tunneling current.

B. A simple approach to the interaction of He and metal surfaces

The problem we want to address in this section is a He atom approaching a metal surface. We start assuming that the He atom only interacts with a metal surface atom: this implies that we consider a He atom on the top position of the metal surface.

In our approach we consider the interaction between an s orbital of a metal atom and the 1s level of He. Let us describe the s-metal band by a mean level E_M, and an occupancy per spin, N_M. We analyze the interaction between the metal band and He in the following way.

(i) One-electron terms. This contribution appears when we consider the overlap and the hybridization between the metal level E_M and the He orbital. As regards to the overlap, following Eqs. (38) we find the contributions

$$\delta E_M^S=\frac{S^2}{4}[(\varepsilon_M^0+U_M^0\langle n_{M-\sigma}\rangle+J^0\langle n_{\mathrm{He}-\sigma}\rangle)-(\varepsilon_{\mathrm{He}}^0+U_{\mathrm{He}}\langle n_{\mathrm{He}-\sigma}\rangle+J^0\langle n_{M-\sigma}\rangle)]-ST \tag{43a}$$

and

$$\delta E_{\mathrm{He}}^S=\frac{S^2}{4}[(\varepsilon_{\mathrm{He}}^0+U_{\mathrm{He}}^0\langle n_{\mathrm{He}-\sigma}\rangle+J^0\langle n_{M-\sigma}\rangle)-(\varepsilon_M^0+U_M^0\langle n_{M-\sigma}\rangle+J^0\langle n_{\mathrm{He}-\sigma}\rangle)]-ST\ , \tag{43b}$$

where obviously subscript He refers to the rare-gas atom. Notice that ε_M^0 includes the interaction between the metal electron and the He nucleus, and similarly, $\varepsilon_{\mathrm{He}}^0$ includes the interaction between one He electron and the metal nucleus. Then, we define the metal and the He free-atom levels as E_M and E_{He} and rewrite Eqs. (43a) as follows:

$$\begin{aligned}\delta E_M^S&=\frac{S^2}{4}[(E_M+I_{M,\mathrm{He}}+J^0\langle n_{\mathrm{He}-\sigma}\rangle)-(E_{\mathrm{He}}+I_{\mathrm{He},M}+J^0\langle n_{M-\sigma}\rangle)]-ST\\&\cong\frac{S^2}{4}(E_M-E_{\mathrm{He}}-J^0N_M)-ST\ ,\end{aligned} \tag{44a}$$

where we have taken $I_{M,\mathrm{He}}\sim 2J^0$, $I_{\mathrm{He},M}=-J^0$, $\langle n_{\mathrm{He}-\sigma}\rangle=1$, and $\langle n_{M-\sigma}\rangle=N_M$. Similarly

$$\delta E_{\mathrm{He}}^S=\tfrac{1}{4}S^2(E_{\mathrm{He}}-E_M+J^0N_M)-ST\ . \tag{44b}$$

On the other hand, the hybridization contribution to the total energy due to the coupling of the helium 1s state with the states of the metal[18] can be calculated up to the second-order perturbation theory, yielding

$$\delta E_M^T=T^2/(E_M-E_{\mathrm{He}}-J^0N_M) \tag{45a}$$

and

$$\delta E_{\mathrm{He}}^T=-T^2/(E_M-E_{\mathrm{He}}-J^0N_M)\ . \tag{45b}$$

Notice that in these equations the difference of energies between orbitals E_M and E_{He} has been shifted by the term J^0N_M, which is the correction related to the fact that if one electron jumps between levels E_M and E_{He}, one of these two levels has to be empty. On the other hand, if we take $N_M=\frac{1}{2}$ (half-occupied band) the correction ($J^0/2$) plays the role of an image potential for the helium level.

Combining Eqs. (44) and (45) we obtain the following results:

$$\delta E_M^S=\frac{S^2}{2}(E_M-E_{\mathrm{He}}-J^0N_M)-ST+\frac{T^2}{E_M-E_{\mathrm{He}}-J^0N_M}, \tag{46a}$$

$$\delta E_{\mathrm{He}}^S=-\frac{S^2}{4}(E_M-E_{\mathrm{He}}-J^0N_M)-ST-\frac{T^2}{E_M-E_{\mathrm{He}}-J^0N_M}\ . \tag{46b}$$

Now, we can use Eq. (31) in order to calculate T since in the physisorption problem the metal-adsorbate distance is large. A word of caution has to be put here: Eq. (31) was calculated for a one-electron model. In the present approach, we have found that the He level is renormalized to $E_{\mathrm{He}}+J^0N_M$, by "image effects." Then, instead of Eq. (31) we find

$$T=\tfrac{1}{2}S(E_{\mathrm{He}}+J^0N_M-E_M)\ . \tag{47}$$

Then, using Eqs. (46) and (47) we find

$$\begin{aligned}\delta E_M&=\frac{1}{E_M-E_{\mathrm{He}}-J^0N_M}[T-\tfrac{1}{2}S(E_M-E_{\mathrm{He}}-J^0N_M)]^2\\&=S^2(E_M-E_{\mathrm{He}}-J^0N_M)\end{aligned} \tag{48a}$$

and

$$\begin{aligned}\delta E_{\mathrm{He}}&=\frac{1}{E_M-E_{\mathrm{He}}-J^0N_M}[T+\tfrac{1}{2}S(E_M-E_{\mathrm{He}}-J^0N_M)]^2\\&=0\ .\end{aligned} \tag{48b}$$

These equations show that all the one-electron effects on the He level cancel each other[15] at large distances. On the other hand, the metal level is shifted to higher energies by $S^2(E_M-E_{\mathrm{He}}-J^0N_M)$. These results show that the one-electron contribution to the repulsion between one metal atom and He is $2N_MS^2(E_M-E_{\mathrm{He}}-J^0N_M)$, since $2N_M$ is the number of electrons in the level E_M.

Many-body contributions can be included in the same way as in the He-He case. Two different contributions appear; one is the exchange contribution given by [see Eq. (36)]:

$$E_x = 2N_M(-J_c^0 + J^0 S^2) \ . \tag{49a}$$

In the limit of large distances, J^0 goes like $1/d$ and Eq. (49a) can be approximated by

$$E_x = -2N_M J_c^0 \ . \tag{49b}$$

Finally we have to include the electrostatic term V_{elec} defined by the interaction between the classical charges on each atom. All the different terms yield the following repulsive energy:

$$V_{\text{rep}} = 2N_M S^2(E_M - E_{\text{He}}) - 2N_M J_c^0 + V_{\text{elec}} \quad \text{for } d \to \infty \ . \tag{50}$$

The different contributions appearing in this equation can be easily calculated if we assume the He orbital to be very localized in comparison with the metal wave function. Thus, assuming

$$\psi_{\text{He}} = (\beta^3/\pi)^{1/2} e^{-\beta r}$$

a straightforward calculation yields the following result:

$$V_{\text{rep}} = 2N_M S^2(E_M - E_{\text{He}} - \tfrac{3}{8}\beta) \ . \tag{51}$$

On the other hand, S can be related to the metal density, n, at the He site. Then, we get the following equation:

$$V_{\text{rep}} = (64\pi/\beta^3)(E_M - E_{\text{He}} - \tfrac{3}{8}\beta)n \tag{52a}$$

showing that the metal-He repulsion is proportional to the metal density at the He site. Typical values of E_M, E_{He}, and β are the following:

$$\begin{aligned} \beta &= 1.6875 \text{ a.u.} \ , \\ E_{\text{He}} &= -0.8965 \text{ a.u.} \ , \\ E_M &= -0.14 \text{ a.u.} \end{aligned} \tag{52b}$$

This yields

$$V_{\text{rep}} = \alpha n \ , \tag{53}$$

where $\alpha = 140$ eV a_0^3.

We should comment at this point that although Eqs. (53) have been obtained by assuming the He atom interacting with a single metal atom, the same result holds for the case of several metal atoms. This can be easily shown by noticing that the interactions between He and the metal atoms are additive in the metal density, and assuming that the effects of interference between metal atoms can be neglected (see below). The values for α as calculated in a local-density approach range between 200 and 750 eV a_0^3 (Refs. 16–18). It should be noted, however, that Eq. (52) has been obtained in the limit of very large distances. In other words, for the distances of interest, $d \sim 8$ a.u., the image potential is not negligible, and its effects on V_{rep} are important. We pass to discuss a more accurate description of the repulsive potential between the metal and the He atom.

C. Full He-metal interaction

A better interaction can be obtained by improving the calculation of the different terms contributing to the repulsive energy. In a more complete approach we describe the metal using the **k** eigenfunctions ϕ_K^M, and the corresponding eigenvectors $\varepsilon(k)$. Thus, we introduce the metal Hamiltonian

$$H_M = \sum_{\mathbf{k}\sigma} \varepsilon(k) C_{k\sigma}^\dagger C_{k\sigma} \ . \tag{54}$$

Then, we consider the metal as a single atom with many different levels, interacting with the He atom. To this system we can apply the discussion of Sec. II, and calculate the different contributions to the interaction energy.

As regards to the one-electron contributions associated with the metal-atom overlap, we find that the **k** level is shifted by the following energy:

$$\delta\varepsilon^S(k) = \tfrac{1}{4} S_{k,\text{He}}^2[\varepsilon(k) - E_{\text{He}}^{\text{eff}}] - S_{\mathbf{k},\text{He}} T_{\mathbf{k},\text{He}} \ , \tag{55}$$

where $S_{\mathbf{k},\text{He}}$ is the overlap between a k eigenfunction and the He level, and $T_{\mathbf{k},\text{He}}$ the corresponding hopping element. In Eq. (55), we have introduced $E_{\text{He}}^{\text{eff}}$, the atomic 1$s$-He level corrected by the image potential as discussed above. The 1s-He level is also shifted due to the overlap by the following amount:

$$\delta\varepsilon_{\text{He}}^S = \sum_k \{ \tfrac{1}{4} S_{k,\text{He}}^2 [E_{\text{He}}^{\text{eff}} - \varepsilon(k)] - S_{\mathbf{k},\text{He}} T_{\mathbf{k},\text{He}} \} \ . \tag{56}$$

Combining Eqs. (55) and (56) and taking into account the k-level occupancy we find that the overlap between the metal and He orbitals contributes in the following amount to the interaction energy:

$$\begin{aligned} \delta V^S = \tfrac{1}{2} &\sum_{\mathbf{k}\text{ empty}} S_{\mathbf{k},\text{He}}^2 [E_{\text{He}}^{\text{eff}} - \varepsilon(k)] \\ &- 2 \sum_{\mathbf{k}\text{ empty}} S_{\mathbf{k},\text{He}} T_{\mathbf{k},\text{He}} - 4 \sum_{\mathbf{k}\text{ occ}} S_{\mathbf{k},\text{He}} T_{\mathbf{k},\text{He}} \ , \end{aligned} \tag{57}$$

where a factor of 2 has been introduced due to the electron spin, and the different sums in **k** refer either to empty or occupied states of the metal. Equation (57) can be written as a function of the metal atomic orbitals, ϕ_i^M, by means of the equation:

$$\phi_k^M = \sum C_k^i \phi_i^M \ . \tag{58}$$

Introducing Eq. (58) into (57) and neglecting the overlap between metal orbitals, we reach the following equations

$$\begin{aligned} \delta V^S = \tfrac{1}{2} &\sum_i S_{i,\text{He}}^2 \int_{E_F}^{\infty} (E_{\text{He}}^{\text{eff}} - \varepsilon) n_i(\varepsilon) d\varepsilon \\ &- 2 \sum_i S_{i,\text{He}} T_{i,\text{He}} \int_{E_F}^{\infty} n_i(\varepsilon) d\varepsilon \\ &- 4 \sum_i S_{i,\text{He}} T_{i,\text{He}} \int_{-\infty}^{E_F} n_i(\varepsilon) d\varepsilon \ , \end{aligned} \tag{59}$$

where $n_i(\varepsilon)$ is the local density of states in the metal atom i. This equation reproduces the results of the last section if we replace $(E_{\text{He}}^{\text{eff}} - \varepsilon)$ by $(E_{\text{He}} + J^0 N_M - E_M)$. Notice that in obtaining Eq. (59) we have neglected the interferences between the different metal atoms: in this approximation, the interaction potential appears as the sum of the interactions between the He atom and the different metal atoms. We should also mention that in our actual calculation, the repulsive potential is given by the interaction of metal atoms with the approaching He atom; on a top position, one metal atom is practically controlling the interaction, while in a center coordinated position there are those few metal atoms having the same distance to He. This allows us to write $E_{\mathrm{He}}^{\mathrm{eff}}=E_{\mathrm{He}}+J^0N_M$ as discussed in the preceding section, where N_M is the orbital occupancy per spin of the nearest-neighbor metal atom to He, and J^0 the Coulomb interaction between one electron in this orbital and another in the 1s He level.

On the other hand, we have to consider the hybridization energy between the He-orbital and the metal states. This is defined by the hopping terms:

$$\sum_{\mathbf{k},\sigma} T_{\mathbf{k},\mathrm{He}}(C_{k\sigma}^{\dagger}C_{\mathrm{He}\sigma}+C_{\mathrm{He}\sigma}^{\dagger}C_{k\sigma})$$

and the effective 1s-He level $E_{\mathrm{He}}^{\mathrm{eff}}=E_{\mathrm{He}}+J^0N_M$. This hybridization energy can be calculated using conventional Green-function techniques; the reader is referred to Ref. 30.

Still, we have to define the hopping parameters, $T_{k,\mathrm{He}}$, or $T_{i,\mathrm{He}}$ if we use a localized description of the metal orbitals. $T_{i,\mathrm{He}}$ has been obtained using the Bardeen tunneling current as discussed above. Thus, we write

$$T_{i,\mathrm{He}}=\gamma T_{i,\mathrm{He}}^{B}$$

and adjust γ using the limit of large distances given by Eq. (47b).

The exchange contribution can be calculated using the same approach given in Sec. II B. The main difference with the calculations of that section is that we now use the multizeta atomic wave function of Clementi-Roetti tables.[26]

Finally, let us mention that in order to calculate the total He-metal interaction we have to include the van der Waals potential. We have used the results of Refs. 28 and 29, where the different saturation effects associated with that interaction are included.

We have applied this approach to the calculation of the interaction of He with the Ni(110), Cu(110), and Ag(110) surfaces. In our calculation we have considered two different surface sites: the on-top position and the fourfold coordinated site. From our analysis we conclude that, for each site, the repulsive potential can be written in the local form:

$$V_{\mathrm{rep}}\cong\alpha n(z) ,$$

where $n(z)$ is the electronic metal density. These results show, however, a dependence of α on the He position with respect to the metal surface. In Table I we show our results for α, as calculated for the different surfaces on the different metals sites.

TABLE I. Values of $[V_{\mathrm{rep}}=\alpha n(z)]$ for different surfaces and for the two helium position on metal surfaces.

Metal	Top position α ($\mathrm{eV}a_B^3$)	Center position α ($\mathrm{eV}a_B^3$)
Ni(110)	271	335
Cu(110)	342	407
Ag(110)	495	581

TABLE II. Theoretical ΔZ_T and experimental $\Delta Z_E(8)$ corrugations for different metal surfaces as seen by a He atom having 21 meV.

Metal	ΔZ_T (Å)	ΔZ_E (Å)
Ni(110)	0.11	0.074
Cu(110)	0.12	0.11
Ag(110)	0.26	0.24

The main point to be noticed about Table I is the change of α with the metal site, showing an important increase when going from the top to the center position. We think these changes are basically due to the non-negligible overlap between the metal wave function near the center of the atom and the He-1s orbital. This change of α is critically related to the surface corrugations as measured with the surface scattering of He atoms.[31,32] Takada and Kohn[19] have stressed that this experimental evidence can only be reasonably explained if α is assumed to change along the metal surface: this is what our results of Table I seem to indicate. In Table II we give the results of our calculation for the corrugation of different metal surfaces, defined as the difference in the direction perpendicular to the surface between the classical turning points for the top and center position, for a given He energy: we have chosen this energy to be 21 meV.

Our results show a fair agreement with the experimental evidence.[31,32] This seems to be a critical test to the method proposed in this paper to calculate the interaction between atom and surfaces.

IV. CONCLUSIONS

In this paper we have presented a first-principles tight-binding (TB) approach, whereby the different parameters of the basic TB Hamiltonian can be calculated from the properties of the constituent atoms, using no adjustable parameter. The basic approach is a kind of bond theory with the hopping parameters and the diagonal levels of the orbitals forming the bond, related to the tunneling current and the overlap between those orbitals. Many-body effects can also be introduced in this tight-binding approach, and we show how to obtain the basic parameters of the interaction Hamiltonian using the wave functions of the constituent atoms.

We have applied this approach to the calculation of the interaction potential between a He atom and a metal surface. The results found in this paper show a good agreement with the experimental evidence and other theoretical calculations based on a local-density formalism approach. We believe that these results allow us to conclude that the method presented in the paper can be applied with great advantage at least for surface problems. Work along these lines for other chemisorbed species on metal surfaces is in progress in our laboratory.

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