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Electronic structure of interstitial impurities near surfaces

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We report calculations of the band contribution to the dissolution and segregation energy for interstitial impurities near a surface, from adsorbate to bulk position, within the tight-binding model, for different classes of environment. The application to the nickel (001) surface—hydrogen system contains the following ingredients: (1) the description of the host by a charge-conserving procedure, with a fivefold-degenerate d band; (2) the description of the substitutional impurity, by a localized perturbation restricted to its own site, adjusted by the Friedel sum rule. The recursion method has been used for computing the self-energies. Extensions of the phase shift in the interstitial case to the complex-energy plane are given.

I. INTRODUCTION

The subject of the electronic structure of dilute interstitial impurities in bulk or near surfaces and interfaces is central in many actual technological fields: energetics (hydrogen storage), metallurgy (segregation, temper embrittlement, heat treatment), chemisorption, catalysis, and semiconductor and device physics. Let us recall (without claim of completeness) some recent results in these fields.

Rasolt and Perrot[1] analyzed, within the "spherical solid model," the relaxation of a hydrogen atom, and its heat of dissolution in bulk aluminum, for different diffusion equilibrium positions and migration paths. Interstitial H in metals has also been studied as a molecular, finite cluster.[2,3] A more satisfactory approach is to embed such a cluster into the host.[4,5] These concepts have also been used in chemisorption.[6–8]

Pseudopotential and jellium models have been applied to the dissolution of H in normal metals,[9,10] and even in transition metals.[11] The tight-binding method is also widely used, in all fields; its credibility is reinforced by the linear muffin-tin orbital—atomic-spheres-approximation method (LMTO-ASA) band-structure models, which may provide first-principles tight-binding band parameters, and has even been extended to the one-impurity bulk model;[12,13] the related linearized—augmented-plane-wave (LAPW) method is used for surfaces.[14]

In semiconductor physics, tight-binding methods are also useful for defects.[15] Progress has been made in interstitial cases by introducing the extraorbital atom,[16] or lattice,[17] concepts, and different bases in the state before and after the coupling of adatoms.[18]

In surface physics and catalysis, much work on chemisorption, experimental as well as theoretical, is available. If the theories of impurities in the bulk were adapted to chemisorption (the Anderson model by Newns,[19] and tight-binding model by Allan,[20] Grimley,[21] and Einstein[22]), considerable progress would have been made in this field beyond the Hartree-Fock model, multielectronic effects being necessary for the interpretation of experimental data such as photoemission. One may refer to Ref. 23 for a recent review of the status of work in this field.

This paper is the extension of our previous work[24,25] on the electronic structure of substitutional impurities near surfaces in the tight-binding model, for the interstitial case. The general framework, and even our use of the substrate Ni, will be the same (a tight-binding degenerate d band). In the initial state (semi-infinite medium without impurity adatom), the atomic-d-level shifts near the surface are determined "self-consistently" within the empirical tight-binding model.[26] Moreover, global neutrality must be achieved. In fact, a simplified version, where only the atomic levels of the surface plane are shifted, is used.[27,28] In the final state, with the coupled impurity, global change neutrality[29] will again be ensured by adjusting the impurity adatom level. This rather naive model, which may be considered as a paramagnetic Hartree-Fock model, has the virtue that it is quite parameter free, and that it allows a systematic study, versus the adatom position and environment, of the band contribution to dissolution and segregation energy, with the structural effects induced by the surface. The specific features associated with d-band degeneracy are (i) nondiagonal intrasite interorbital contributions to the phase shift, and (ii) the possible presence of surface states (resonances) within the spectral range of the host.

At first, the choice of the nickel substrate does not seem to be very adequate for studying dissolution and segregation energies within a d-band model only, since it is known that conduction s electrons contribute appreciably to the adsorption and dissolution energies;[11] however, the segregation energies, which are differences of the dissolution energies at different sites [cf. (2.16)], may still be significant owing to the smooth behavior of the s contribution reported in Ref. 11.

A formal account of tight-binding theory of chemisorption that may be adapted to our interstitial problem in the neighborhood of a surface can be found in Ref. 30. We use a simplified version of it, with unit overlap.

In Sec. II we briefly recall the definition and results for the Green functions. Then we define the corresponding phase shifts adapted to the complex-energy plane, a very efficient method for fast and precise calculations of occupation numbers and band energies.[24,25] Attempts to properly define such a phase shift well defined at $\mathrm{Im}z \to 0$, or $|z| \to \infty$, have failed, up to now,[31] in the interstitial case.

We establish the charge-conservation relation[29] in terms of this phase shift, and the band contribution to the dissolution and segregation energy, essential ingredients of our calculation.

In Sec. III the calculation is performed on a minimal model, i.e., hydrogen in paramagnetic nickel bounded by a (001) surface. The H adatom is described by a single 1*s* orbital; the substrate nickel has already been described above.[27,28] The hopping between H and its Ni neighbors is determined by a unique parameter, the $(sd\sigma)$ molecular integral.[32]

The adatom self-energy is computed by the recursion method generalized to the group-orbital concept.[33] This function, the local density of states of hydrogen, its occupation number, and the associated band energies, are presented and discussed, versus the position of the surface and the environment. In conclusion, we discuss the positive points of this calculation, and its limitations.

We recall that our work differs from that of Refs. 30 and 34 in the implementation of two-step charge conservation[24]—one step for the semi-infinite host and one for the localized impurity level—in the systematic study from adsorbate to bulk interstitial position, and in the precision of the calculation.

II. ELECTRONIC STRUCTURE OF AN INTERSTITIAL IMPURITY NEAR A SURFACE

The generalized tight-binding model we use can be considered a particular realization of Anderson's model used in alloy theory and chemisorption. It has the advantage of being able to incorporate easily level shifts of the adatom on its neighbors, induced by Coulomb interactions, for instance. We present briefly, for the sake of definiteness, the main results of Ref. 30 in the case of unit overlap (for simplicity), valid from adsorbate up to bulk atom. We couple two separate systems: (a) an adatom of Hamiltonian H_A^0, with the basis functions being a finite set of localized orbitals $|a\rangle$, of energy ε_a^0. We denote this set $A=\{|a\rangle\}$; (b) a semi-infinite or infinite host, defined by a self-consistent Hamiltonian H_I^0 and an infinite set of states I, the set of atomic orbitals localized on lattice site R; the degeneracy index is assumed to be included in R: $I=\{|R\rangle\}$.

The initial unperturbed Hamiltonian

$$H^0=H_A^0+H_I^0 , \tag{2.1}$$

as well as the corresponding Green function $G^0(z)=(z-H^0)^{-1}$, may be represented in matrix form:

$$\underline{H}^0=\begin{bmatrix} \underline{H}_A^0 & \underline{0} \\ \underline{0} & \underline{H}_I^0 \end{bmatrix} . \tag{2.2}$$

In the final state, after coupling, both subspaces are perturbed and coupled:

$$H=H^0+V , \tag{2.3}$$

$$V=\Delta H_A+\Delta H_I+V_{AI}+V_{IA} . \tag{2.4}$$

The first two terms act on their respective subspaces only; they correspond to the atomic-level shifts induced by the crystal field and occupations of the adatom and by the occupation variations on the host neighboring levels.

The coupling terms V_{AI} and V_{IA} $(=V_{AI}^\dagger)$ describe the hopping between adatom states and neighboring host orbitals $|R\rangle$,

$$V_{AI}=\sum_{a\in A} |a\rangle\beta_{aR}\langle R| . \tag{2.5}$$

It may be shown that the Green-function, $G=(z-H)^{-1}$, matrix in the final state can be written as

$$\underline{G}=\begin{bmatrix} \underline{G}_A & \underline{G}_{AI} \\ \underline{G}_{IA} & \underline{G}_I \end{bmatrix} \tag{2.6}$$

in the set $A\cup I$, with

$$\underline{G}_A(z)=[z\underline{\mathbb{1}}-\underline{H}_A^1-\underline{\Delta}(z)]^{-1} , \tag{2.7a}$$

$$\underline{G}_I(z)=[z\underline{\mathbb{1}}-\underline{H}_A^1-\underline{Y}(z)]^{-1} , \tag{2.7b}$$

and

$$\underline{H}_\alpha^1=\underline{H}_\alpha^0+\Delta\underline{H}_\alpha,\ \ \alpha=A,I . \tag{2.7c}$$

The chemisorption matrix (adatom self-energy) is

$$\underline{\Delta}(z)=\underline{V}_{AI}(z\underline{\mathbb{1}}-\underline{H}_I^1)^{-1}\underline{V}_{IA} . \tag{2.7d}$$

The dual quantity in subspace I is

$$\underline{Y}(z)=\underline{V}_{IA}(z\underline{\mathbb{1}}-\underline{H}_A^1)^{-1}\underline{V}_{AI} . \tag{2.7e}$$

These two quantities, as far as separate subspaces are concerned (as in charge or energy properties), can be considered to be complex energy-dependent optical potentials. We refer to the literature for the off-diagonal matrix elements.[30] The determination of the $(z-H_\alpha^1)^{-1}$ in their respective subspaces is a well-known problem.

The density of states is given by

$$n(E)=-\frac{1}{\pi}\lim_{z\to E+i0}\ \operatorname*{Tr}_{A\cup I}\underline{G}(z) . \tag{2.8}$$

In fact, for the total charge and the variations of the band energy, the relevant quantity is the phase shift. It may be shown that the complex phase shift Z (Refs. 24 and 25) verifies

$$\operatorname*{Tr}_{A\cup I}(\underline{G}-\underline{G}^0)=\frac{d}{dz}Z , \tag{2.9a}$$

$$Z=Z_A+Z_I , \tag{2.9b}$$

$$Z_A(z)=\operatorname*{Tr}_{A}\ln\{[z\underline{\mathbb{1}}-\underline{H}_A^1-\underline{\Delta}(z)](z\underline{\mathbb{1}}-\underline{H}_A^0)^{-1}\} , \tag{2.9c}$$

$$Z_I(z)=\operatorname*{Tr}_{I}\ln(\underline{\mathbb{1}}-\Delta\underline{H}_I^1\underline{G}_I^0) . \tag{2.9d}$$

We also recall the identity used to evaluate (2.9c)—(2.9d) if the dimension of the space over which the trace is performed is greater than 1,

$$\mathrm{Tr}\ln \underline{A} = \ln \det \underline{A} \ . \tag{2.9e}$$

We now establish the charge-conservation relation[29] with the nonstandard definition of the phase shift, in a metallic system: (i) The Fermi energy E_F is conserved before and after coupling, for the infinite system. However, for the isolated atom in the initial state, an "atomic Fermi energy" E_A, consistent with the highest occupied state and its occupancy, exists. (ii) The total variation of charge between the initial and final states vanishes; in the complex-energy-plane formulation,[24,25]

$$N - N_0 = \frac{1}{2\pi i}\int_{C_I} \underset{A\cup I}{\mathrm{Tr}}\,(\underline{G} - \underline{G}^0)dz - \frac{1}{2\pi i}\int_{C_A - C_I} \underset{A}{\mathrm{Tr}}\,[\underline{G}^{\,0}_{A}(z)]dz = 0 \ , \tag{2.10}$$

where C_α is the path turning counterclockwise around the real energy axis from E_α to $-\infty$, and backwards (E_F and E_A, respectively, for C_I and C_A). The last integral in (2.10) is the valence of atom A relative to the matrix:

$$\Delta Z = \frac{1}{2\pi i}\int_{C_A - C_I} \underset{A}{\mathrm{Tr}}\,[\underline{G}^{\,0}_{A}(z)]dz = \begin{cases} \displaystyle\sum_{(a,\,E_a^0 > E_F)} N_a & \text{if } E_A > E_F, \\ \displaystyle -\sum_{(a,\,E_a^0 < E_F)} (1 - N_a) & \text{if } E_A < E_F \ , \end{cases} \tag{2.11}$$

a donor or an acceptor, respectively, according to the inequalities

$$E_A > E_F, E_A < E_F \ .$$

N_a is the occupation number of state a, of energy E_a with (2.9), and the charge-conservation relation becomes

$$\Delta Z = \frac{1}{2\pi i}[Z(E_F + i0) - Z(E_F - i0)] \ . \tag{2.12}$$

The band contribution to the dissolution energy can be written similarly as[25]

$$E_b = \frac{1}{2\pi i}\int_{C_I} z \underset{A\cup I}{\mathrm{Tr}}\,(\underline{G} - \underline{G}^0)dz - \frac{1}{2\pi i}\int_{C_A - C_I} z \underset{A}{\mathrm{Tr}}\,[\underline{G}^{\,0}_{A}(z) - \underline{\mathbb{1}}]dz \ . \tag{2.13}$$

After some manipulations we obtain

$$E_b = E_f\,\Delta Z - \frac{1}{2\pi i}\int_{C_I} Z(z)dz + E_p \ , \tag{2.14}$$

with the promotion energy [the last term of (2.13)]

$$E_p = \begin{cases} \displaystyle\sum_{(a,\,E_a^0 > E_F)} E_a^0 N_a & \text{if } E_A > E_F, \\ \displaystyle\sum_{(a,\,E_a^0 < E_F)} E_a^0 (1 - N_a) & \text{if } E_A < E_F \ . \end{cases} \tag{2.15}$$

We recall that the quantities G^0, Δ, and E_0 depend on the position relative to the surface, R. This quantity E_b contributes to the heat of dissolution in the bulk (∞).

Within our severe approximation,[24,25] the band contribution to the segregation energy E_s is simply the difference between the dissolution energy at position R and the bulk one (∞):

$$E_s(R) = E_b(R) - E_b(\infty) = \frac{-1}{2\pi i}\int_{C_I} [Z(R;z) - Z(\infty;z)]dz \ . \tag{2.16}$$

The optimum contour C_I is used[25] in the numerical evaluations of E_s and E_b in Sec. III, the advantage being avoidance of the ambiguities of determination which arise in the conventional integral of the phase shift on the real axis, since only the well-defined ReZ is required on the Bromwitch path

$$E_F + iy,\ y \in [0, +\infty] \ .$$

III. APPLICATION TO AN INTERSTITIAL HYDROGEN IMPURITY NEAR A Ni(01) SURFACE

We perform the simplified calculations outlined in the Introduction for different families of environment (octahedral, tetrahedral, and saddle-point positions, which are known to be, respectively, the stable-, metastable-, and unstable-equilibrium positions in the bulk).[35] The last class is usually invoked in determining the barrier height in a diffusion process. Owing to the symmetry breaking by the surface, this last class is subdivided into two subclasses. Shown in Table I are the considered positions and

TABLE I. The four studied geometries of an interstitial atom in fcc crystals. The label n indexes the position of the interstitial atom (in units $a/2$ of the lattice parameter), for the (001) surface. Usually, $n = -1$ refers to an adsorption position, but does not exist for saddle-point site 1, which is not coupled to the system, in our model. $(x,y,0)$ is the surface plane.

Site	Surface plane
Octahedral (n even)	$(1,0,2p)$[a]
Octahedral (n odd)	$(1,1,2p+1)$[b]
Tetrahedral	$(\frac{1}{2},\frac{1}{2},\frac{1}{2}+n)$,
Saddle point 1	$(\frac{1}{2},\frac{1}{2},n)$
Saddle point 2	$(\frac{1}{2},0,n+\frac{1}{2})$

[a] $n = 2p$.

[b] $n = 2p + 1$.

how they are labeled. We neglect any distortion around the impurity or geometrical relaxation of the host near the surface in this approach, as well as the renormalization of the neighboring atomic levels.

We solved this problem in the same spirit as the calculation of the local Green function, namely by the generalized recursion method:[36]

$$\Delta=\langle a \mid V_{AI} G_I^0 V_{IA} \mid a \rangle \qquad (2.7\text{d}')$$

may be considered the matrix element of G_I^0 between $(V_{IA} \mid a \rangle)$ states, and then solved accordingly. This scheme was given by Kelly[33] in the case of chemisorption. The normalized $V_{IA} \mid a \rangle$ function is known as the group orbital $\mid g \rangle$. We incorporated the programmed evaluation of the group orbital, in any environment, into the recursion method, in order to evaluate Δ for all the distances and geometries. By the recursion method, we build Δ as a continued fraction. About 10 levels are necessary to develop the structure. We go up to 25 levels in order to have a resolution of $\frac{1}{50}$th of the bandwidth. We terminated these continued fractions using the prescription of Pettifor and Beer.[37] This method of calculation is even valid for self-energies, with renormalized neighboring atomic levels (2.5). We recall that Δ is scaled by the molecular integral $(sd\sigma)^2$. We use a unique $(sd\sigma)$ value, that of Switendick[38] proposed for stoichiometric NiH, i.e., $(sd\sigma)=-0.074$ Ry, in presenting the self-energies Δ versus the position of the surface and environment in Fig. 1. This allows to compare directly the coordination effects on the structure.

The following features may be noted:

(i) The amplitudes are roughly proportional to the coordination. This is mainly true for adsorption and surface positions.

(ii) Fast convergence toward the bulk shape after the adsorbate first interstitial position.

(iii) The self-energy is proportional to the group-orbital Green function g; indeed,

$$\Delta(z)= \mid \langle a \mid V_{AI} \mid g \rangle \mid^2 G_{gg}^1(z) \; , \qquad (2.7\text{d}'')$$

$$\Delta(z)= \sum_{R,R'} \langle a \mid V_{AI} \mid R \rangle G_{RR'}^1(z) \langle R' \mid V_{IA} \mid a \rangle \; . \qquad (2.7\text{d}''')$$

The self-energy has been often approximated in alloy theory by (2.6c) with the sum R,R' restricted to $R=R'$, or R,R' up to first-nearest neighbors, by evaluation of the

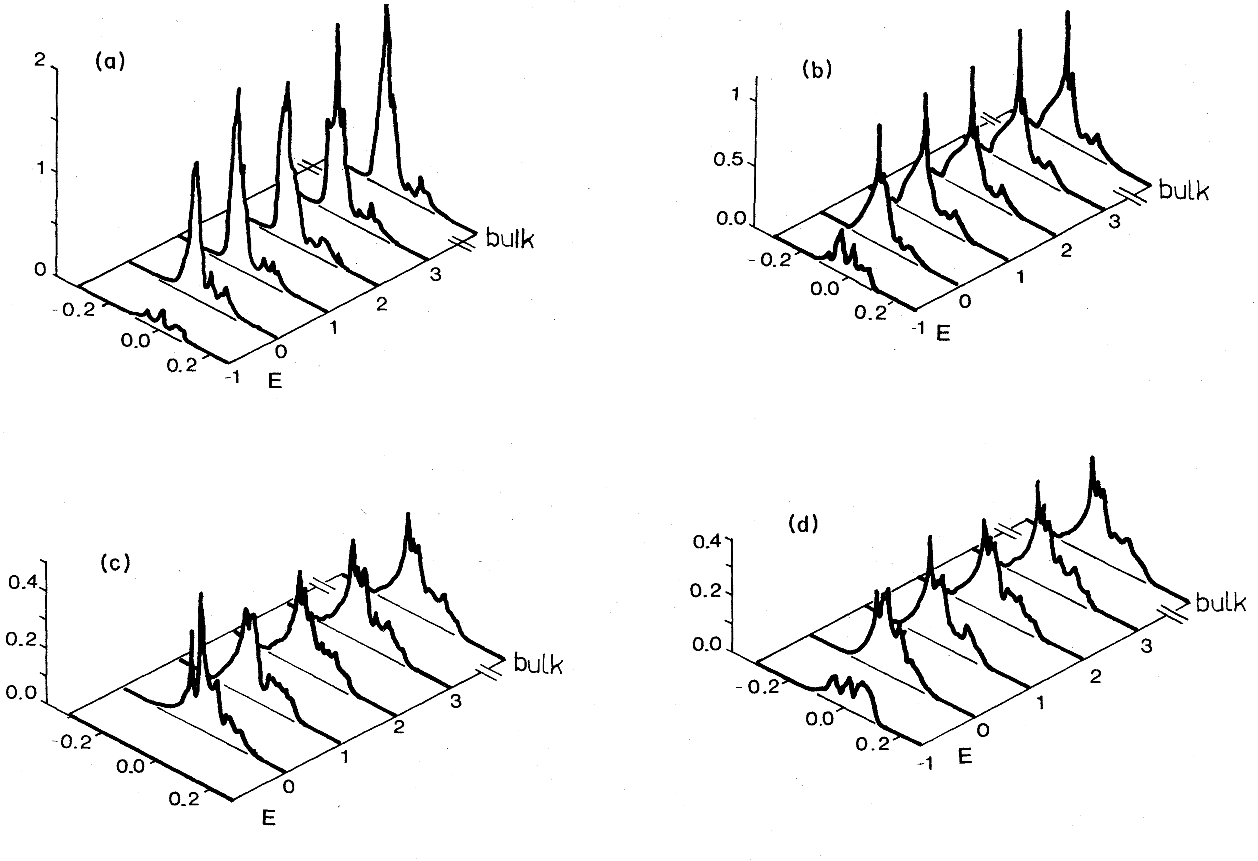

FIG. 1. Chemisorption function $(-\text{Im}\Delta)$ vs energy (E) and position of the impurity (with the same definition for the labels n as in Table I), for the four geometries of interstitial H in Ni(001): (a) octahedral site; (b) tetrahedral site; (c) saddle-point site 1; (d) saddle-point site 2. The value of $(sd\sigma)$ is -0.074 Ry (Ref. 38). The real part of Δ, not represented here, may be obtained by the Hilbert transformation of ImΔ.

corresponding Green-function matrix elements. These approximations are not really satisfied, except in exceptional cases, where the coordination is sufficiently low that the approximations become exact, and are even computationally heavier than the procedure (2.5c) adopted here.[39] See, for instance, saddle point 2 of Fig. 1(d), which is proportional to the $3z^2-r^2$ orbital density of states.[34]

We briefly recall the remaining steps of our calculation, for a given family of sites:

(1) Choose the value of the $(sd\sigma)$ hopping parameter between the adatom H and its Ni neighbors. In the calculations presented here, we adopted an unique value.[38] Another point of view is to vary $(sd\sigma)$ with the distance H-Ni; Boudeville *et al.*[40] proposed an exponential law:

$$(sd\sigma)=(sd\sigma)_0\exp\{-q[(R/R_0)-1]\}\ ,$$

where $(sd\sigma)_0$ and R_0 are reference values, and $q\sim3$. The range of validity of this law, however, is limited; its application to the unrelaxed saddle-point positions, which are very close to their neighbors, leads to unphysical binding energies (of the order of a rydberg).

(2) Determine the H 1*s* level ε_I by the sum rule (2.12). This simulates, in a global way, some crystal-shift effects and Coulomb and exchange corrections to H.

(3) Compute the local Green function of the H 1*s* state, $\langle 1s\,|\,G(z)\,|\,1s\rangle=[z-\varepsilon_I-\Delta(z)]^{-1}$ [Eq. (2.7a)]. Its imaginary part (local density of states) is represented in Fig. 2, versus position. The corresponding occupations of the H 1*s* state (ionicities) are obtained integrating by (2.7a) along the path C_I.[25]

(4) The dissolution energies (2.14)—(2.16) for the bulk interstitial positions, and the segregation energies (2.17) versus position, are computed along the same path using Gaussian quadrature on the Bromwitch line. In our model, the expression of E_s is very simple:

$$E_s=-\frac{1}{2\pi i}\int_{C_I}\ln\left[\frac{z-\varepsilon_I(R)-\Delta(R;z)}{z-\varepsilon_I(\infty)-\Delta(\infty,z)}\right]dz\ . \qquad (3.1)$$

The corresponding results are reported in Table II.

Let us now discuss the different results.

In Fig. 2, due to sum rule (2.12), the 1*s* local densities of states (LDOS's) are pinned at the Fermi level at the topmost peak. The H 1*s* LDOS is very structured: for octahedral [Fig. 2(a)] and tetrahedral [Fig. 2(b)] sites, a bonding resonance occurs for the adsorption, which turns into a molecular bound state deeper in the metal. Owing to the shapes of Δ, with our parameters, no antibonding molecular states occur above the band. We recall that very structured LDOS's may also be obtained by introducing multielectronic corrections, at least for the adatom.[41]

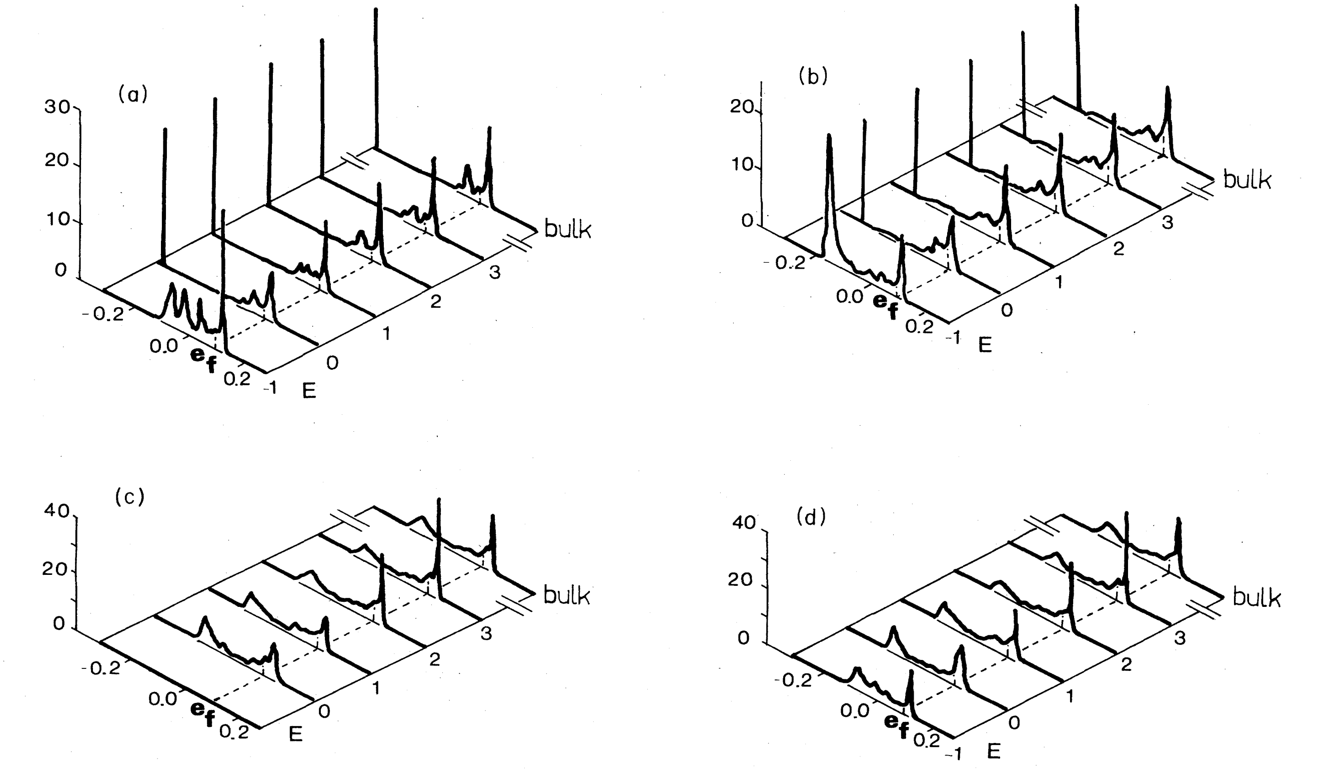

FIG. 2. Local density of states of the hydrogen interstitial site in Ni(001), vs energy and position of the impurity (same conventions as in Fig. 1).

TABLE II. Band contributions to the segregation energy of a hydrogen interstitial in Ni(001) vs its position (with the same conventions as in Fig. 1 and Table I). Last line denotes values for absolute dissolution energy in the bulk (in Ry), with the origin of energies at E_d^0 (Ref. 46) and the vacuum level at 0.4327 Ry.

n	Octahedral site	Tetrahedral site	Saddle-point site 1	Saddle-point site 2
−1	0.3606	0.4266		0.0054
0	−0.0376	−0.0026	0.0019	−0.0092
1	−0.0130	0.0045	−0.0248	−0.0188
2	0.0037	−0.0052	−0.0024	−0.0024
3	−0.0106	−0.0043	0.0094	0.0071
Bulk	0.1246	0.2925	0.4509	

It is therefore important to be able to discriminate the origin of the structures observed experimentally, many-body and/or band-structure effects. We note also that the structures obtained for saddle-point positions at fixed $(sd\sigma)$ are weaker, without a molecular bound state, due to the low coordination. The ionicity of the H adatom is negative and rather high in this model: 0.5, 0.7, and 0.8 for saddle-point, tetrahedral, and octahedral positions in bulk, respectively. This high ionicity is a general flaw of Hartree-Fock models; models with strong correlations on H favor the neutrality of H.[42]

It is possible to adopt this approximation of local neutrality in step 2 instead of (2.12). However, the relations (2.17) for band segregation would lose their simplicity since global neutrality is then usually violated.

The band contribution to segregation energy presented in Table II shows the following trends:

(1) For the octahedral family, there is a low bonding energy in adsorption positions, but strong subsurface bonding on the following planes (0 and 1), and a barrier on plane 2. These results agree with the model used for the kinetics of H adsorption.[43]

(ii) The other families behave similarly.

It is not possible to attach significance to the absolute values between the different families of sites, since the parameter $(sd\sigma)$ should be varied, and the lattice distortions are different for the various environments.

A better evaluation of the dissolution energies would also require proper treatment of 4s electrons, which are known to contribute significantly to the binding energy in the case of Ni.[43] The introduction of repulsive ion-ion interactions within a Born-Mayer—type expression, and geometrical lattice distortion, may also be considered.[44]

IV. CONCLUSION

This paper is the extension of our previous work on substitutional impurities near surfaces, in the interstitial case.[24,25] We performed here precise and systematic calculations of the band contribution to dissolution and segregation energy within the tight-binding model.

The main ingredients of the calculation are the recursion method extended to self-energies,[33] complex-energy-plane integration of the Green function and of the proper extension of the phase shift in the interstitial case, and the Friedel sum rule.[29] The effects of the geometrical structure and of the degeneracy of the bands, from adsorption up to bulk interstitial position, are well demonstrated, mainly on the band contribution to the segregation energy. We recall that the degeneracy introduces off-diagonal contributions to the Green functions and the phase shifts for a general surface orientation. It allows also sharp resonances within the band.

It is, in principle, possible to improve the model via the following:

(i) By performing self-consistent calculations within the Hartree-Fock approximation, with intra-atomic and interatomic Coulomb and exchange contributions[26,45] to the impurity and the host. Such self-consistent calculations are unstable and the results sometimes deceptive.[26]

(ii) By introducing 4s conduction electrons, which are known to contribute in the case of H in Ni.[2,11]

(iii) By introducing correlations on the adatoms and, eventually, on the host.[23,41]

It is also necessary to estimate the repulsive contributions, i.e., lattice distortions, in order to obtain absolute values of segregation energy and to estimate the barrier heights involved in diffusion.

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