PHYSICAL REVIEW B VOLUME 17, NUMBER 4 15 FEBRUARY 1978

Ab initio self-consistent-field method using linear combinations of atomic orbitals for the calculation of surface states of three-dimensional crystals

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(Received 16 June 1977)

The resolvent method developed previously for the *ab initio* self-consistent-field linear-combination-of-atomic-orbitals (SCF LCAO) treatment of a cluster of impurities imbedded in a one-dimensional periodic polymer has been applied to the end of a semi-infinite linear chain. Generalizing the expressions obtained to the case when the chain is periodically repeated in the other two dimensions a method has been worked out for the *ab initio* SCF LCAO computation of the surface and chemisorption states of a three-dimensional semi-infinite crystal. The matrix equations derived seem rather suitable to immediate numerical applications.

INTRODUCTION

In a previous paper[1] (hereafter called I), an *ab initio* self-consistent-field linear-combination-of-atomic-orbitals (SCF LCAO) method was described for the calculation of the extra states due to a cluster of impurities (with an arbitrary number of impurity orbitals) imbedded in an one-dimensional periodic system. This resolvent method (which was a generalization to the SCF LCAO case of the method of Koster and Slater[2] and that of Kertesz and Biczo[3]) can provide also the surface states belonging to the two ends of a finite linear chain, if we intersect the loop formed by the chain at some point.[4] In this paper it will be shown how one can generalize the same procedure for the calculation of the surface states of a semi-infinite three-dimensional crystal in the Hartree-Fock (*ab initio* SCF LCAO) level. In this respect one should mention that the resolvent method has been applied already before the study of surface states in the simple tight-binding (LCAO) approximation by Koutecky.[5]

It should be emphasized that in the present paper only the resolvent method will be used which means that only surface levels not lying inside the bulk energy bands can be obtained. Further no attempt will be made to find out how much localized are the wave functions belonging to the surface states.[6] In connection with this it should be mentioned that Hoshen and Kopelman,[7] using a partition of the Hamiltonian, have already investigated successfully in the case of a simple-cubic molecular crystal the localization of surface exciton states in terms of the exciton-transfer integral J and the environmental-shift integral D (in the nearest-neighbor approximation). The same problem was treated (using the method of localized perturbation) also by Ueba and Ichimura.[8] They have found conditions not only for the localization (existence) of surface exciton states, but also a criterion to determine whether the surface exciton states lie above or below the bulk exciton states. Rather probably one could apply these methods also for the investigation of the localization and of the position (whether they are different from the bulk band states) of the electronic ground-state Hartree-Fock surface states. The treatment of these problems and numerical applications of the method will be discussed in subsequent publications.

It should be mentioned that a SCF theory of the surface states of three-dimensional crystals is already published in several papers. All these works apply, however, either a model Hamiltonian[9,10] or a general operator formalism[11,12] which is not very suitable for immediate applications. On the other hand, the present *ab initio* SCF LCAO method with its matrix formulation of the problem, as we shall see, facilitates very much numerical calculations.

PROBLEM OF THE FINITE LINEAR CHAIN

Let us assume that we have a three-dimensional periodic crystal with $2N_1+1$, $2N_2+1$, and $2N_3+1$ unit cells in each direction and m orbitals in the unit cell. Let us further assume that though N_2 and $N_3 \to \infty$, N_1 does not. Let us consider now a linear chain of cells in the first direction. The position of this in the crystal chain should be characterized by the integers q_2 and q_3 ($\vec{R} = q_2 a_2 \vec{i} + q_3 a_3 \vec{j}$, where a_2 and a_3, and $\vec{i}$ and $\vec{j}$, are the elementary translations and unit vectors in the second and third directions, respectively). In Fig. 1 we show this chain in the crystal. Introducing periodic boundary conditions the coefficients of the Bloch orbitals of the electrons delocalized in the chain can be calculated with the aid of the matrix equation[13]

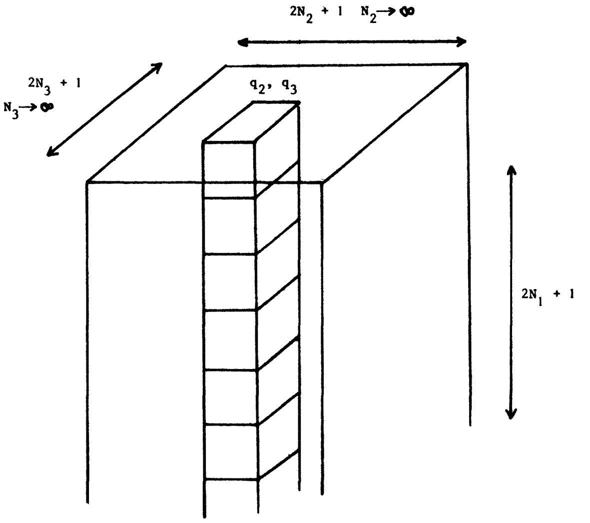

FIG. 1. A linear chain of cells in the three-dimensional crystal.

$$\underline{F}_0(k_1, q_2, q_3)\underline{d}_i(k_1, q_2, q_3) = \underline{\epsilon}_i(k_1, q_2, q_3)\underline{S}_0(k_1, q_2, q_3)\underline{d}_i(k_1, q_2, q_3)\,, \tag{1}$$

where

$$\underline{F}_0(k_1, q_2, q_3) = \sum_{q_1=-\infty}^{\infty} \underline{F}_0(q_1, q_2, q_3)e^{ik_1q_1a_1}\,, \tag{2a}$$

$$\underline{S}_0(k_1, q_2, q_3) = \sum_{q_1=-\infty}^{\infty} \underline{S}_0(q_1, q_2, q_3)e^{ik_1q_1a_1}\,, \tag{2b}$$

with

$$[\underline{F}_0(q_1, q_2, q_3)]_{f,g} = \langle \chi_f{}^{(0,q_2,q_3)}|\hat{F}^P|\chi_g{}^{(q_1,q_2,q_3)}\rangle\,, \tag{3a}$$

$$[\underline{S}_0(q_1, q_2, q_3)]_{f,g} = \langle \chi_f{}^{(0,q_2,q_3)}|\chi_g{}^{(q_1,q_2,q_3)}\rangle\,. \tag{3b}$$

$\hat{F}^P$ is the Fock operator of the periodic linear chain and $\chi_f{}^{(0,q_2,q_3)}$is the fth orbital in the cell characterized by the integers $0, q_2, q_3$.

If we now intersect the chain at the crystal surface ($q_1 = 0$), we obtain instead of the original loop a finite chain. We can write then the Hamiltonian matrix of the whole finite chain in the form

$$\underline{H} = \underline{H}_0^P + \underline{H}'\,, \tag{4}$$

where $\underline{H}_0^P$ is the Hamiltonian matrix of the original periodic chain (loop)[14] and the matrix $\underline{H}'$ (which) gives the deviation from the periodic case) is defined (see also I) in the first-neighbor interactions approximation by

$$\underline{H}' = \left[\begin{array}{cccccc}
\tilde{\underline{F}}(0) & \tilde{\underline{F}}(1) & \cdots\underline{0}\cdots & & & \underline{F}_0(2N_1) - \underline{F}(1)^{\mathrm{tr}} \\
\tilde{\underline{F}}(1) & \underline{0} & & & & \\
\vdots & & \vdots & & & \vdots \\
\underline{0} & & \cdots\underline{0}\cdots & & & \underline{0} \\
\vdots & & \vdots & & & \vdots \\
 & & & & \underline{0} & \tilde{\underline{F}}(1)^{\mathrm{tr}} \\
\underline{F}_0(2N_1)^{\mathrm{tr}} - \underline{F}(1) & \cdot & \cdots\underline{0}\cdots & & \tilde{\underline{F}}(1) & \tilde{\underline{F}}(0)
\end{array}\right]. \tag{5}$$

Here

$$\tilde{\underline{F}}(0) = \underline{F}_0(0) - \underline{F}(0)\,, \quad \tilde{\underline{F}}(1) = \underline{F}_0(1) - \underline{F}(1)\,. \tag{6}$$

The matrices $\underline{F}(0)$ and $\underline{F}(1)$ occur in the hypermatrix $\underline{H}_0^P$ which can be written in the first-neighbor interactions approximation as

$$\underline{H}_0^P = \left[\begin{array}{ccccccc}
\underline{F}(0) & \underline{F}(1) & \underline{0} & \cdots & & & \underline{F}(1)^{\mathrm{tr}} \\
\underline{F}(1)^{\mathrm{tr}} & \underline{F}(0) & \underline{F}(1) & & & & \vdots \\
0 & \underline{F}(1)^{\mathrm{tr}} & \underline{F}(0) & & & & \\
\vdots & & \ddots & & & & \\
 & & & & \underline{F}(1)^{\mathrm{tr}} & \underline{F}(0) & \underline{F}(1) \\
\underline{F}(1) & & & \cdots & (\underline{0}) & \underline{F}(1)^{\mathrm{tr}} & \underline{F}(0)
\end{array}\right]. \tag{7}$$

From (7) it is clear that the elements of the matrix $\underline{F}(0)$ (suppressing the indices q_2 and q_3),

$$[\underline{F}(0)]_{f,g} = \langle \chi_f^{(0)} | \hat{F}^P | \chi_g^{(0)} \rangle = \langle \chi_f^{(q_1)} | \hat{F}^P | \chi_g^{(q_1)} \rangle , \tag{8}$$

give interactions within the unit cell, while the matrix $\underline{F}(1)$ provides the first-neighbor interactions. The matrix $\underline{F}_0(0) \neq \underline{F}(0)$ corresponds to the end of the chain, and its elements are defined as

$$[\underline{F}_0(0)]_{f,g} = \langle \tilde{\chi}_f^{(0)} | \hat{F}^s | \tilde{\chi}_g^{(0)} \rangle . \tag{9}$$

Here $\tilde{\chi}_f^{(0)}$ can be different from $\chi_f^{(0)}$ due to chemisorption [in the case if the end cell has a larger number of orbitals ($\tilde{m} = m + m_{\text{chem}}$, where m_{chem} is the number of orbitals in the chemisorbed molecule) than the bulk cells]. Further generally $\underline{\hat{F}}^S \neq \underline{\hat{F}}^P$, due both to the change of the potential at the chain end due to possible changes in the geometry in the end cell. Correspondingly the elements

$$[\underline{F}_0(1)]_{f,g} = \langle \tilde{\chi}_f^{(0)} | \hat{F}^S | \chi_g^{(1)} \rangle \tag{10}$$

of the matrix $\underline{F}_0(1)$ give the interactions between orbitals centered in the end cell and in the next-neighbor cell, respectively.

In full analogy to (4) we can write

$$\underline{S} = \underline{S}_0^P + \underline{S}' , \tag{11}$$

where the hypermatrix $\underline{S}_0^P$ can be given by (7) if we substitute in it the corresponding overlap matrices $\underline{S}(0)$ and $\underline{S}(1)$, respectively. The deviation matrix $\underline{S}'$ has (in the first-neighbor interactions approximations) again the form of (5) and we can write it down if we substitute into (5), instead of $\underline{\tilde{F}}(0)$ and $\underline{\tilde{F}}(1)$, the corresponding overlap matrices

$$\underline{\tilde{S}}(0) = \underline{S}_0(0) - \underline{S}(0) , \quad \underline{\tilde{S}}(1) = \underline{S}_0(1) - \underline{S}(1) . \tag{12}$$

In Eq. (12) the elements of $\underline{S}_0(0)$ and $\underline{S}_0(1)$ can be easily obtained if we substitute into (9) and (10) instead of $\hat{F}^S$ the unity operator $\hat{1}$.[15] Further it should be mentioned that in the first-neighbor interactions approximation, the matrix $\underline{F}_0(2N_1)$ and the corresponding matrix $\underline{S}_0(2N_1)$ (which give the interactions between the orbitals belonging to the two different end cells of the chain) should be neglected.

With the help of these definitions we can formulate the problem of our finite open chain as

$$\underline{H}\underline{c} = (\underline{H}_0^P + \underline{H}')\underline{c} = \lambda \underline{S}\underline{c} = \lambda(\underline{S}_0^P + \underline{S}')\underline{c} . \tag{13}$$

Let us multiply this equation from the left by $\underline{U}_1^\dagger$ (the unitary matrix which block diagonalizes $\underline{H}_0^P$ and $\underline{S}_0^P$). By inserting $\underline{U}_1\underline{U}_1^\dagger = \underline{1}$ and collecting the periodic matrices on the left-hand side, we obtain

$$\underline{U}_1^\dagger \underline{H}_0^P \underline{U}_1 \underline{U}_1^\dagger \underline{c} - \lambda \underline{U}_1^\dagger \underline{S}_0 \underline{U}_1 \underline{U}^\dagger \underline{c} = -\underline{U}_1^\dagger \underline{H}' \underline{c} - \lambda \underline{U}_1^\dagger \underline{S}' \underline{c} , \tag{14}$$

or by introducing the notations

$$\underline{H}_0^{\text{BD}} = \underline{U}_1^\dagger \underline{H}_0^P \underline{U}_1 , \quad \underline{S}_0^{\text{BD}} = \underline{U}_1^\dagger \underline{S}_0^P \underline{U}_1 ,$$

we can write

$$(\underline{H}_0^{\text{BD}} - \lambda \underline{S}_0^{\text{BD}}) \underline{U}_1^\dagger \underline{c} = -\underline{U}_1^\dagger (\underline{H}' - \lambda \underline{S}') \underline{c} . \tag{15}$$

The blocks of the unitary matrix $\underline{U}_1$ are defined[13] as

$$[\underline{U}_1]_{p,q} = \frac{1}{(2N_1+1)^{1/2}} \exp\left(\frac{2\pi i p_1 q_1}{2N_1+1}\right) . \tag{16}$$

If we introduce the resolvent matrix

$$\underline{Z}(q_2, q_3) \equiv \underline{U}_1 [\underline{H}_0^{\text{BD}}(q_2, q_3) - \lambda \underline{S}_0^{\text{BD}}(q_2, q_3)]^{-1} U_1^\dagger \tag{17}$$

and multiply Eq. (16) from the left by

$$\underline{U}_1(\underline{H}_0^{\text{BD}} - \lambda \underline{S}_0^{\text{BD}})^{-1} ,$$

we obtain the equation

$$\underline{c}(q_2, q_3) = -\underline{Z}(q_2, q_3)[\underline{H}'(q_2, q_3) - \lambda \underline{S}'(q_2, q_3)] \times \underline{c}(q_2, q_3) . \tag{18}$$

HALF-INFINITE LINEAR CHAIN

In the case of a half-infinite chain ($N_1 \to \infty$, but one end), we can repeat the preceding derivation, only now our deviation matrix $\underline{H}'$ is defined as

$$\underline{H}' = \begin{bmatrix} \underline{0} & -\underline{F}(1) & \underline{0} & \cdots & \underline{0} & \cdots \\ -\underline{F}(1)^{\text{tr}} & \underline{\tilde{F}}(0) & \underline{\tilde{F}}(1) & & & \\ \underline{0} & \underline{\tilde{F}}(1)^{\text{tr}} & \underline{0} & \ddots & & \\ \vdots & & & & & \\ \underline{0} & & & & \underline{0} & \\ \vdots & & & & & \ddots \end{bmatrix} \tag{19}$$

and $\underline{S}'$ has a similar expression. Substituting these expressions for $\underline{H}'$ and $\underline{S}'$ into (19) we obtain the following equations for the determination of the subvectors (having only m components) of $\underline{c}$:

$$\begin{aligned} -\underline{c}_{-1} &= \underline{M}_{-1,-1}\underline{c}_{-1} + \underline{M}_{-1,0}\underline{c}_0 + \underline{M}_{1,1}\underline{c}_1 , \\ -\underline{c}_0 &= \underline{M}_{0,-1}\underline{c}_{-1} + \underline{M}_{0,0}\underline{c}_0 + \underline{M}_{0,1}\underline{c}_1 , \\ -\underline{c}_1 &= \underline{M}_{1,-1}\underline{c}_{-1} + \underline{M}_{1,0}\underline{c}_0 + \underline{M}_{1,1}\underline{c}_1 , \\ -\underline{c}_i &= \underline{M}_{i,-1}\underline{c}_{-1} + \underline{M}_{i,0}\underline{c}_0 + \underline{M}_{i,1}\underline{c}_1 \quad (i = 2, 3, \ldots) . \end{aligned} \tag{20}$$

By performing the matrix multiplications in (18) it is easy to show that the matrices $\underline{M}_{q,-1}$, $\underline{M}_{q,0}$ and $\underline{M}_{q,1}$ ($q = -1, 0, 1$) are defined as

$$\underline{M}_{q,-1} = \underline{Z}_{q,0}[-\underline{F}(1) + \lambda \underline{S}(1)]^{\text{tr}} , \tag{21a}$$

$$\underline{M}_{q,0} = \underline{Z}_{q,-1}[-\underline{F}(1) + \lambda \underline{S}(1)] + \underline{Z}_{q,0}[\underline{\tilde{F}}(0) - \lambda \underline{\tilde{S}}(0)] + \underline{Z}_{q,1}[\underline{\tilde{F}}(1) - \lambda \underline{\tilde{S}}(1)]^{\text{tr}} , \tag{21b}$$

$$\underline{M}_{q,1} = \underline{Z}_{q,0}[\underline{\tilde{F}}(1) - \lambda \underline{\tilde{S}}(1)] \quad (q = -1, 0, 1) . \tag{21c}$$

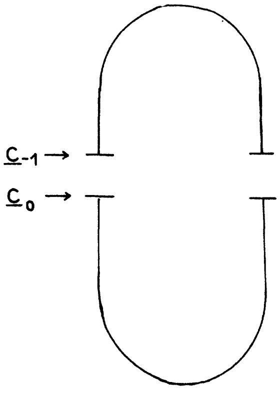

FIG. 2. The position of the "−1" cell.

In the system of Eqs. (20) one has to take into account that the part of the LCAO wave function, which has coefficients given by the subvector $\underline{c}_{-1}$, does not correspond to any physical reality because in a semifinite chain the electron belonging to the surface states of the end cannot get to the other end of the chain (which is in infinity) or to the space outside the chain (we are discussing here always-bound electrons). [We can visualize this situation also with a finite loop which has been intersected in two points (see Fig. 2).] To rule out the occurrence of these unphysical parts of the wave functions and also the occurrence of the unphysical solutions (spurious states) of the system of Eqs. (20), one has to leave out the first equation and take into account only the second and third terms in the subsequent equations.[16] In this way we can rewrite our Eqs. (20) as

$$\begin{aligned}
-\underline{c}_0 &= \underline{M}_{0,0}\underline{c}_0 + \underline{M}_{0,1}\underline{c}_1 ,\\
-\underline{c}_1 &= \underline{M}_{1,0}\underline{c}_0 + \underline{M}_{1,1}\underline{c}_1 ,\\
-\underline{c}_i &= \underline{M}_{i,0}\underline{c}_0 + \underline{M}_{i,1}\underline{c}_1 \quad (i=2,3,\ldots) .
\end{aligned} \tag{22}$$

The definition of the matrices $\underline{M}_{0,0}$, $\underline{M}_{0,1}$, etc., remains however, also in this case the same [see Eqs. (21)]. If we want to solve Eqs. (22) only for $\underline{c}_0$ and $\underline{c}_1$ we obtain the following matrix equation:

$$\underline{M}(\lambda)\begin{pmatrix}\underline{c}_0\\ \underline{c}_1\end{pmatrix} = \begin{pmatrix}\underline{M}_{0,0}+\underline{1} & \underline{M}_{0,1}\\ \underline{M}_{1,0} & \underline{M}_{1,1}+\underline{1}\end{pmatrix}\begin{pmatrix}\underline{c}_0\\ \underline{c}_1\end{pmatrix} = \underline{0} . \tag{23}$$

SURFACE STATES OF A THREE-DIMENSIONAL CRYSTAL

Let us remember that the half-infinite chain treated in the previous section can be periodically repeated in the other two dimensions an infinite number of times ($N_2 \to \infty$, $N_3 \to \infty$; see Fig. 1.) If we introduce periodic boundary conditions in these two other dimensions, all the matrices $\underline{M}_{q,0}$ and $\underline{M}_{q,1}$ ($q=0,1,2,3,\ldots$) occurring in Eqs. (22) will become cyclic hypermatrices. This can be easily proved if we take into account that $\underline{F}(1)$, $\underline{S}(1)$, $\underline{\tilde{F}}(0)$, $\underline{\tilde{S}}(0)$, $\underline{\tilde{F}}(1)$, $\underline{\tilde{S}}(1)$, and $\underline{Z}_{p_1,s}$ ($p_1=0,1,\ldots$; $s=-1,0,1$) occurring in Eqs. (21b) and (21c) are cyclic hypermatrices, and the product of cyclic hypermatrices is also a cyclic hypermatrix. If we have periodic (simple translation or a combined symmetry consisting of a simple translation and another symmetry operation, e.g., rotation) symmetry in directions 2 and 3, we can immediately see that the first six of the mentioned matrices are cyclic hypermatrices. The matrices $\underline{Z}_{p,s}$ are defined as

$$\underline{Z}_{p_1,s} = \frac{1}{\omega_1}\int_{\omega_1} \frac{\exp[ia_1(p_1-s)k_1]}{\underline{F}_0(k_1)-\lambda\underline{S}_0(k_1)}\,dk_1$$

$$(p_1=0,1,2,\ldots;\, s=-1,0,1) \tag{24}$$

[see Eq. (3.13) of I], where $\underline{F}_0(k_1)$ and $\underline{S}_0(k_1)$ are again cyclic hypermatrices due to the periodicity in dimensions 2 and 3. The inverse of a cyclic matrix is also a cyclic matrix, but the inverse of a cyclic hypermatrix is not necessarily a cyclic hypermatrix. One can show, however, by inspecting the elements of the matrices $\underline{Z}_p$, [see Eq. (3.23) of I, which was derived by fully diagonalizing the matrices $\underline{H}_0(k_1)$ and $\underline{S}_0(k_1)$],

$$\begin{aligned}
\{[\underline{Z}(q_2,q_3)]_{p_1,s}\}_{f,g} = \sum_{i,l,q,r=1}^{m} & v_{i,f}(p_1,q_2,q_3)v^{*}_{i,q}(p_1,q_2,q_3)\\
&\times [s(p_1,q_2,q_3)_i]^{-1/2} v_{l,r}(p_1,q_2,q_3)v^{*}_{l,g}(p_1,q_2,q_3)[s(p_1,q_2,q_3)_l]^{-1/2}\\
&\times \frac{1}{\omega_1}\int_{\omega_1} dk_1 \exp[ik_1a_1(p_1-s)] \sum_{j=1}^{n^*} b^{*}_{j,q}(k_1,k_2,k_3)b_{j,r}(k_1,k_2,k_3)\\
&\times [\epsilon(k_1,k_2,k_3)_j - \lambda(k_2,k_3)]^{-1} \quad (f,g=1,\ldots,m),
\end{aligned} \tag{25}$$

that if we build up from those [the definitions of the different quantities occurring in (25) were given in I, so we do not repeat them here] the matrices $\underline{Z}(q_2,q_3)_{p_1,s}$, and from these blocks the matrices $\underline{Z}_{p_1,s}$, they are cyclic hypermatrices.

Performing the matrix multiplications in (23) and knowing that all the four matrices $\underline{M}_{0,0}$, $\underline{M}_{0,1}$, $\underline{M}_{1,0}$, and $\underline{M}_{1,1}$ are cyclic hypermatrices, we can write

$$\underline{U}_{2,3}^{\dagger}(\underline{M}_{0,0}+\underline{1})\underline{U}_{2,3}\underline{U}_{2,3}^{\dagger}\underline{c}_0+\underline{U}_{2,3}^{\dagger}\underline{M}_{0,1}\underline{U}_{2,3}\underline{U}_{2,3}^{\dagger}\underline{c}_1=\underline{0}, \tag{26a}$$

$$\underline{U}_{2,3}^{\dagger}\underline{M}_{1,0}\underline{U}_{2,3}\underline{U}_{2,3}^{\dagger}\underline{c}_0+\underline{U}_{2,3}^{\dagger}(\underline{M}_{1,1}+\underline{1})\underline{U}_{2,3}\underline{U}_{2,3}^{\dagger}\underline{c}_1=\underline{0}, \tag{26b}$$

where the unitary matrix $\underline{U}_{2,3}$ which block diagonalizes the matrices $\underline{M}_{q,0}$ and $\underline{M}_{q,1}$ ($q=0, 1$) is defined through its blocks as (if we assume $N_1=N_2=N_3=N$)[13]

$$(\underline{U}_{2,3})_{p_2,p_3;q_2,q_3} =(2N+1)^{-1}\exp[i2\pi(p_2q_2+p_3q_3)(2N+1)^{-1}]\underline{1}. \tag{27}$$

Introducing the notations

$$\underline{M}_{q,s}^{\mathrm{BD}}=\underline{U}_{2,3}^{\dagger}\underline{M}_{q,s}\underline{U}_{2,3}, \quad \underline{\tilde{D}}_q=\underline{U}_{2,3}^{\dagger}\underline{c}_q \quad (q, s=0, 1), \tag{28}$$

we can rewrite Eqs. (26) as

$$(\underline{M}_{0,0}^{\mathrm{BD}}+\underline{1})\underline{\tilde{D}}_0+\underline{M}_{0,1}^{\mathrm{BD}}\underline{\tilde{D}}_1=\underline{0}, \tag{29a}$$

$$\underline{M}_{1,0}^{\mathrm{BD}}\underline{\tilde{D}}_0+(\underline{M}_{1,1}^{\mathrm{BD}}+\underline{1})\underline{\tilde{D}}_1=\underline{0}. \tag{29b}$$

Taking into account the definitions (21) of the $\underline{M}_{q,0}$ and $\underline{M}_{q,1}$ ($q=0, 1$) matrices we can write for instance $\underline{M}_{1,1}^{\mathrm{BD}}$ as

$$\begin{aligned}\underline{M}_{1,1}^{\mathrm{BD}}&=\underline{U}_{2,3}^{\dagger}\underline{M}_{1,1}\underline{U}_{2,3}\\&=\underline{U}_{2,3}^{\dagger}\underline{Z}_{1,0}\underline{U}_{2,3}\underline{U}_{2,3}^{\dagger}[\underline{\tilde{F}}(1)-\lambda\underline{\tilde{S}}(1)]\underline{U}_{2,3}\\&=\underline{Z}_{1,0}^{\mathrm{BD}}[\underline{\tilde{F}}(1)^{\mathrm{BD}}-\lambda\underline{\tilde{S}}(1)^{\mathrm{BD}}].\end{aligned} \tag{30}$$

Since the product of block diagonal matrices is again a block diagonal matrix, the matrix equations (29) can be reduced to such matrix equations which have only the order of the number of orbitals in the unit cell (m).[13] If we assume further that $N_2=N_3\to\infty$ and introduce the continuous variables

$$k_2=2\pi q_2/(2N+1)a_2, \quad k_3=2\pi q_3/(2N+1)a_3, \tag{31}$$

we can write

$$[\underline{M}_{0,0}(k_2,k_3)+\underline{1}]\underline{\tilde{d}}_0(k_2,k_3) +\underline{M}_{0,1}(k_2,k_3)\underline{\tilde{d}}_1(k_2,k_3)=\underline{0}, \tag{32a}$$

$$\underline{M}_{1,0}(k_2,k_3)\underline{\tilde{d}}_0(k_2,k_3) +[\underline{M}_{1,1}(k_2,k_3)+\underline{1}]\underline{\tilde{d}}_1(k_2,k_3)=\underline{0}. \tag{32b}$$

With the notation $\vec{k}'=k_2\vec{i}+k_3\vec{j}$, we can write Eqs. (32) in the form of the hypermatrix equation

$$\underline{M}(\lambda(\vec{k}'),\vec{k}')\underline{\vec{d}}(\vec{k}') =\begin{pmatrix}\underline{M}_{0,0}(\vec{k}')+\underline{1} & \underline{M}_{0,1}(\vec{k}')\\ \underline{M}_{1,0}(\vec{k}') & \underline{M}_{1,1}(\vec{k}')+\underline{1}\end{pmatrix}\begin{pmatrix}\underline{\vec{d}}_0(\vec{k}')\\ \underline{\vec{d}}_1(\vec{k}')\end{pmatrix}=\underline{0}. \tag{33}$$

From the criterion of the existence of the nonvanishing solution for the vectors $\underline{\vec{d}}(\vec{k}')$ one obtains the equation

$$\det[\underline{M}(\lambda(\vec{k}'),\vec{k}')]=0 \tag{34}$$

for the determination of the $2m$ surface energy bands $\lambda_i(\vec{k}')$.

To form the matrix $\underline{M}(\vec{k}')$ one has to write down the individual matrices $\underline{M}_{0,0}(\vec{k}')$, $\underline{M}_{0,1}(\vec{k}')$, $\underline{M}_{1,0}(\vec{k}')$, and $\underline{M}_{1,1}(\vec{k}')$, respectively. The last of these, $\underline{M}_{1,1}(\vec{k}')$, is if we write it out in more detail,

$$\underline{M}_{1,1}(\vec{k}')=\underline{Z}_{1,0}(\vec{k}')[\underline{\tilde{F}}(1,\vec{k}')-\lambda(\vec{k}')\underline{\tilde{S}}(1,\vec{k}')], \tag{35}$$

where, as one can show,[13,17]

$$\underline{Z}_{1,0}(\vec{k}')=\sum_{q_2q_3=-\infty}^{\infty}\exp[i(k_2q_2a_2+k_3q_3a_3)]\underline{Z}_{1,0}(q_2,q_3) \tag{36}$$

with [see Eq. (24) in the case of $p_1=1, s=0$]

$$\underline{Z}_{1,0}(q_2,q_3) =\frac{1}{\omega_1}\int_{\omega_1}\frac{\exp[ia_1(1-0)k_1]}{\underline{F}_0(k_1,q_2,q_3)-\lambda(\vec{k}')\underline{S}_0(k_1,q_2,q_3)}dk_1. \tag{37}$$

[An alternative way to define $\underline{Z}_{1,0}(q_2,q_3)$ is to construct it from its elements (25), substituting in them again $p_1=1$ and $s=0$]. Further $\underline{F}_0(k_1,q_2,q_3)$ and $\underline{S}_0(k_1,q_2,q_3)$ were defined by Eq. (2),

$$\underline{\tilde{F}}(1,\vec{k}')=\sum_{q_2,q_3=-\infty}^{\infty}\exp[i(k_2q_2a_2+k_3q_3a_3)] \times[\underline{F}_0(1,q_2,q_3)-\underline{F}(1,q_2,q_3)] \tag{38}$$

and analogous expressions are valid for $\underline{\tilde{F}}(0,\vec{k}')$, $\underline{\tilde{S}}(1,\vec{k}')$, and $\underline{\tilde{S}}(0,\vec{k}')$, respectively.

SELF-CONSISTENT-FIELD PROCEDURE FOR THE CALCULATION OF SURFACE STATES

To be able to calculate the surface states in a SCF way we need the definitions of the elements of the matrices $\underline{F}(q_1,q_2,q_3)=\underline{F}(\vec{q})$, $\underline{F}_0(0,q_2,q_3)$, and $\underline{F}_0(1,q_2,q_3)$, respectively. The elements of the matrix $\underline{F}(\vec{q})$ belonging to the periodic problem are[13,17] (see also I)

$$\begin{aligned}[\underline{F}(\vec{q})]_{f,g}&=\langle\chi_f^{\vec{0}}|-\frac{1}{2}\Delta-\sum_{q_1}\sum_{\alpha}^{M_0}\frac{{}^0Z_\alpha}{|\vec{r}-\vec{r}_{\alpha_1}^{\vec{q}_1}|}|\chi_g^{\vec{q}}\rangle\\&\quad+\sum_{\vec{q}_1,\vec{q}_2}\sum_{u,v=1}^{m}p(\vec{q}_1-\vec{q}_2)_{u,v}\\&\quad\times(\langle\chi_f^{\vec{0}}\chi_u^{\vec{q}_1}|\chi_g^{\vec{q}}\chi_v^{\vec{q}_2}\rangle\\&\quad-\frac{1}{2}\langle\chi_f^{\vec{0}}\chi_u^{\vec{q}_1}|\chi_v^{\vec{q}_2}\chi_g^{\vec{q}}\rangle),\end{aligned} \tag{39}$$

where the elements of the generalized-charge-bond-order matrix are defined as (Refs. 9 and 10 and I)

$$p(\vec{q}_1-\vec{q}_2)_{u,v}=\frac{1}{\omega}\int_{\omega}\exp[i\vec{k}(R_{\vec{q}_1}-R_{\vec{q}_2})]\times d^*(\vec{k})_{j,u}\,d(\vec{k})_{j,v}\,d\vec{k} \tag{40}$$

(ω is the volume of the first Brillouin zone in the $\vec{k}$ space). In the case of the first-neighbor interactions approximation used here in the formulation of the problem, we have to substitute for $\vec{q}$ either $(0,q_2,q_3)$ or $(1,q_2,q_3)$.

The elements of the additional matrix $F_0(0,q_2,q_3)$ are given by

$$[\underline{F}_0(0,q_2,q_3)]_{f,g}=\langle\tilde{\chi}_f^{\vec{0}}|-\frac{1}{2}\Delta-\sum_{\alpha=1}^{M}\sum_{q_5,q_6}\frac{Z_\alpha}{|\vec{r}-\vec{r}_\alpha^{\,(0,q_5,q_6)}|}-\sum_{\alpha=1}^{M_0}\sum_{q_5,q_6}\frac{{}^0Z_\alpha}{|\vec{r}-\vec{r}_\alpha^{\,(1,q_5,q_6)}|}|\tilde{\chi}_g^{(0,q_2,q_3)}\rangle$$
$$+\sum_{q_4,q_7=0}^{1}\;\sum_{q_5,q_6,q_8,q_9=-\infty}^{\infty}\;\sum_{u,v=1}^{\tilde{m}}\tilde{p}(q_4,q_5,q_6;q_7,q_8,q_9)_{u,v}$$
$$\times(\langle\tilde{\chi}_f^{\vec{0}}\bar{\chi}_u^{(q_4,q_5,q_6)}|\tilde{\chi}_g^{(0,q_2,q_3)}\bar{\chi}_v^{(q_7,q_8,q_9)}\rangle-\frac{1}{2}\langle\;\rangle_{\text{exch}}), \tag{41}$$

where $\tilde{\chi}_f^{\vec{0}}=\tilde{\chi}_f^{(0,q_2,q_3)}$ is the fth atomic orbital in the surface cell characterized by q_2, q_3,

$$\bar{\chi}_u^{(q_5,q_5,q_6)}=\begin{cases}\tilde{\chi}_u^{(q_4,q_5,q_6)} & \text{if } q_4=0\\ \chi_u^{(q_4,q_5,q_6)} & \text{if } q_4=1,\end{cases} \tag{42}$$

${}^0\underline{Z}_\alpha$ and M_0 is the nuclear charge of the αth nucleus and the number of nuclei, respectively, in the bulk cell, while Z_α and M are the same in the surface cell (which may be constituted from a pure surface cell and a chemisorbed molecule). Correspondingly, as mentioned before, $\tilde{m}=m+m_{\text{chem}}$, where m_{chem} is the number of orbitals in the chemisorbed molecule. Finally,

$$\tilde{p}(q_4,q_5,q_6;q_7,q_8,q_9)_{u,v}=\sum_{j=1}^{\tilde{n}^*}\frac{1}{\omega_{2,3}}\int_{\omega_{2,3}}dk_2\,dk_3\,d^*_{j,q_4,u}(k_2,k_3)\,\tilde{d}_{j,q_7,v}(k_2,k_3)$$
$$\times\exp\{i[k_2a_2(q_5-q_8)+k_3a_3(q_6-q_9)]\}\quad(q_4=0,\ q_7=0\text{ or }1), \tag{43}$$
$$\tilde{n}^*=\tfrac{1}{2}[n^*(q_4)+n^*(q_7)].$$

We can immediately obtain also the elements of the matrix $\underline{F}(1,q_2,q_3)$ if we substitute in (41) everywhere the orbital $\chi_g^{(1,q_2,q_3)}$ instead of $\tilde{\chi}_g^{(0,q_2,q_3)}$.

After having all the necessary expressions for the *ab initio* SCF LCAO treatment of the surface (and chemisorption states) of a three-dimensional crystal, one can proceed in the following way:

(i) One has to solve first the SCF problem of the three-dimensional periodic infinite crystal.

(ii) Next one has to obtain the $\lambda_i(\vec{k}')$ solutions of Eq. (34). Very probably this is numerically the most difficult step of the procedure. One promising way to do it is, as van der Avoird *et al.*[11] have suggested it, to solve the eigenvalue problem of the Hermitian matrix $\underline{M}^H$ [$\underline{M}(\lambda)$ is not Hermitian]:

$$\underline{M}^H(\lambda(\vec{k}'))\underline{d}_j(\lambda(\vec{k}'))=[\underline{H}'(\vec{k}')-\lambda(\vec{k}')\underline{S}'(\vec{k}')]\times\underline{M}(\lambda(\vec{k}'))\underline{d}_j(\lambda(\vec{k}'))=E_j(\lambda(\vec{k}'))\underline{d}_j(\lambda(\vec{k}')), \tag{44}$$

where

$$\underline{H}'(\vec{k}')=\begin{pmatrix}\underline{\tilde{F}}(0,k_2,k_3) & \underline{\tilde{F}}(1,k_2,k_3)\\ \underline{\tilde{F}}(1,k_2,k_3) & \underline{0}\end{pmatrix} \tag{45}$$

and $\underline{S}'(\vec{k}')$ has an analogous expression.[18] By substituting into (44) different trial values of $\lambda(\vec{k}')$, one can find out the zero eigenvalues $E_j(\lambda(\vec{k}'))=0$ of this equation. The values $\lambda(\vec{k}')$ which provide these zero eigenvalues will be the roots of the equation $\det[\underline{M}(\lambda(\vec{k}'))]=0$.

(iii) After having found the roots $\lambda_i(\vec{k}')$, one can substitute these back into Eq. (33) and solve that for the different vectors $\underline{\tilde{d}}_{i,0}(\vec{k}')$ and $\underline{d}_{i,1}(\vec{k}')$, respectively.

(iv) With the aid of the vectors $\underline{\tilde{d}}_{i,0}(\vec{k}')$ and $\underline{d}_{i,1}(\vec{k}')$, one can form again the matrices $\underline{F}_0(0,q_2,q_3)$ and $\underline{F}_0(1,q_2,q_3)$, and with the latter ones the matrix $\underline{M}(\lambda(\vec{k}'))$. In this way the whole procedure can be repeated until self-consistency is reached.

One can hope that after coding the described method one can obtain, in the near future, surface states for three-dimensional crystals in an *ab initio* SCF way. Comparing the results of these planned calculations with those of cluster calculations and of two-dimensional (layer orbital) calculations on simple metals (like Be crystal), one will be able on the one hand to decide better when these approximations are justified. On the other hand, the results of these calculations will give also better answers on the following questions:

(i) How many neighbors perpendicular to the surface have to be taken into account in different types of systems (metals, covalently bound crystals, etc.) to describe correctly the surface and chemisorption states; (ii) how much are the surface states localized or delocalized in these systems; and (iii) how much effect may the (usually experimentally not well-known) possible changes have in the geometry of the surface cells as compared to the bulk cells on the surface states. All these studies will serve of course the better understanding of the surface properties and in final analysis of the catalytic properties of different solids.

ACKNOWLEDGMENT

The author would like to express his gratitude to Professor J. Koutecký for very interesting and useful discussions and for putting at his disposal the manuscript of his recent review article[12] before its publication.

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[15] If the geometry of the end cell remains unchanged and there is no chemisorption, $\underline{S}_0(0) = \underline{S}(0)$, $\underline{S}_0(1) = \underline{S}(1)$, and therefore $\underline{\tilde{S}}(0) = \underline{\tilde{S}}(1) = \underline{0}$.

[16] Instead of this intuitive argument one can also give a more rigorous derivation of this procedure with the aid of projection-operator technique (see also Ref. 12).

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[18] One can show on the basis of the definition of $\underline{M}(\lambda(\vec{k}'))$ [see Eqs. (21b), (21c), (33), and (35)–(38)] that $\underline{M}^H(\lambda(\vec{k}')) = (\underline{H}' - \lambda \underline{S}')\underline{M}$ is Hermitian.