

## Resolvent method for quantitative calculations on surface states and adsorption: General method

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A new method is presented for the calculation of surface and adsorption effects on one-electron states in crystals. Conceptually, this method is similar to the Koster-Slater resolvent method for impurity states, which has often been applied to surface states in semi-infinite crystals. The elaboration is very different, however. The proposed scheme works for finite crystals, the resolvent matrix is calculated numerically instead of analytically, and the applicability of the method depends on a suitable algorithm for the numerical solution of the Koster-Slater equations. Such an algorithm is described. In comparison with the resolvent method for semi-infinite crystals, this method permits a more quantitative treatment of real crystals, such as transition metals or semiconductors. On the other hand, compared with standard molecular-orbital methods on finite clusters, it can handle much larger crystals.

### I. INTRODUCTION

Although many important processes occur on the surfaces of solids, as for instance chemisorption and heterogeneous catalysis on transition metals or semiconductors, the understanding of these processes is far from being complete. Experimentally, more and more data are becoming available for adsorption on well-defined surfaces,<sup>1-11</sup> but the interpretation of these data is very difficult. From this situation arises a considerable need for theoretical calculations on surfaces and adsorption and, in particular, for improvement of the methods to yield more quantitative information on real crystals.

The majority of the quantum-theoretical methods for the study of surface and adsorption states on crystals are based on the linear combination of atomic orbitals (LCAO) or tight-binding<sup>12</sup> formalism. They can be divided into two types: the "solid-state" approach and the "molecular" approach. The first group starts from solid-state band calculations on infinite periodic crystals (satisfying Born-Von Kármán cyclic boundary conditions with an infinite number of unit cells). These infinite crystals are then reduced to semi-infinite crystals with a surface, and the influence of the perturbation which effects this surface formation is mostly taken into account by a resolvent or Green's-function technique. A description of these methods can be found in several review articles.<sup>13,14</sup> The resolvent method applied to this problem is based on Koster-Slater treatment of impurity states in crystals.<sup>15</sup> This type of approach requires the use of an analytical resolvent, to be constructed from the infinite-crystal solutions. For this reason one has to introduce various approximations such as neglect of nonorthogonality of the basis orbitals and of many interactions between them. In practice, one often falls back on the use of a model Hamilto-

nian depending only on a few parameters,<sup>16-23</sup> or one calculates model crystals with one orbital per atom,<sup>24-26</sup> or even one-dimensional chains.<sup>13,27</sup> The same type of model crystals have also been studied by different methods, without using the resolvent technique.<sup>28-33</sup> It is doubtful whether such models will yield a valuable description of real crystals such as transition metals, which have rather localized *d* electrons on the one hand, and diffuse conduction electrons on the other. Moreover, these methods only calculate "pure" surface or adsorption states with wave functions localized at the surface and energies lying outside the crystal bands. Most states, however, remain within the crystal bands and are not completely localized, but are still affected by surface formation or by adsorption. As Koutecký<sup>13</sup> points out, these states must be included when calculating total surface energies or adsorption energies: although they shift only by infinitely small amounts, we have an infinite number of them (in the semi-infinite crystal model).

The second class of methods is of the molecular type. Assuming that the effects of the surface or adsorption are localized, which is probably true in many cases and has been confirmed both by theory<sup>34-36</sup> and experiment,<sup>3,4,7,10</sup> one applies molecular-orbital methods to a cluster of crystal atoms, possibly interacting with one or more adsorbed atoms.<sup>37-43</sup> Although this approach takes into account all interactions within a (semiempirical) molecular-orbital (MO) formalism, it suffers from the drawback that the clusters must remain rather small (up to about 15 transition-metal atoms or 30 first- or second-row atoms). This gives rise to undesirable boundary effects. One can try to compensate for such effects, for instance, by saturating the "dangling" bonds with hydrogen atoms or by connecting them to other dangling bonds,<sup>39</sup> but it

would be better to increase also the size of the clusters.

As we are especially interested in chemisorption and catalysis on transition-metal surfaces, in which both the  $d$  electrons and the conduction electrons play a role,<sup>40,44</sup> we have developed a method which does not require the simplifying parametrization of the "solid-state" methods and still calculates larger crystals than the "molecular" methods. It avoids unwanted boundary effects and, moreover, it calculates all one-electron states in crystals having a surface, possibly with adsorption, also those states which are not strictly localized at the surface. By application of the presented method one can obtain quantitative information about properties of solid surfaces and about adsorption phenomena. This might also be helpful for the interpretation and correlation of experimental data for adsorbed atoms and molecules.<sup>1-11</sup>

## II. DESCRIPTION OF THE METHOD

The proposed method works for finite crystals (in practice up to about 1000 atoms) with two surfaces parallel to a chosen crystal plane. This plane is defined by two elementary lattice translations,  $\vec{a}_1$  and  $\vec{a}_2$ , which can be the primitive translations of the bulk crystal or linear combinations of them.<sup>13</sup> The third elementary translation  $\vec{a}_3$ , which is nonparallel to the surface, carries from one crystal layer to another. The number of layers is finite; the dimensions of the crystal parallel to the surface could be infinite, but we find it advantageous to keep these dimensions finite as well, while still avoiding undesirable boundary effects by imposing Born-Von Kármán cyclic boundary conditions on the finite number of unit cells ( $\vec{a}_1, \vec{a}_2$ ). This implies that we assume the crystal wave functions to satisfy the relations

$$\psi(\vec{r}) \equiv \psi(\vec{r} - N_1 \vec{a}_1) \equiv \psi(\vec{r} - N_2 \vec{a}_2), \quad (1)$$

$N_1$  and  $N_2$  being the number of unit cells in the directions  $\vec{a}_1$  and  $\vec{a}_2$ , respectively. Working in an LCAO model, we denote the basis atomic orbitals as

$$|\chi_p(m_1, m_2, m_3)\rangle = \chi_p(\vec{r} - m_1 \vec{a}_1 - m_2 \vec{a}_2 - m_3 \vec{a}_3), \quad (2)$$

where the index  $p=1, \dots, \nu$  labels the different atomic orbitals in one unit cell with the origin ( $m_1 \vec{a}_1 + m_2 \vec{a}_2 + m_3 \vec{a}_3$ ). Now, because of the periodic boundary conditions the crystal wave function can be expressed as

$$|\psi^{k_1, k_2}\rangle = \sum_{m_3} \sum_{p=1}^{\nu} |a_p^{k_1, k_2}(m_3)\rangle c_{p, m_3}^{k_1, k_2}, \quad (3)$$

with

$$|a_p^{k_1, k_2}(m_3)\rangle = \sum_{m_1=1}^{N_1} \sum_{m_2=1}^{N_2} |\chi_p(m_1, m_2, m_3)\rangle e^{i(k_1 m_1 + k_2 m_2)}.$$

The summation over  $m_3$  runs over all layers of the crystal. The two-dimensional Bloch orbitals  $|a_p^{k_1, k_2}(m_3)\rangle$  are called "layer orbitals"; the components of the wave vector,  $k_1$  and  $k_2$ , must satisfy

$$k_1 = 2\pi n_1 / N_1, \quad k_2 = 2\pi n_2 / N_2$$

with

$$n_1 = 1, 2, \dots, N_1, \quad n_2 = 1, 2, \dots, N_2.$$

Expression (3) is equivalent to the statement that layer orbitals with different  $(k_1, k_2)$  are noninteracting, which is so because they belong to different irreducible representations of the finite cyclic group that is the translation group of this crystal. So we see that the periodic boundary conditions, besides eliminating end effects, result in a considerable simplification of the wave equations, also for finite crystals. Actually, this assumption of finite, but cyclic, crystals is nonphysical, which is probably not very serious, however, as it corresponds exactly to collecting a finite selection from the infinite crystal solutions—namely, those Bloch waves of which the wavelength is a divisor of the total crystal dimensions.

The method for calculating the one-electron states of this crystal now proceeds as follows. We start with a crystal of  $N_3$  layers, which is also periodic in the third ( $\vec{a}_3$ ) direction. This completely periodic crystal is called the "unperturbed" system. The extra periodicity facilitates the solution of the secular equations for this system if we use three-dimensional Bloch orbitals as a basis:

$$|b_p^{k_1, k_2, k_3}\rangle = \sum_{m_3=1}^{N_3} |a_p^{k_1, k_2}(m_3)\rangle e^{i k_3 m_3}, \quad (4)$$

with

$$k_3 = 2\pi n_3 / N_3, \quad n_3 = 1, 2, \dots, N_3.$$

We then define a perturbation  $V = V^S + V^T$  which has the following effects:

(i)  $V^S$  removes so many layers from the periodic crystal that the two surface layers on both sides of the crystal interact only with inside layers. Thus we have created two "Shockley" surfaces,<sup>45</sup> just as the removal of a segment from a circle creates two "ends."

(ii)  $V^T$  adds the effect of a surface potential to the atoms near the surface. If this effect is non-zero, we shall speak of "Tamm" surfaces.<sup>46</sup>

This perturbation effects complete layers so that the periodicity parallel to the surface is conserved. The influence of the perturbation is taken into account in an exact way by the resolvent or Green's-function method, the resolvent being constructed from the "unperturbed" periodic crystal solutions. The combination of this method with the LCAO model was first used by Lifshitz<sup>47</sup> and by Baldock<sup>30</sup>

and formulated more generally by Koster and Slater.<sup>15</sup> In our case, we obtain a set of simultaneous equations containing the resolvent matrix and the perturbation matrix over layer orbitals, which we shall call the "Koster-Slater equations." These equations can be regarded as the matrix representation of a homogeneous integral equation.<sup>48</sup> The Koster-Slater treatment of the LCAO problem, which in fact is a way to deal with the effect of "local" changes in the secular matrix, also shows some resemblance to a matrix-partitioning technique by Löwdin.<sup>49</sup>

In case of adsorption, we define an extra unperturbed problem which consists of a set of secular equations for noninteracting adsorbate layers. Adding the interactions between the crystal and the adsorbate layers and the interactions among different adsorbate layers to the perturbation, i. e.,  $V = V^S + V^T + V^A$ , we can also take adsorption effects into account by the resolvent method. As long as the adsorbed layers have the same two-dimensional periodicity as the crystal layers, all equations can be solved for each  $(k_1, k_2)$  separately.

Conceptually, this method is similar to the semi-infinite crystal treatments.<sup>13,14</sup> The practical elaboration is very different, however, for the following reasons:

(i) All matrix elements between atomic orbitals are calculated explicitly, within a given (possibly semiempirical) LCAO model. An arbitrary range can be specified, outside which the interactions are neglected. (We have used for this range, for instance, the fourth-nearest-neighbor distance for the fcc crystals nickel and copper.) We work with nonorthogonal basis functions because orthogonal orbitals, even of the localized type such as Löwdin<sup>50</sup> or Wannier<sup>51</sup> orbitals, always involve some amount of delocalization. This effect is usually neglected, but it can be quite large—for instance, in case of conduction electrons.

(ii) We do not require the unperturbed problem to be solved analytically. Instead, we use a numerical method (matrix diagonalization) to obtain these solutions from a set of secular equations.

(iii) The Koster-Slater equations which are constructed from a numerical resolvent matrix (and perturbation matrix) must be solved numerically as well. The dimension of these equations is determined by the number of layers which are directly affected by the surface or by adsorption; so it is smaller than the dimension of the secular problem over all layer orbitals. Since the Koster-Slater equations are nonlinear in the energy, however, the applicability of the method depends on a suitable algorithm for their numerical solution. We have found one in the procedure developed by Williams<sup>52</sup> for solving the Korringa-Kohn-Rostoker (KKR) equations<sup>53,54</sup> in solid-state band calcula-

tions. Although the physical background of these equations is quite different from the surface or adsorption problem, they have almost the same mathematical structure as the Koster-Slater equations occurring in our problem. In the next sections the latter equations will be derived for surfaces and for adsorption, in a manner which is generalized to nonorthogonal basis functions. We bring them into a standard form adapted to the algorithm just mentioned and we show the function of this algorithm. Because of the special character of our problem, where the perturbation has to annihilate interactions between different nonorthogonal orbitals, the perturbation matrix in the resolvent method depends on the (unknown) energy of the perturbed problem, and therefore Williams's algorithm had to be generalized.

### III. SURFACES

Since the periodicity of the crystal permits the solution of all equations for each two-dimensional wave vector  $(k_1, k_2)$  separately, we shall omit these indices in the notation for the layer orbitals

$$|a_p(m)\rangle = |a_p^{k_1, k_2}(m)\rangle,$$

and for the Bloch orbitals

$$|b_p^k\rangle = |b_p^{k_1, k_2, k}\rangle.$$

Except for the calculation of the matrix elements, the three-dimensional-crystal problem becomes identical to the calculation of a linear chain.

The "unperturbed" crystal is described in terms of layer orbitals by the following secular equations:

$$\sum_{m'=1}^{N_3} \sum_{p'=1}^{\nu} [\langle a_p(m) | H | a_{p'}(m') \rangle - E_i^{(0)} \langle a_p(m) | a_{p'}(m') \rangle] c_{p'i}^{(0)}(m') = 0, \\ m = 1, \dots, N_3, \quad p = 1, \dots, \nu. \quad (6)$$

The solutions  $E_i^{(0)}$  and  $c_{p'i}^{(0)}(m)$  are numbered by  $i = 1, \dots, N_3\nu$ . The explicit form of the one-electron Hamiltonian  $H$  depends on the type of LCAO method used. Taking advantage of the periodicity of the unperturbed crystal, one can solve, instead of this  $(N_3\nu)$ -dimensional secular problem, a set of  $N_3$  secular problems of dimension  $\nu$  over Bloch orbitals:

$$\sum_{p'=1}^{\nu} [\langle b_p^k | H | b_{p'}^k \rangle - E_j^{(0)}(k) \langle b_p^k | b_{p'}^k \rangle] c_{p'j}^{(0)}(k) = 0, \\ p = 1, \dots, \nu. \quad (7)$$

The solutions are now labelled by  $j = 1, \dots, \nu$  and  $k = 2\pi n_3 / N_3$ , with  $n_3 = 1, \dots, N_3$ . The solutions of Eq. (6) can then be expressed as

$$E_i^{(0)} = E_j^{(0)}(k), \\ c_{p'i}^{(0)}(m) = e^{i km} c_{p'j}^{(0)}(k), \quad (8)$$

where  $i, j$ , and  $k$  run as indicated above. The eigenvectors are orthogonal and are assumed to be normalized:

$$\sum_{p=1}^{\nu} \sum_{p'=1}^{\nu} c_{pj}^{(0)}(k) \langle b_p^k | b_{p'}^{k'} \rangle c_{p'j'}^{(0)}(k') = \delta_{kk'} \delta_{jj'}, \quad (9)$$

$$\sum_{m=1}^{N_3} \sum_{p=1}^{\nu} \sum_{m'=1}^{N_3} \sum_{p'=1}^{\nu} c_{pi}^{(0)}(m) \langle a_p(m) | a_{p'}(m') \rangle c_{p'i'}^{(0)}(m') = \delta_{ii'}. \quad (10)$$

From now on, we shall work only in terms of layer orbitals and introduce a compact matrix notation (matrices are denoted by capitals, column vectors by small letters). The indices run both over layers ( $m=1, \dots, N_3$ ) and over atomic orbitals ( $p=1, \dots, \nu$ ). The unperturbed equations (6) read

$$(\underline{H}^{(0)} - E_i^{(0)} \underline{S}^{(0)}) \underline{c}_i^{(0)} = \underline{0}, \quad (10)$$

with  $E_i^{(0)}$  and  $\underline{c}_i^{(0)}$  given by (8).

For the real system of interest, i.e., a crystal with two surfaces, the energy  $E$  and the wave function  $\underline{c}$  (in terms of layer orbitals) are to be determined from the equation

$$(\underline{H} - E \underline{S}) \underline{c} = \underline{0}. \quad (11)$$

The matrices  $\underline{H}$  and  $\underline{S}$  are changed with respect to  $\underline{H}^{(0)}$  and  $\underline{S}^{(0)}$  only in a few parts. In order to express these changes in mathematical form, it is convenient to distinguish some subsystems in the original crystal of  $N_3$  layers (see Fig. 1).

The subsystem  $\mathcal{R}$  contains the layers which are removed from the periodic crystal by the Shockley perturbation  $V^S$  in order to create a crystal with two surfaces. The remaining crystal is denoted by  $\mathcal{C}$ . In this crystal a set of outer layers  $\mathcal{O}$  is directly affected by this removal (because they were interacting with  $\mathcal{R}$ ) and/or by the Tamm perturbation  $V^T$ . Projection matrices for these systems ( $\underline{P}^R, \underline{P}^C, \underline{P}^O, \underline{P}^{C-O}$ ) are defined as follows<sup>55</sup>: Let  $\underline{P}^m$  be a  $(N_3\nu) \times (N_3\nu)$  dimensional matrix with a  $\nu \times \nu$  unit matrix on the diagonal for layer  $m$  and zero otherwise. Then, for a given subsystem  $\mathfrak{X}$

$$\underline{P}^X = \sum_{m \in \mathfrak{X}} \underline{P}^m. \quad (12)$$

These projection matrices are idempotent, mutually exclusive, and form the following resolution of the  $(N_3\nu) \times (N_3\nu)$  identity matrix:

$$\underline{I} = \underline{P}^R + \underline{P}^C = \underline{P}^R + \underline{P}^O + \underline{P}^{C-O}. \quad (13)$$

The changes in  $\underline{H}$  and  $\underline{S}$  can now be written as

$$\begin{aligned} \text{by } V^S: \quad \underline{\Delta H}^S &= -\underline{P}^R \underline{H}^{(0)} \underline{P}^O - \underline{P}^O \underline{H}^{(0)} \underline{P}^R, \\ \underline{\Delta S}^S &= -\underline{P}^R \underline{S}^{(0)} \underline{P}^O - \underline{P}^O \underline{S}^{(0)} \underline{P}^R; \\ \text{by } V^T: \quad \underline{\Delta H}^T &= \underline{P}^O \underline{T} \underline{P}^O, \\ \underline{\Delta S}^T &= \underline{0}. \end{aligned} \quad (14)$$

The matrix  $\underline{T}$  describes the effects of the surface

potential  $V^T$  which are localized in the outer layers  $\mathcal{O}$ . If the structure of these outer layers would be changed with respect to the bulk structure, the overlap matrix  $\underline{\Delta S}^T$  would be nonzero as well. The fact that  $\underline{H}$  and  $\underline{S}$  are only locally modified (see Fig. 2) is now expressed by means of projection matrices. Because of this fact, it is advantageous, instead of solving the new secular problem (11), to use the resolvent technique.<sup>13,14</sup> Define the perturbation matrix

$$\begin{aligned} \underline{V}(E) &= \underline{V}^S(E) + \underline{V}^T, \\ &= \underline{\Delta H} - E \underline{\Delta S}, \\ &= -\underline{P}^R (\underline{H}^{(0)} - E \underline{S}^{(0)}) \underline{P}^O \\ &\quad - \underline{P}^O (\underline{H}^{(0)} - E \underline{S}^{(0)}) \underline{P}^R + \underline{P}^O \underline{T} \underline{P}^O, \end{aligned} \quad (15)$$

and the resolvent matrix

$$\underline{G}(E) = \sum_{i=1}^{N_3\nu} \underline{c}_i^{(0)} (E - E_i^{(0)})^{-1} \underline{c}_i^{(0)\dagger}, \quad (16)$$

with  $E_i^{(0)}$  and  $\underline{c}_i^{(0)}$  being the solutions of the unperturbed problem (10). Both  $\underline{V}(E)$  and  $\underline{G}(E)$  depend on the energy  $E$  of the perturbed system, which must still be determined. Writing the perturbed equations (11) as

$$\underline{V}(E) \underline{c} = -(\underline{H}^{(0)} - E \underline{S}^{(0)}) \underline{c}, \quad (17)$$

multiplying this by  $\underline{G}(E)$ , and using the relation

$$-\underline{G}(E) (\underline{H}^{(0)} - E \underline{S}^{(0)}) = \underline{I}, \quad (18)$$

which is proved by substituting (16), (10), and the normalization condition (9), we obtain the Koster-Slater equations

$$\underline{G}(E) \underline{V}(E) \underline{c} = \underline{c}. \quad (19)$$

Although this Koster-Slater problem still has the same dimension as the secular problem (11), this

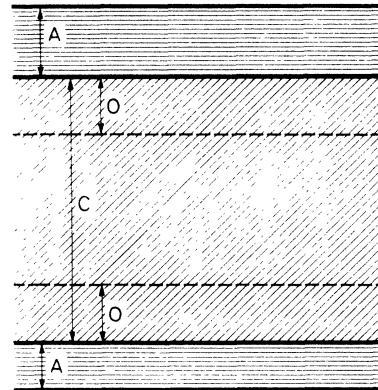


FIG. 1. Schematic drawing of the crystal with adsorbed layers. Layers  $\mathcal{R}$  are not shown because they are nonphysical; they were only added to make the unperturbed crystal periodic.

can be easily reduced if we introduce the following properties:

(i) After removal of the layers  $\mathcal{R}$ , some solutions of the perturbed equations are localized on  $\mathcal{R}$ , others on  $\mathcal{C}$ . We are interested in the latter, which satisfy the relations

$$\underline{P}^R \underline{c} = \underline{0}, \quad \underline{P}^C \underline{c} = \underline{c}. \quad (20)$$

(ii) The matrix  $\underline{V}(E)$  contains many blocks which are zero, as expressed by (15) and shown in Fig. 2.

Usually,<sup>13,14</sup> Eqs. (19) are projected by  $\underline{P}^O$  and then solved in the subspace  $\mathcal{O}$ . In view of our algorithm for numerical solution of these equations, which applies to Hermitian matrices, we multiply the equations (19) by  $\underline{P}^O \underline{V}(E)$ , substitute (15) and (20), and use the properties of the projection matrices (13), to obtain

$$\begin{aligned} \underline{P}^O \underline{W}(E) \underline{P}^O \underline{c} = & \{ \underline{P}^O [ \underline{V}^S(E) \underline{P}^R + \underline{V}^T \underline{P}^O ] \underline{G}(E) \\ & \times [ \underline{P}^O \underline{V}^T + \underline{P}^R \underline{V}^S(E) ] \underline{P}^O - \underline{P}^O \underline{V}^T \underline{P}^O \} \underline{c} = \underline{0}. \end{aligned} \quad (21)$$

The matrix  $\underline{P}^O \underline{W}(E) \underline{P}^O$  contains zeroes except for the submatrix corresponding to the outer crystal layers  $\mathcal{O}$ . Therefore we can reduce Eqs. (21) to a smaller set, only over the space  $\mathcal{O}$ .

$$\underline{W}^O(E) \underline{c} = \underline{0}, \quad (22)$$

where  $\underline{W}^O(E)$  is the (Hermitian) nonzero submatrix of  $\underline{P}^O \underline{W}(E) \underline{P}^O$  over the layers  $\mathcal{O}$ . The equations for the perturbed problem have now been simplified as much as possible and prepared into such a form that a slightly generalized version of Williams's algorithm can be applied to solve for the energies  $E$ . These can be substituted into (21) or (19) and the coefficients  $\underline{c}$  can be calculated by standard methods (solving a set of homogeneous linear equations).

#### IV. ADSORPTION

On the crystal of the previous section we adsorb  $N$  layers of atoms of a different type. These layers are assumed to have the same periodicity in the  $\vec{a}_1$  and  $\vec{a}_2$  directions as the crystal, so that we can construct layer orbitals

$$\begin{aligned} |a_q(n)\rangle &= |a_q^{k_1, k_2}(n)\rangle \\ &= \sum_{m_1=1}^{N_1} \sum_{m_2=1}^{N_2} | \chi_q(m_1, m_2, n) \rangle e^{i(k_1 m_1 + k_2 m_2)}, \end{aligned} \quad (23)$$

which obey the same periodic boundary conditions (1). Atomic orbitals are labelled by  $q=1, \dots, \mu$ ; adsorbed layers by  $n=1, \dots, N$ . The space spanned by the adsorbed-layer orbitals is denoted by  $\mathcal{A}$ ; the corresponding projection matrix by

$$\underline{P}^A = \sum_{n=1}^N \underline{P}^n. \quad (24)$$

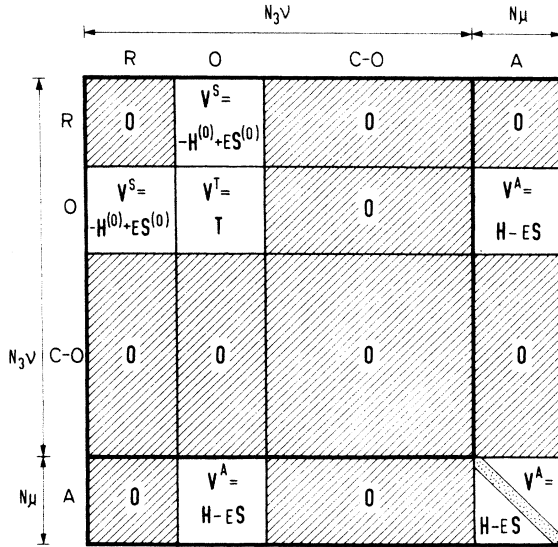


FIG. 2. Block structure of the perturbation matrix  $\underline{V}$ .

Using a matrix notation, we now imply the indices to run over  $N_3$  crystal layers with  $\nu$  layer orbitals each and over  $N$  adsorbed layers with  $\mu$  layer orbitals. Consequently, the resolution of the identity matrix becomes

$$\begin{aligned} \underline{I} &= \underline{P}^R + \underline{P}^C + \underline{P}^A, \\ &= \underline{P}^R + \underline{P}^O + \underline{P}^{C-O} + \sum_{n=1}^N \underline{P}^n. \end{aligned} \quad (25)$$

Adsorption effects can also be treated by the resolvent method. Unless  $N$  is very large, it is most convenient to define an unperturbed problem of isolated adsorbate layers,<sup>56</sup> in addition to the unperturbed crystal problem described by (6) and (7). For an adsorbate layer  $n$  we write

$$\begin{aligned} \sum_{q'=1}^{\mu} (\langle a_q(n) | H | a_{q'}(n) \rangle \\ - E_i^{(0)}(n) \langle a_q(n) | a_{q'}(n) \rangle) c_{q'}^{(0)}(n) = 0, \end{aligned} \quad (26)$$

where the solutions are numbered by  $l=1, \dots, \mu$ . For the total unperturbed system, the secular problem reads

$$\begin{aligned} (\underline{P}^R + \underline{P}^C) [ \underline{H}^{(0)} - E_i^{(0)} \underline{S}^{(0)} ] (\underline{P}^R + \underline{P}^C) \underline{c}_i^{(0)} \\ + \sum_{n=1}^N \underline{P}^n [ \underline{H}^{(0)} - E_i^{(0)}(n) \underline{S}^{(0)} ] \underline{P}^n \underline{c}_i^{(0)}(n) = \underline{0}. \end{aligned} \quad (27)$$

The perturbation  $V^A$  which adds the interactions between the crystal and the adsorbate layers and between adsorbate layers among each other, corresponds to the following matrix:

$$\begin{aligned} \underline{V}^A(E) &= \underline{\Delta H}^A - E \underline{\Delta S}^A, \\ &= \underline{P}^A (\underline{H} - E \underline{S}) \underline{P}^O + \underline{P}^O (\underline{H} - E \underline{S}) \underline{P}^A + \underline{P}^A (\underline{H} - E \underline{S}) \underline{P}^A \\ &\quad - \sum_{n=1}^N \underline{P}^n (\underline{H}^{(0)} - E \underline{S}^{(0)}) \underline{P}^n. \end{aligned} \quad (28)$$

We have assumed that the direct interactions with the adsorbed atoms are restricted to the outer crystal layers  $\emptyset$ . If necessary, the set  $\emptyset$  is extended with respect to the previous section. The resolvent matrix derived from the unperturbed problem (27) reads

$$\begin{aligned} \underline{G}(E) &= (\underline{P}^R + \underline{P}^C) \left( \sum_{i=1}^{N_{3v}} \underline{c}_i^{(0)} (E - E_i^{(0)})^{-1} \underline{c}_i^{(0)\dagger} \right) (\underline{P}^R + \underline{P}^C) + \sum_{n=1}^N \underline{P}^n \left( \sum_{i=1}^{\mu} \underline{c}_i^{(0)}(n) [E - E_i^{(0)}(n)]^{-1} \underline{c}_i^{(0)\dagger}(n) \right) \underline{P}^n, \\ &= \underline{G}(E)^{R+C} + \underline{G}(E)^A. \end{aligned} \quad (29)$$

This resolvent must be substituted into the Koster-Slater equations (19), together with the perturbation matrix

$$\underline{V}(E) = \underline{V}^S(E) + \underline{V}^T + \underline{V}^A(E) \quad (30)$$

given by (15) and (28). Again taking into account the zeroes in this perturbation matrix (see Fig. 2) and the fact that the solutions  $\underline{c}$  are now localized on  $\mathcal{C} + \mathcal{A}$ , we obtain, after multiplication by  $(\underline{P}^A + \underline{P}^O) \underline{V}(E)$ :

$$\begin{aligned} (\underline{P}^O + \underline{P}^A) \underline{W}(E) (\underline{P}^A + \underline{P}^O) \underline{c} &= \{ [\underline{P}^O \underline{V}^S(E) \underline{P}^R + \underline{P}^O \underline{V}^T \underline{P}^O + \underline{P}^A \underline{V}^A(E) \underline{P}^O ] \underline{G}(E)^{R+O} [ \underline{P}^O \underline{V}^A(E) \underline{P}^A + \underline{P}^O \underline{V}^T \underline{P}^O + \underline{P}^R \underline{V}^S(E) \underline{P}^O ] \\ &\quad + [ \underline{P}^O \underline{V}^A(E) \underline{P}^A + \underline{P}^A \underline{V}^A(E) \underline{P}^A ] \underline{G}(E)^A [ \underline{P}^A \underline{V}^A(E) \underline{P}^A + \underline{P}^A \underline{V}^A(E) \underline{P}^O ] \\ &\quad - [ \underline{P}^O \underline{V}^T \underline{P}^O + \underline{P}^A \underline{V}^A(E) \underline{P}^O + \underline{P}^O \underline{V}^A(E) \underline{P}^A + \underline{P}^A \underline{V}^A(E) \underline{P}^A ] \} \underline{c} = \underline{0}. \end{aligned} \quad (31)$$

Defining  $\underline{W}(E)^{O+A}$  as the nonzero submatrix of  $(\underline{P}^O + \underline{P}^A) \underline{W}(E) (\underline{P}^A + \underline{P}^O)$  over the layers  $\emptyset + \mathcal{A}$ , we can solve a smaller problem—namely the one over those layers only:

$$\underline{W}(E)^{O+A} \underline{c}^{O+A} = \underline{0}. \quad (32)$$

Since the matrix  $\underline{W}(E)^{O+A}$  is Hermitian, these equations are of the type that can be solved by the algorithm described in the next section.

#### V. NUMERICAL SOLUTION OF THE KOSTER-SLATER EQUATIONS

The Koster-Slater equations for a crystal with two surfaces and adsorption have been brought into a standard form which can be generalized as

$$\underline{W}(E) \underline{c} = [ \underline{V}(E) \underline{G}(E) \underline{V}(E) - \underline{V}(E) ] \underline{c} = \underline{0}. \quad (33)$$

In the earlier applications of the resolvent method to this problem,<sup>18-22</sup> one solved Eq. (19) for the energy by searching for the roots of the equation

$$\det[ \underline{G}(E) \underline{V}(E) - \underline{I} ] = 0. \quad (34)$$

Instead, we will search for the zeroes in the (real) eigenvalues of the Hermitian matrix  $\underline{W}(E)$ , which, of course, are also the zeroes of  $\det[ \underline{W}(E) ]$  and the solutions of Eq. (34) if  $\underline{V}(E)$  is nonsingular in the subspace considered. These zeroes can be calculated by an elegant algorithm because the matrix  $\underline{W}(E)$  and its eigenvalues  $\lambda_j(E)$  have some special properties (the same kind of properties were proved for the expectation value of a general resolvent by Löwdin<sup>49</sup>):

(i) When an eigenvalue  $\lambda_j(E)$  passes through

zero as a function of  $E$ , it always goes from positive to negative value with increasing  $E$ . In other words, if  $\lambda_j(E_0) = 0$ , it follows that

$$\left( \frac{d\lambda_j(E)}{dE} \right)_{E=E_0} < 0. \quad (35)$$

This is proved in the Appendix.

(ii) The eigenvalues of  $\underline{W}(E)$  have poles, as do the matrix elements of  $\underline{W}(E)$  and those of  $\underline{G}(E)$ , at  $E = E_i^{(0)}$ , the eigenvalues of the unperturbed problem. One can prove (see the Appendix) that the number of eigenvalues  $\lambda_j(E)$  which have a pole at a certain  $E_i^{(0)}$  equals the degeneracy  $d_i^{(0)}$  of this unperturbed energy. Moreover, it can be shown that at the poles the eigenvalues  $\lambda_j(E)$  always pass from  $-\infty$  to  $+\infty$  with increasing  $E$ .

These properties easily lead to the following theorem: The number of zeroes  $E_0$  of all eigenvalues  $\lambda_j(E)$  of  $\underline{W}(E)$  in a given energy interval  $E_1 < E_2$  is equal to

$$n_0(E_1, E_2) = n_+(E_1) - n_+(E_2) + \sum_i^{E_1 < E_i^{(0)} < E_2} d_i^{(0)}, \quad (36)$$

when  $n_+(E_1)$  and  $n_+(E_2)$  are the number of positive eigenvalues of  $\underline{W}(E_1)$  and  $\underline{W}(E_2)$ , respectively.

Using this theorem, the values of the energy roots  $E_0$  can be determined by repeated bisection of the interval, until the required accuracy is reached. As the positions of the poles  $E_i^{(0)}$ , and their degeneracies  $d_i^{(0)}$  are known from the unperturbed equations, the only problem that remains is to calculate the number of positive eigenvalues  $n_+(E)$  of the matrix  $\underline{W}(E)$  at given points  $E$ . Sever-

al procedures are possible: (i) complete diagonalization of the matrix  $\underline{W}$  and counting the number of positive eigenvalues; (ii) tri-diagonalization of  $\underline{W}$  and using the Sturm sequence property<sup>57</sup> for the parameter  $\mu = 0$ ; and (iii) bringing  $\underline{W}$  into upper-triangular form by the Gauss elimination process<sup>58</sup> and counting the number of positive diagonal elements. This number can be proved to equal the number of positive eigenvalues of  $\underline{W}$  (see the Appendix).

Applying standard techniques to perform these manipulations on the complex Hermitian matrix  $\underline{W}$ , it appears that the third procedure is about three times faster than the second and about twenty times as rapid as the first. (They all increase in time with the third power of the dimension of  $\underline{W}$ .)

An advantage of the algorithm based on formula (36) for calculating the energy solutions of (33) is that it also calculates those energies of the perturbed system which coincide with an unperturbed energy and, thus, with a pole in the resolvent. In this case, one or more eigenvalues  $\lambda_j(E)$  of  $\underline{W}(E)$  go to zero, which corresponds to a solution of Eq. (33), whereas some other eigenvalues go to infinity. Such solutions cannot be found by the usual methods, which look for the zeroes of the determinant in (34). As pointed out in the Introduction, this advantage is of practical importance, since we wish to calculate also those one-electron energies lying within the crystal-bulk bands.

## VI. DISCUSSION

In the previous sections we worked out a method for the quantitative calculation of one-electron states in finite crystals, with or without adsorption. We can now compare this method in more detail with the more traditional methods mentioned in the Introduction.

In comparison with the resolvent method for semi-infinite crystals, this method is more suitable for quantitative calculations on real crystals, such as semiconductors or transition metals. It does not neglect overlap effects between atomic orbitals and calculates all interaction matrix elements explicitly, up to a given distance. Moreover, it calculates, not merely the strictly localized surface or adsorption states lying outside the crystal-energy bands, but *all* one-electron states.

One can object to the finite-crystal model on the grounds that it does not take into account really long-range effects. We do not think that this omission is very serious, however, because: (i) one can treat crystals up to about  $10 \times 10 \times 10$  atoms; (ii) one can test the model by comparing crystals of different sizes; and (iii) the effects of the surface and, particularly, of chemisorption seem to be rather localized. Moreover, it could well be argued that crystals of this size are already of

physical interest themselves.

Compared with quantitative MO calculations on finite clusters, we have a great reduction in computation time, which enables us to treat much larger clusters and to take into account interactions over a more extended range. This is illustrated by the following arguments for crystals without adsorption: If we have a cluster of  $N_1 \times N_2 \times N_3 = N$  atoms and perform a traditional MO calculation, the number of matrix elements over atomic orbitals that must be evaluated is proportional to  $N^2 = N_1^2 N_2^2 N_3^2$ ; the time for solving the secular problem is proportional to  $N^3 = N_1^3 N_2^3 N_3^3$ . If we impose periodic boundary conditions in two directions and use two-dimensional Bloch orbitals, as we do in our method, we have to calculate a number of matrix elements over atomic orbitals which is proportional to  $N_1 N_2 N_3^2$ . Transformation to Bloch orbitals takes only a negligible time. The time for solution of the secular problem then becomes proportional to  $N_1 N_2 N_3^3$ . By using the resolvent method, as described in this paper, the latter time can be even further reduced. The time for solution of the unperturbed periodic-crystal problem is proportional to  $N_1 N_2 N_3$ . The dimension of the Koster-Slater equations is smaller than the dimension of the secular problem by a factor  $N_0/N_3$ , where  $N_0$  is the number of outer crystal layers directly interacting with the surface. The time for solving the Koster-Slater equations is hard to estimate, as the algorithm contains some steps which are proportional to  $N_0^3$  and other steps proportional to  $N_3^x$ , with  $x$  approximately equal to 1.5. At any rate, it follows that the Koster-Slater problem increases less rapidly with the crystal size than the secular problem, but since the Koster-Slater equations are more complex, the proportionality constant is larger. Therefore we conclude that the application of the resolvent method becomes advantageous when the ratio  $N_3/N_0$  surpasses a certain limit. If this is not the case, we rather solve the secular problem over layer orbitals, which is still much better than the traditional cluster calculations both in time saved and in the avoidance of undesirable boundary effects.

Besides the general resolvent method for surface states and adsorption, we have developed efficient special methods for the case where the effects of the surface potential (the Tamm perturbation) on the one-electron states become negligible. The perturbed wave functions themselves may give rise to a surface potential, however. These methods will be described in a future paper.

The complete procedure for calculating the one-electron states of a crystal with two surfaces and, possibly, some adsorbed layers, as derived in this paper, has been programmed in FORTRAN for an IBM 370 computer. The structure of the program

is shown schematically in Fig. 3. Calculations for hydrogen adsorption on nickel and copper surfaces are underway.

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#### APPENDIX

The applicability of the algorithm for numerical solution of the Koster-Slater equations rests on a number of properties of which the proof shall be outlined in this Appendix.

We wish to find the energies  $E_0$  and the coefficients  $\underline{c}_0$  for which the equation

$$\underline{G}(E)\underline{V}(E)\underline{c} = \underline{c} \quad (\text{A1})$$

becomes an identity:

$$\underline{G}(E_0)\underline{V}(E_0)\underline{c}_0 = \underline{c}_0. \quad (\text{A2})$$

These solutions are obtained by looking at the eigenvalue problem

$$\underline{W}(E)\underline{c}(E) = [\underline{V}(E)\underline{G}(E)\underline{V}(E) - \underline{V}(E)]\underline{c}(E) = \lambda(E)\underline{c}(E) \quad (\text{A3})$$

and searching for those energies  $E_0$  for which  $\lambda(E_0) = 0$ . The first property that we invoke reads

$$\left(\frac{d\lambda}{dE}\right)_{E_0} < 0. \quad (\text{A4})$$

Williams<sup>52</sup> has proved this as follows for orthonormal bases and  $\underline{V}$  not depending on  $E$ :

$$\begin{aligned} \frac{d\lambda}{dE} &= \frac{d}{dE} \underline{c}(E)^\dagger \underline{W}(E) \underline{c}(E), \\ &= \frac{d\underline{c}^\dagger}{dE} \underline{W}\underline{c} + \underline{c}^\dagger \frac{d\underline{W}}{dE} + \underline{c}^\dagger \frac{d\underline{W}}{dE} \underline{c}. \end{aligned} \quad (\text{A5})$$

For  $E = E_0$ , we can substitute the identity (A2) to obtain

$$\left(\frac{d\lambda}{dE}\right)_{E_0} = \underline{c}_0^\dagger \left(\frac{d\underline{W}}{dE}\right)_{E_0} \underline{c}_0 = \underline{c}_0^\dagger \underline{V} \left(\frac{d\underline{G}}{dE}\right)_{E_0} \underline{V} \underline{c}_0. \quad (\text{A6})$$

On the same orthonormal basis the resolvent matrix  $\underline{G}(E)$  reads

$$\underline{G}(E) = \sum_i \underline{c}_i^{(0)} (E - E_i^{(0)})^{-1} \underline{c}_i^{(0)\dagger} \quad (\text{A7})$$

and its derivative becomes

$$\frac{d\underline{G}}{dE} = -\underline{G}\underline{G}. \quad (\text{A8})$$

Substituting this result into (A6) and using the identity (A2) again, we find that

$$\left(\frac{d\lambda}{dE}\right)_{E_0} = -\underline{c}_0^\dagger \underline{V} \underline{G}(E_0) \underline{G}(E_0) \underline{V} \underline{c}_0 = -\underline{c}_0^\dagger \underline{c}_0 = -1. \quad (\text{A9})$$

In our problem, with a nonorthonormal basis and  $\underline{V}(E)$  dependent on  $E$ , we obtain some extra terms in the derivative of Eq. (A6):

$$\begin{aligned} \left(\frac{d\lambda}{dE}\right)_{E_0} &= \underline{c}_0^\dagger \left(\frac{d\underline{W}}{dE}\right)_{E_0} \underline{c}_0, \\ &= \underline{c}_0^\dagger \left(\frac{d\underline{V}}{dE} \underline{G} \underline{V}\right)_{E_0} \underline{c}_0 + \underline{c}_0^\dagger \left(\underline{V} \underline{G} \frac{d\underline{V}}{dE}\right)_{E_0} \underline{c}_0 \\ &\quad + \underline{c}_0^\dagger \left(\underline{V} \frac{d\underline{G}}{dE} \underline{V}\right)_{E_0} \underline{c}_0 - \underline{c}_0^\dagger \left(\frac{d\underline{V}}{dE}\right)_{E_0} \underline{c}_0. \end{aligned} \quad (\text{A10})$$

Two of these terms cancel after using (A2), so that

$$\left(\frac{d\lambda}{dE}\right)_{E_0} = \underline{c}_0^\dagger \left(\underline{V} \frac{d\underline{G}}{dE} \underline{V}\right)_{E_0} \underline{c}_0 + \underline{c}_0^\dagger \left(\frac{d\underline{V}}{dE}\right)_{E_0} \underline{c}_0. \quad (\text{A11})$$

Using the fact that  $\underline{V}(E)$  is linear in  $E$ , and that [according to Eqs. (15) and (28)]  $d\underline{V}/dE$  equals a submatrix of the overlap matrix, and substituting the expression (16) or (29) for  $\underline{G}(E)$ , we have proved, similarly to the proof just given, that

$$\left(\frac{d\lambda}{dE}\right)_{E_0} < 0.$$

The second important property of the eigenvalues  $\lambda(E)$  of  $\underline{W}(E) = \underline{V}(E)\underline{G}(E)\underline{V}(E) - \underline{V}(E)$  is their behavior at the poles  $E_i^{(0)}$  of  $\underline{G}(E)$ . In the neighborhood of a pole  $E_i^{(0)}$ , we write  $E = E_i^{(0)} + \epsilon$ , with  $\epsilon$  very small. For  $\epsilon \rightarrow 0$  all matrix elements of  $\underline{G}(E)$ , and also those of  $\underline{W}(E)$ , go to infinity. In each matrix element of  $\underline{G}(E)$ , given by Eq. (A7), only  $d_i^{(0)}$  terms in the sum behave as  $\epsilon^{-1}$ , whereas the rest remains finite. (Remember that  $d_i^{(0)}$  is the degeneracy of  $E_i^{(0)}$ .) In the limit of  $\epsilon \rightarrow 0$  we can write  $\underline{G}(E)$  effectively as

$$\underline{G}(E) = \epsilon^{-1} \sum_{i=1}^{d_i^{(0)}} \underline{c}_i^{(0)} \underline{c}_i^{(0)\dagger}. \quad (\text{A12})$$

This matrix projects the total space onto a subspace of dimension  $d_i^{(0)}$ ; so it has the rank  $d_i^{(0)}$ . Also the matrix  $\underline{W}(E)$  must have this rank, because the term linear in  $\underline{V}(E)$  is small with respect to  $\epsilon^{-1}$  and the transformation  $\underline{V}(E)\underline{G}(E)\underline{V}(E)$  with nonsingular  $\underline{V}(E)$  does not change the rank. Consequently, only  $d_i^{(0)}$  eigenvalues  $\lambda(E)$  behave as  $\epsilon^{-1}$ , while the other remain small. Since the matrix  $\underline{G}(E)$  given by Eq. (A12) is positive definite for  $\epsilon \downarrow 0$  and negative definite for  $\epsilon \uparrow 0$ , we conclude that at each pole  $E_i^{(0)}$  just  $d_i^{(0)}$  eigenvalues  $\lambda(E)$  pass from  $-\infty$  to  $+\infty$ .

These two properties are sufficient to calculate the number of zeroes in the eigenvalues  $\lambda(E)$  of  $\underline{W}(E)$  in a given interval  $(E_1, E_2)$ , when the number of positive  $\lambda(E)$  is known in the end points  $E_1, E_2$



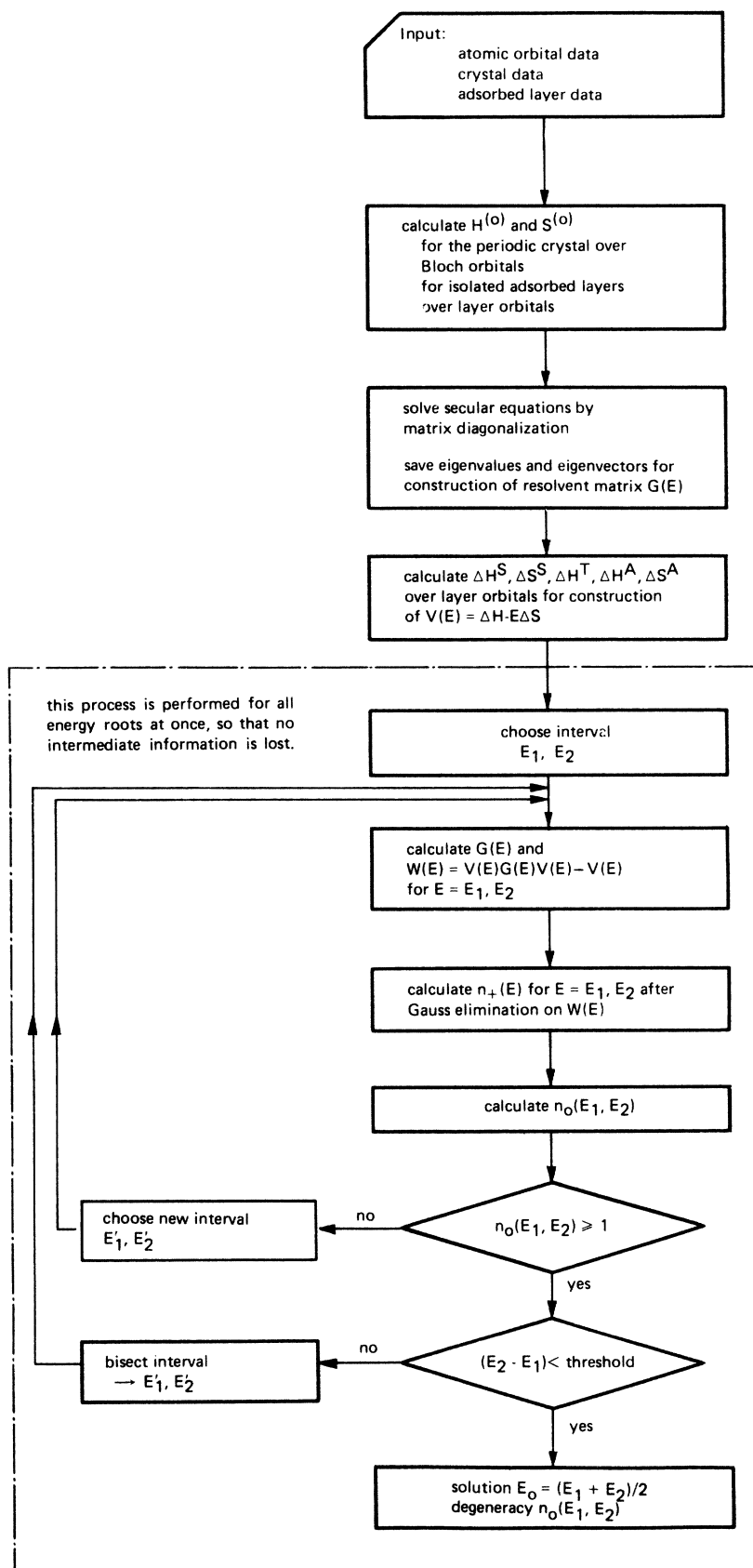


FIG. 3. Flow chart of the FORTRAN program for computing the one-electron energies in finite crystals, with or without adsorption.

[Eq. (36)].

The fastest method to calculate the number of positive eigenvalues of a given complex Hermitian matrix  $\underline{W}$  (dimension  $n$ ) is by the Gauss elimination process,<sup>58</sup> which brings  $\underline{W}$  into an upper-triangular form. The number of positive diagonal elements of the triangular matrix equals the number of positive eigenvalues of  $\underline{W}$ . This is shown most easily for tri-diagonal Hermitian matrices  $\underline{W}'$ . For such a matrix one can calculate the Sturm sequence for any parameter  $\mu$ , which is the sequence of determinants  $D_i(\mu)$  of the principal minors of  $\underline{W}' - \mu \underline{I}$  with increasing size,  $i=0, 1, \dots, n$ ;  $D_0(\mu)=1$ . It has been proved<sup>57</sup> that the number of agreements in sign between the consecutive elements  $D_i(\mu)$  equals the number of eigenvalues of  $\underline{W}'$  which are strictly greater than  $\mu$ . So the number of positive eigenvalues of  $\underline{W}'$  is directly calculated by putting  $\mu=0$ . Actually, this property can be used if we bring  $\underline{W}$  into tri-diagonal form—for instance, by the Householder method.<sup>59</sup> This method is slower, however, than the Gauss elimination process.

Instead of using the Sturm sequence for  $\mu=0$  (i. e., the elements  $D_i$ ), and counting the agreements in sign, one can count the number of positive

quotients  $D_i/D_{i-1}$ .<sup>60</sup> Now, these quotients are exactly the elements which we obtain on the diagonal after Gauss elimination on a general matrix.<sup>58</sup> Thus we have only to prove that the Sturm-sequence property also holds for the determinants  $D_i$  of the principal minors of a general Hermitian matrix  $\underline{W}$ . The proof for tri-diagonal matrices<sup>57</sup> is based on the separation theorem<sup>61</sup> for the eigenvalues of a Hermitian matrix and those of its principal minors, which for such matrices is valid in the strict sense. For general Hermitian matrices it holds only in the non-strict sense,<sup>61</sup> i. e., with  $\leq$  signs instead of  $<$  signs. If none of the determinants  $D_i$  of the principal minors would be equal to zero, however, none of the principal minors can have a zero eigenvalue either, and we effectively have strict separation around zero. On that condition, the Gauss elimination method can be used to calculate the number of positive eigenvalues of  $\underline{W}$ . If any of the elements  $D_i$  does equal zero, the elimination process would fail anyway. In this situation, we can invoke the technique of pivoting,<sup>58</sup> which for our purpose is only permitted if we interchange rows and columns simultaneously, i. e., keep the same elements on the diagonal.

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<sup>55</sup>We have chosen the matrix formulation of the theory because for nonorthogonal basis functions it takes a simpler appearance than the operator formalism. In operator form, the projection operators would read

$$P^X = \sum_{m \in \mathfrak{X}} \sum_{p=1}^{\nu} \sum_{m'=1}^{N_3} \sum_{p'=1}^{\nu} |a_p(m)\rangle \langle a_{p'}(m')|,$$

and they satisfy the relations

$$P^X |a_p(m)\rangle = |a_p(m)\rangle \text{ if } m \in \mathfrak{X}, \\ = 0 \text{ if } m \notin \mathfrak{X}.$$

<sup>56</sup>If we want to calculate adsorption energies, the reference system should contain noninteracting adsorbate atoms (or molecules) instead of layers. The energy correction corresponding to layer formation can be calculated immediately from the solutions of Eq. (26).

<sup>57</sup>J. H. Wilkinson, *The Algebraic Eigenvalue Problem* (Clarendon, Oxford, 1965), p. 300.

<sup>58</sup>Reference 57, p. 200.

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<sup>60</sup>W. Barth, R. S. Martin, and J. H. Wilkinson, in *Handbook for Automatic Computation II. Linear Algebra*, edited by J. H. Wilkinson and C. Reinsch (Springer-Verlag, New York, 1971), p. 249.

<sup>61</sup>Reference 57, p. 103.