Resolvent method for quantitative calculations on surface states and adsorption. II. Adsorption on Shockley surfaces

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Recently, a method has been developed for the quantitative calculation of surface and adsorption effects on one-electron states in finite crystals. This method, which is based on the linear-combination-of-atomic-orbitals or tight-binding scheme, uses the Koster-Slater resolvent method for computing the energies and orbital coefficients. Since the resolvent matrix is constructed numerically, an algorithm was described to solve the Koster-Slater equations numerically as well. The present paper shows a particularly efficient manner to prepare the Koster-Slater equations for this algorithm, which is applicable to crystals with Shockley surfaces and adsorption.

I. INTRODUCTION

The electronic properties of solid surfaces and the phenomena occurring on adsorption have been the subject of much research, both experimental and theoretical. Experimentally, more and more data are becoming available for adsorption on well-defined surfaces, but the interpretation and correlation of these data, which should lead to a better understanding of adsorption interactions, leave many open questions. Theoretically, two types of methods have been applied to this problem, both using mainly the linear-combination-of-atomic-orbitals (LCAO) or tight-binding scheme. The first group of methods calculates the surface and adsorption states in a semi-infinite crystal model. Although these methods are very useful for the interpretation of general phenomena, such as the occurrence of strictly localized surface states, they must introduce various simplifying approximations and, therefore, they remain rather qualitative and cannot do justice to the complexity of interesting crystals such as transition metals. Particularly, the interpretation of spectroscopic data for adsorbed atoms or molecules calls for a more quantitative treatment. Also, the calculation of total surface and adsorption energies is practically impossible by these methods.

A more quantitative approach is followed by the methods of the second kind, applying molecular-orbital (MO) techniques to finite clusters of atoms. Results from such calculations are distorted by undesirable boundary effects, however, because the clusters have to stay rather limited in size.

In a previous paper we proposed a LCAO method which works on finite crystals, just as the cluster methods, and calculates all interaction matrix elements between atomic orbitals explicitly within the (semiempirical) MO scheme that is used. By invoking different features from the semi-infinite crystal methods, such as periodic boundary conditions parallel to the surface and the application of the Koster-Slater resolvent technique, we have considerably reduced the time required for actual computations. Therefore, we can treat larger crystals than the usual cluster calculations and take into account interactions over a more extended range. Typical aspects of our procedure, described in Ref. 22, are the numerical calculation of the resolvent matrix and the algorithm for the numerical solution of the Koster-Slater equations. These are still the most time-consuming steps, though, and we must make them as efficient as possible. In the present paper, we describe simplified procedures for finite crystals having two surfaces without extra surface potentials and, also, for adsorption on these “Shockley” surfaces. First, we shall give a brief account of the general method and show in which parts improvements will be made.

II. GENERAL METHOD

The crystal and the adsorbed layers are assumed to be periodic in two directions, \( \vec{a}_1 \) and \( \vec{a}_2 \), with finite numbers of unit cells, \( N_1 \) and \( N_2 \), respectively. Besides eliminating boundary effects in these directions, this periodicity implies that, working in a LCAO model, we have a set of basis layer orbitals

\[
|a_p(m)\rangle = \sum_{m_1=1}^{N_1} \sum_{m_2=1}^{N_2} |\chi_p(m_1, m_2, m)\rangle e^{i(m_1k_1 + m_2k_2)},
\]

which are noninteracting for different \((k_1, k_2)\). The atomic orbitals \( |\chi_p(m_1, m_2, m)\rangle \) are centered in the unit cell with the origin \( m_1\vec{a}_1 + m_2\vec{a}_2 + m\vec{a}_3 \), the index \( p = 1, \ldots, \nu \) labels different atomic orbitals in the unit cell. On the basis of these layer orbitals we introduce a matrix representation, the matrix index running over all crystal layer orbitals (layers: \( m = 1, \ldots, N_3 \); atomic orbitals: \( p = 1, \ldots, \nu \) and, in case of adsorption, also over the adsorbed layer orbitals (layers: \( n = 1, \ldots, N \); atomic orbitals: \( p = 1, \ldots, \nu \)).
\[ q = 1, \ldots, \mu \]. (Capitals denote matrices, small letters column vectors.)

Using the resolvent method in order to find the solutions, \( E \) and \( c \), of the secular equations for this system

\[ (H - ES)c = 0 \]  

we need an "unperturbed" system, which is most conveniently defined as the crystal periodic in three directions together with some isolated adsorbate layers. The reason for this choice is that the unperturbed equations

\[ (H^{(0)} - E^{(0)}S^{(0)})c = 0 \]

are particularly simple for this special system, even if they must be solved numerically.\(^{22}\) From the numerical solutions of the unperturbed problem we can construct the resolvent matrix by a finite summation over \( i = 1, \ldots, N_3 \mu \) or, in case of adsorption, over \( i = 1, \ldots, N_3 \nu + N_1 \mu \):

\[ G(E) = \sum_i c_{i}^{(0)}(E - E^{(0)})^{-1}c_{i}^{(0)*}. \]

The perturbation which carries the unperturbed system into the real system of interest has the following effects.

(a) It removes so many layers \( R \) from the periodic crystal, that the remaining crystal \( C \) has two surfaces, which are only interacting with inside layers (just as the removal of a segment from a circle creates two ends). These surfaces are called "Shockley" surfaces. The perturbation \( V^S \) which annihilates the interactions between \( R \) and \( C \) actually has only matrix elements between layers \( R \) and some outer crystal layers \( O \), the inner layers \( C-O \) are not directly affected. This is so because we assume the interaction matrix elements between (localized) atomic orbitals to become negligible beyond a given distance.

(b) It adds a surface potential \( V^T \) which modifies the \( H \)-matrix elements of the outer layers \( O \). In the present paper we shall discuss the case that this "Tamm" perturbation \( V^T \) effectively equals zero.

(c) In case of adsorption, it adds the interactions between the adsorbed layers \( A \) and the crystal layers and between adsorbed layers among each other. This interaction \( V^A \) is localized within the adsorbed layers \( A \) and the outer crystal layers \( O \).

The total perturbation \( V^S + V^T + V^A \) modifies the unperturbed secular matrices \( H^{(0)} \) and \( S^{(0)} \) only in certain regions, by amounts \( \Delta H \) and \( \Delta S \). This is most easily expressed by projection matrices \( P^S \), \( P^T \), \( P^C \), and \( P^A = \sum_{n=1}^{N} P^n \), which have unit matrices in the diagonal blocks corresponding to the regions indicated and zero otherwise. Multiplication by a projection matrix \( P^n \) means restriction of the indices to the layer orbitals contained in the region \( X \). Now, we can write the effects of the perturbation as

\[
\begin{align*}
\Delta H^S &= -P^S H^{(0)} P^O - P^O H^{(0)} P^S, \\
\Delta S^S &= -P^S S^{(0)} P^O - P^O S^{(0)} P^S, \\
\Delta H^T &= P^O T P^O, \\
\Delta H^A &= P^A T P^O + P^O T P^A + P^A H P^A - \sum_{n=1}^{N} P^n H^{(0)} P^n, \\
\Delta S^A &= P^A S P^O + P^O S P^A + P^A S P^A - \sum_{n=1}^{N} P^n S^{(0)} P^n.
\end{align*}
\]

The matrix \( T \) describes the effect of the surface potential on the outer layers \( O \). If we define the matrix

\[ V(E) = \Delta H - E \Delta S, \]

which depends on the energy of the perturbed system, the perturbed secular equations (2) can be written

\[ V(E)c = -(H^{(0)} - ES^{(0)})c. \]

Multiplying these equations by the resolvent matrix (4) and using the properties of the latter,\(^{22}\) we obtain the Koster-Slater equations

\[ G(E)V(E)c = c. \]

The dimension of these equations is considerably reduced with respect to the original secular problem (2) if we substitute the matrix \( V(E) \) as given by (5) and (6) and realize that the solutions \( c \) which we are seeking are located in the crystal region \( C \) (in case of adsorption, in the region \( C+A \)). This is worked out in the following sections.

At this point we only recall that Eq. (8) can be solved numerically for \( E \) and \( c \) by the following procedure. Equation (8) is multiplied by \( V(E) \) to obtain

\[ W(E)c = [V(E)G(E)V(E) - V(E)]c = 0. \]

Then we search for the zeroes in the (real) eigenvalues of the complex Hermitian matrix \( W(E) \), which are the energy solutions of (9). Substituting these into (8) or (9) we calculate the coefficients \( c \) by standard techniques (solving a set of homogeneous linear equations). The algorithm to calculate the energies \( E \), which is based on the properties of the eigenvalues of \( W(E) \), is described in paper I.\(^{22}\) This algorithm uses a bisection procedure: select an interval \( (E_1, E_2) \); calculate the number of roots in this interval \( n_0(E_1, E_2) \); if \( n_0(E_1, E_2) > 0 \) bisect the interval, etc., until the required accuracy is reached. In each cycle we have to construct the matrices \( G(E) \) and \( V(E) \) for a given energy \( E \) and to perform the operations required for the calculation of \( W(E) = V(E)G(E)V(E) - V(E) \). These operations are rather time consuming, the more since they
have to be performed in complex arithmetic, which is a serious limit on the practical applicability of this method. In the following sections we show for Shockley surfaces and adsorption how to avoid a considerable part of these operations and, thereby, to make the procedure much more efficient.

### III. SHOCKLEY SURFACES

According to our procedure for general surfaces we would (more precisely) multiply Eq. (8) by $P^0V(E)$ with $V(E) = V^S(E) + V^T$, substitute (5) and (6) and solve Eq. (9) in the subspace $O$. If $V^T$ equals zero, the matrix $P^0V(E)$ becomes equal to $P^0V^S(E)P^R$ and its rank is determined by $\dim(R)$, the dimension of the space $R$, which is smaller than $\dim(O)$. Generally, $\dim(O) = 2 \times \dim(R)$ because the dimension of the space is larger than $\dim(O)$.

For this reason the matrix

$$W^0(E) = P^0V^S(E)P^R(G(E)P^R)P^0V^S(E)P^O$$

becomes singular in the subspace $O$ and we cannot apply the algorithm to find the energy solutions $E$ by looking for the zeroes in the eigenvalues of $W(E)$, since half of the eigenvalues are identically zero. This difficulty could easily be removed by choosing the matrix $W^0(E)$ in the unperturbed (periodic) crystal.

When the Tamm perturbation is zero, i.e., $H = H_0$, the dimension of the space is larger than $\dim(R)$.

It is more efficient, though, to use a special equation for Shockley surfaces which is much faster to solve than the general one.

We start with Eq. (8), substitute $V(E) = V^S(E)$ given by (5) and (6) and use the fact that $P^0c = c$, because the solutions $c$ are located on the crystal $C$. Use of the relations between the projection matrices, $P^0P^R = 0$; $P^0P^C = P^0$; yields

$$G(E)P^R = P^C.$$

Multiplying this equation by $P^R$, denoting the matrix $P^RG(E)P^R$ by $G^{RR}(E)$ and incorporating the Shockley perturbation into a new set of coefficients

$$d^R(E) = P^R V^S(E) P^O c,$$

we are left with the equation

$$G^{RR}(E)d^R(E) = 0.$$

This equation can be solved in the subspace $R$. The matrix $G^{RR}(E)$ is Hermitian and has the correct properties, so that the algorithm of Paper I can be applied to $G^{RR}(E)$ instead of $W^0(E)$ for the calculation of the energy solutions $E$. This procedure is much faster for two reasons. In the first place, the dimension of $G^{RR}(E)$ is twice as small as the dimension of $W^0(E)$ and, therefore, the Gauss elimination process which is part of the algorithm requires less time. Secondly, the matrix $G^{RR}(E)$ is just the restriction of $G(E)$ to the layers $R$, so we can omit the matrix operations needed in each bi-section cycle for the construction of $W(E)$.

According to a proof by Freeman, yields all energy roots $E_0$ for the crystal with Shockley surfaces. The coefficients $c$ can be calculated by substituting these roots back into (13), solving the set of homogeneous linear equations for the coefficients $d^R(E_0)$ and substituting these coefficients into (11), multiplied by $P^O c$.

$$c = P^C G(E_0) P^R d^R(E_0).$$

### IV. ADSORPTION

We want to follow a similar procedure for adsorption on Shockley surfaces. In this case, the unperturbed system consists of the periodic crystal $R + C$ and some isolated adsorbate layers, $n = 1, \ldots, N$, and the resolvent matrix can be written

$$G(E) = (P^R + P^C) G(E) (P^C + P^R) + \sum_{n=1}^{N} P^n G(E) P^n.$$

When the Tamm perturbation is zero, i.e., $H = H_0$, for the crystal layers $O$ as well as for individual adsorbed layers $n \in A$, the perturbation matrix reads

$$V(E) = P^R V^S(E) P^O + P^R V^S(E) P^R + P^0 V^A(E) P^A + P^O V^A(E) P^O + \sum_{n=1}^{N} \sum_{n'=1}^{N} P^n V^A(E) P^{n'} c, \quad n \neq n'.$$

According to the general method, we would have to solve Eq. (9) in the subspace $O + A$, with the matrix $W(E) = V(E) G(E) V(E) - V(E)$ constructed from (15) and (16). In most practical cases, where we do not have too many adsorbed layers, the dimension of this subspace is larger than $\dim(R) + 2 \times \dim(A)$, which appears to be the rank of the matrix $W(E)$ in these systems. So we have tried to replace the matrix $W(E)$ by a smaller matrix of the size $\dim(R) + 2 \times \dim(A)$ and to avoid, at the same time, many of the matrix operations required for the construction of $W(E)$ from the expressions (15) and (16).

We start by substituting (15) and (16) into the Koster-Slater equations (8), using the property that $c$ is now located in $C + A$: $(P^C + P^A)c = c$, and the relations between the projection matrices. If we multiply the resulting equations by $P^R$, $P^A$, and $P^O$, respectively, we find the equations

$$P^R G(E) P^R V^S(E) P^O c + P^R G(E) P^O V^A(E) P^A c = 0,$$

$$\sum_{n=1}^{N} P^n G(E) P^n V^A(E) P^O c + \sum_{n=1}^{N} \sum_{n'=1}^{N} P^n G(E) P^n V^A(E) P^{n'} c = P^O c, \quad n \neq n'.$$
Before proceeding with the preparation of these equations to suit the algorithm for the calculation of \( E \), we introduce some additional definitions. The matrices describing the interactions between the crystal and the adsorbed layers are denoted as

\[ Y_a(E) = V_a V^\dagger_a(E) V^\dagger_0 + V^\dagger_0 V_a(E) P^a c = P^a c. \]  

Equation (17c) reads

\[ \mathcal{P}_G(E) = P^R G^R(E) P^{0c} + P^G(E) P^A(E) P^A c = P^0 c. \]

The interaction matrix between different adsorbed layers, which has zero diagonal blocks, is divided into two triangular matrices:

\[ V^{AO}(E) = P^A V^A(E) P^O; \quad V^{OA}(E) = V^{AO}(E)^\dagger. \]  

These matrices obey the relations

\[ V^{AA'}(E) = \sum_{n=1}^{N} \sum_{n'=1}^{n} P^n V^A(E) P^{n'}, \quad V^{AA'}(E) = V^{AA'}(E)^\dagger. \]  

Different parts of the resolvent matrix are denoted as

\[ G^{RR}(E) = P^R G(E) P^R; \quad G^{RO}(E) = P^R G(E) P^O, \quad \text{etc.,} \]

and the diagonal block matrix over adsorbed layers as

\[ G^A(E) = \sum_{n=1}^{N} P^n G(E) P^n. \]

Using these definitions, (17) reads

\[ \mathcal{G}^{RR}(E) P^R V^A(E) P^0 c + \mathcal{G}^{RO}(E) V^A(E) c = 0, \]

\[ \mathcal{G}^{AO}(E) V^A(E) c + \mathcal{G}^A(E) V^{AA'}(E) c + \mathcal{G}^{AO}(E) V^A(E) c = P^A c, \]

\[ \mathcal{G}^{OR}(E) P^R V^A(E) P^0 c + \mathcal{G}^{OO}(E) V^A(E) c = P^0 c. \]

Equation (22c) is replaced by the sum of multiplying (22c) by \( V^{AO}(E) \) and (22b) by \( V^{AA'}(E) \). Then we substitute the new variables:

\[ d^R(E) = P^R V^A(E) P^0 c, \]

\[ d^A(E) = [V^{AO}(E) + V^{AA'}(E)] c, \]

\[ c^A = P^A c, \]

which are linearly independent if \( \text{dim}(O) + \text{dim}(A) \geq \text{dim}(R) + 2 \times \text{dim}(A) \), obtaining:

\[ \mathcal{G}^{RR}(E) d^R(E) + \mathcal{G}^{RO}(E) V^A(E) c^A = 0, \]

\[ \mathcal{G}^{AO}(E) d^O(E) + [V^{AO}(E) + V^{AA'}(E)] c^A = 0, \]

\[ V^{AO}(E) \mathcal{G}^{OR}(E) d^R(E) + [V^{AA'}(E) \mathcal{G}^{AO}(E) - P^A \mathcal{G}^{AA'}(E)] d^A(E) + [V^{AO}(E) \mathcal{G}^{OO}(E) V^A(E)] c^A = 0. \]

If these equations are written in matrix form (Fig. 1) it is easily verified that the matrix multiplying the new coefficients is Hermitian. The algorithm applied to \( W(E) \) in the general method in order to find the roots of Eq. (9) can now be applied to this matrix. Again, this is more efficient since the matrix of Fig. 1 usually has a smaller dimension and its construction requires much less operations. A large part is just the restriction of \( \mathcal{G}(E) \) to the

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**FIG. 1.** Structure of the equations for adsorption on Shockley surfaces.
subspaces $R$ and $A$, most of the remaining parts are simpler than $W(E)$, which is readily seen by comparison with Eq. (31) of Paper I. Especially when we have just a single adsorbed layer, this simplification becomes obvious because the matrix $Y_{AA}^T(E)$ does not exist.

V. CONCLUSION

Summarizing the preceding sections, we conclude that for Shockley surfaces and adsorption the Koster-Slater equations (8) may be prepared in such a form that the numerical algorithm for the calculation of the perturbed energies can be applied. The $E$-dependent matrix multiplying the coefficients of the perturbed wave function, or linear combinations of these [Eq. (23)], is Hermitian. This is not attained by multiplication with the perturbation matrix yielding the matrix $W(E)$ of Eq. (9), which is singular in this case, but by some specific manipulations and substitutions yielding Eqs. (13) and (24). The advantages of the latter procedure are that the matrices in (13) and (24) have smaller dimensions and are much easier to construct than the matrix $W(E)$ of Eq. (9). This is of crucial importance since the construction of these matrices and their triangularization must be carried out in each cycle of the bisection algorithm for determining the energy roots. The procedures described in this paper were incorporated into the computer program of Paper I.

When the Tamm perturbation, accounting for the effect of the surface potential on the one-electron states does not equal zero, the matrix $W(E)$ is non-singular in the subspace $O$, or $O + A$ for adsorption, in which Eq. (9) should be solved. Still, by the same kind of substitutions described in this paper one can try to simplify the form of $W(E)$ and, thus, save much time in calculating the energies.

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