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Use of Orthogonalized Atomic Orbitals in the Koster-Slater Method for Impurities*

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It is proposed to use orthogonalized atomic orbitals as approximate Wannier functions in the Koster-Slater method for treating impurites in crystals. The method used to compute such orbitals can also be applied to the computation of arbitrary elements of the Green's function of the host crystal. The procedures are illustrated by reference to the "hydrogen metal."

I. INTRODUCTION

The advent of the Koster-Slater method for the calculation of localized impurity states[1-3] represented an important step forward in the solution of the problem of an impurity in a crystal. Since the method requires that one know both the impurity potential and the full set of energy bands and corresponding wave functions for the perfect crystal, it is not surprising that practically all applications have been confined to some kind of model systems. Several papers have also been published with critical discussions of the method and its conceptual implications.

In the Koster-Slater method the impurity function is expanded in the Wannier functions of the perfect crystal. These form a complete set only if all bands and all lattice sites are taken into account. An important question then is how quickly this expansion converges. Keeping the computational difficulties in mind, it is natural that one has tried to truncate it as much as possible. This is done first of all by considering only one band, and secondly by assuming that the impurity potential is sufficiently localized in "Wannier space" to allow the neglect of all matrix elements except the one associated with the impurity site. This is the one-band one-site approximation. Izyumov[4] has given a comprehensive survey of this approximation. In particular, he discusses the changes in the density of states due to the impurity states and the electron density near the impurity. Izyumov uses this approximation to treat three different physical problems: the influence of an impurity on the bands of a metal, the spin-wave spectrum of a ferromagnetic crystal, and the phonon spectrum of a crystal.

Turner and Goodings[5] studied the effect of the one-site approximation on the matrix elements of the impurity potential in the Bloch representation. They showed that in this approximation the impurity matrix is independent of the wave vectors $\vec{k}$.

Beeby[6] showed that for an impurity potential confined to the central cell the one-band approximation is poor. From that result he drew the conclusion that the one-band and the one-site approximations are inconsistent. It should be noted, however, that the one-site approximation in Wannier space corresponds to a potential which is *not* negligible outside the central cell. This has been stressed by Stoddart, March, and Stott,[7] who have analyzed in detail the implications of the one-site approximation. They found that the range of the impurity potential is the same as the range of the Wannier functions in the band under consideration.

Clogston[8] discussed the connection between the Koster-Slater method and the phase-shift analysis of Friedel[9] for metallic compounds. By applying a condition of self-consistency on the perturbation, he derived expressions for the susceptibility and the Knight shift of dilute transition-metal alloys.

Kilby[10] set up a variational version of the Koster-Slater method, which simplified the calculations considerably, and still seemed to give fair agreement with the original treatment. As an example he treated the case of a localized impurity in diamond, using an eight-band model due to Leman and Friedel.[11]

Two detailed investigations of a much more realistic type than those mentioned have been carried out by Callaway and Hughes[12] and Faulkner.[13] The former studied the inclusion of several bands and several sites in a calculation of the bound states of a neutral vacancy in silicon. The bands of the perfect crystal were obtained in a pseudopotential approximation, from which explicit Wannier functions were calculated. By taking full advantage of the symmetry, the authors were able to carry through this major computation. The results definitely show the necessity of including Wannier functions for more than one band and seem to indicate that for the case studied only a few *sites* were needed. An important aspect of the paper by Callaway and

Hughes is the discussion of the phases of the Bloch functions and of the question how to define an energy band.

Faulkner[13] considered the GaP:N system. He carried out detailed calculations both for the one-band one-site case and for the case of two bands and several sites. He showed that the simple approximation could be used to correlate a number of experimental results, but he also stressed the importance of taking the response of the host crystal to the impurity into account. In his construction of the Wannier functions Faulkner used a procedure slightly different from that of Callaway and Hughes, which forced him to use more sites than the other authors.

The explicit computation of the Wannier functions is one of the central problems in the Koster-Slater method. To calculate those functions using the basic definition is far from trivial, as can be seen in both Refs. 12 and 13. It might therefore be interesting to approach this problem from another direction. In the linear-combination-of-atomic-orbitals (LCAO) approximation, the Wannier functions are the orthogonalized atomic orbitals (OAO), introduced by Löwdin.[14] Methods for the explicit evaluation of these OAO have been developed.[15,16] In this paper we propose to use OAO as approximate Wannier functions in the Koster-Slater method, and we show with a simple example what such a calculation involves.

The computation of the OAO involves the matrix $\underline{\Delta}^{-1/2}$, where $\underline{\Delta}$ is the overlap matrix of the atomic orbitals. The methods and programs developed to compute $\underline{\Delta}^{-1/2}$ or any other "reasonable" function of $\underline{\Delta}$ can also be used to compute the Green's function associated with the perfect crystal. This has nothing to do with the use of OAO as Wannier functions but can be done for any Green's function of this type provided the orbital energies $\epsilon(\vec{k})$ are known.

Until recently the LCAO method has not been used to calculate accurate bands, but this situation now seems to be changing.[17] The procedures proposed in the present paper are applicable to the case when an LCAO band calculation is available. Explicit Wannier functions can then be obtained from a combination of the OAO with the LCAO coefficients.

A by-product of the approximation of the Wannier functions by OAO is the fact that we can write the Koster-Slater equations in terms of atomic orbitals. This is probably not desirable in general, but there might be cases where a one-site approximation in the atomic-orbital (AO) representation is more reasonable than in the Wannier representation.

The paper is planned as follows. In Sec. II we describe the construction of the OAO and the adaptation of the method to invert the overlap matrix to the calculation of the Green's function. In Sec. III we review the Koster-Slater method and discuss how to calculate the perturbation matrix in terms of the OAO. A simple numerical example is given to illustrate the procedures. In Sec. IV we discuss the Koster-Slater method in the AO representation with reference to a numerical example.

II. WANNIER FUNCTIONS AND GREEN'S FUNCTIONS FROM ATOMIC ORBITALS

Given a set of Bloch functions

$$\underline{\Psi}=[\psi(\vec{k}_1,\vec{r}),\psi(\vec{k}_2,\vec{r}),\ldots]\ , \tag{1}$$

and the unitary matrix $\underline{U}$ with elements

$$U(\vec{m},\vec{k})=G^{-3/2}e^{2\pi i\vec{k}\cdot\vec{m}}\ , \tag{2}$$

where G^3 is the number of unit cells in the Born-von Kármán region and $\vec{m}$ is a direct lattice vector, we can construct the corresponding set of Wannier functions[14c]

$$\underline{W}=[W(\vec{m}_1,\vec{r}),W(\vec{m}_2,\vec{r}),\ldots] \tag{3}$$

from

$$\underline{W}=\underline{\Psi}\,\underline{U}^{\dagger}\ . \tag{4}$$

If the Bloch functions are normalized LCAO functions, they can be written as

$$\underline{\Psi}=\underline{\varphi}\,\underline{U}\ , \tag{5}$$

where the φ's are the orthogonalized atomic orbitals obtained from the basic atomic orbitals as[14]

$$\underline{\varphi}=\underline{\Phi}\,\underline{\Delta}^{-1/2},\qquad \underline{\Delta}=\langle\underline{\Phi}|\underline{\Phi}\rangle\ . \tag{6}$$

Combining Eqs. (4)–(6), we get for the Wannier functions in the LCAO case

$$\underline{W}=\underline{\varphi}=\underline{\Phi}\,\underline{\Delta}^{-1/2}\ . \tag{7}$$

In general, we have to consider several bands, labeled μ, and several sets of LCAO Bloch sums $\underline{\Psi}_n$:

$$\underline{\Psi}_n=\underline{\varphi}_n\underline{U}\ ,\qquad \underline{\Psi}_\mu=\textstyle\sum_n\underline{\Psi}_n\underline{C}_{n\mu}\ . \tag{8}$$

Here the matrix $\underline{C}_{n\mu}$ consists of the LCAO coefficients which are determined from the variation principle. The OAO $\underline{\varphi}_n$ might be the result of a combination of symmetric and successive orthogonalization.[14c] In this general case the Wannier functions corresponding to the μth band are given by

$$\underline{W}_\mu=\underline{\Psi}_\mu\,\underline{U}^{\dagger}\ ,\quad W_\mu(\vec{m},\vec{r})=\textstyle\sum_n\varphi_n(\vec{m},\vec{r})c_{n\mu}\ . \tag{9}$$

For a detailed discussion of these quantities we refer to Ref. 14(c).

Methods for the explicit evaluation of $\underline{\Delta}^{-1/2}$ and $\underline{\Delta}^{-1}$ in terms of the matrix elements

$$\Delta(\vec{m},\vec{n}) = \int \phi^*(\vec{m},\vec{r})\phi(\vec{n},\vec{r})\,dv \tag{10}$$

have been developed by Löwdin, Pauncz, and de Heer[15] for the one-dimensional case and by Calais and Appel[16] for the three-dimensional case. The latter method is based on the fact that since $\underline{\Delta}$ is a cyclic matrix, it is diagonalized by the unitary matrix $\underline{U}$, Eq. (2):

$$(\underline{U}^\dagger\underline{\Delta}\,\underline{U})(\vec{k},\vec{k}') = \delta(\vec{k},\vec{k}')\textstyle\sum_n \Delta(\vec{n},0)e^{-2\pi i\vec{k}\cdot\vec{n}} = \delta(\vec{k},\vec{k}')\,d(\vec{k}) \; . \tag{11}$$

Any "reasonable" function of $\underline{\Delta}$ can then be obtained from

$$f(\underline{\Delta}) = \underline{U}\,f(\underline{d})\underline{U}^\dagger \; , \tag{12a}$$

in other words,

$$f(\underline{\Delta})(\vec{m},\vec{n}) = G^{-3}\textstyle\sum_{\vec{k}} f[d(\vec{k})]\,e^{2\pi i\vec{k}\cdot(\vec{m}-\vec{n})} \; . \tag{12b}$$

In the case $f(\underline{\Delta}) = \underline{\Delta}^{-1}$ and $f(\underline{\Delta}) = \underline{\Delta}^{-1/2}$ the sum in (12b) is converted to an integral, which is evaluated by means of a special kind of numerical integration. Programs are available at the Quantum Chemistry Group of the University of Uppsala.

It should be stressed that this method of calculating functions of $\underline{\Delta}$ works very well also in the case of metals when the overlap integrals (10) are quite large and when many of them have to be taken into account.

In the more general case shown in Eqs. (8) and (9), the LCAO Wannier functions are linear combinations of orbitals $\varphi_n(\vec{m},\vec{r})$ which have been obtained from a combination of different types of orthogonalization. The corresponding procedures involve matrix multiplications of matrices like $\underline{\Delta}$ where the rows and colums are labeled by the direct lattice vectors $\vec{m}$. Programs for such procedures are also available.

To study the form of the OAO shown in Eqs. (7) or (9), it is desirable to expand the AO's from which they are made up, in spherical harmonics centered at, for example, the origin. Symmetry will simplify the summation over atomic sites implied in (7). Procedures for carrying out this are described in Ref. 14c and have been summarized by Calais.[18]

We illustrate the procedures described in the present paper with "hydrogen metal," a bcc lattice with hydrogen atoms. For such a host crystal the OAO corresponding to the 1s AO's,

$$\phi(\vec{m},\vec{r}) = (\eta^3/\pi)^{1/2}e^{-\eta|\vec{r}-\vec{m}|} \; , \tag{13}$$

can be written as[19]

$$\varphi(\vec{r}) = \phi_0(r)Y_{00}(\vartheta,\varphi) + \phi_4(r)C_4(\vartheta,\varphi) + \cdots \; , \tag{14}$$

where

$$\begin{aligned}\phi_0(r) &= 2\sum_\kappa N_\kappa\Delta^{-1/2}(\kappa)\,\alpha_0(R_\kappa/r) = \sum_\kappa A_0(\kappa)\,\alpha_0(R_\kappa/r) \; ,\\ \phi_4(r) &= \frac{4\sqrt{\pi}}{9}\sum_\kappa N_\kappa\Delta^{-1/2}(\kappa)\,C_4(\Theta_\kappa,\Phi_\kappa)\,\alpha_4(R_\kappa/r)\\ &= \sum_\kappa A_4(\kappa)\,\alpha_4(R_\kappa/r) \; ,\\ C_4(\vartheta,\varphi) &= \frac{\sqrt{21}}{6}\,Y_{40}(\vartheta,\varphi) + \frac{\sqrt{30}}{12}\,[Y_{44}(\vartheta,\varphi) + Y_{4,-4}(\vartheta,\varphi)] \; .\end{aligned} \tag{15}$$

Here κ denotes the order of the neighbors, N_κ denotes the number of the neighbors of order κ, $\Delta^{-1/2}(\kappa) = \Delta^{-1/2}(\vec{m},0)$, where $\vec{m}$ is one of the neighbors of order κ, and $(R_\kappa,\Theta_\kappa,\Phi_\kappa)$ are the polar coordinates of one of the neighbors of order κ. The functions $\alpha_l(R_\kappa/r)$ are the expansion coefficients of the spherical harmonics $Y_{lm}(\vartheta,\varphi)$ in the expansion of (13) around the origin. These functions $\alpha_l(R_\kappa/r)$ are illustrated in Ref. 14c, p. 104. In Table I we give some values for the other quantities in (15) for the case when $\eta = 1$ and the nearest-neighbor distance in the crystal is $2\sqrt{3}$ a.u.

The methods and programs for the calculation of $\underline{\Delta}^{-1}$ can also be used to calculate the Green's function for the perfect crystal in the Wannier representation. The one-electron equations for the perfect crystal,

$$\mathcal{H}\psi(\vec{k},\vec{r}) = \epsilon(\vec{k})\psi(\vec{k},\vec{r}) \; , \tag{16}$$

imply

$$(\mathcal{H}-E)\underline{\Psi} = \underline{\Psi}\,[\underline{\epsilon} - E\cdot\underline{1}\,], \tag{17}$$

where $\underline{\epsilon}$ is a diagonal matrix with elements $\epsilon(\vec{k})$. The Green's function in the Wannier representation is then

$$\begin{aligned}\underline{G} = \langle\underline{W}|\,(\mathcal{H}-E)^{-1}|\,\underline{W}\rangle &= \underline{U}\langle\underline{\Psi}|\,(\mathcal{H}-E)^{-1}|\,\underline{\Psi}\,\rangle\underline{U}^\dagger\\ &= \underline{U}\,[\underline{\epsilon} - E\cdot\underline{1}]^{-1}\underline{U}^\dagger \; ,\end{aligned} \tag{18}$$

in other words

$$G(\vec{m},\vec{n};E) = G^{-3}\sum_{\vec{k}}\frac{e^{2\pi i\vec{k}\cdot(\vec{m}-\vec{n})}}{\epsilon(\vec{k}) - E} \; . \tag{19}$$

TABLE I. Coefficients of the functions $\alpha_0(R_\kappa/r)$ and $\alpha_4(R_\kappa/r)$ in Eq. (15) for nearest-neighbor distance $R_1 = 2\sqrt{3}$ a.u.

κ	N_κ	R_κ	$\Delta^{-1/2}(\kappa)$	$A_0(\kappa)$	$A_4(\kappa)$
0	1	0	1.191 729	2.383 458	⋯
1	8	$2\sqrt{3}$	−0.107 871	−1.725 936	0.292 935
2	6	4	−0.041 712	−0.500 544	−0.121 459
3	12	$4\sqrt{2}$	0.014 756	0.354 144	−0.022 540
4	24	$2\sqrt{11}$	0.006 742	0.323 616	0.017 703
5	8	$4\sqrt{3}$	0.009 012	0.144 192	−0.024 473
6	6	8	0.000 604	0.007 248	0.001 845

This is of the same form as (12b) with $f[d(\vec{k})]$ replaced by $[\epsilon(\vec{k})-E]^{-1}$.

The particular kind of numerical integration used to compute (12) is applicable when the integrand can be written as a function of cosine of the integration variable. This can be done when the lattice has inversion symmetry so that $e^{2\pi i\vec{k}\cdot\vec{m}}$ can be combined with $e^{-2\pi i\vec{k}\cdot\vec{m}}$ to yield $\cos(2\pi\vec{k}\cdot\vec{m})$.

In the case of inversion symmetry the denominator of (19) can be written in this form, since $\epsilon(\vec{k})$ can always be expanded in a Fourier series:

$$\epsilon(\vec{k})=\sum_{\vec{m}}\xi(\vec{m})\,e^{-2\pi i\vec{k}\cdot\vec{m}}\ , \tag{20}$$

where $\xi(\vec{m})$ are the matrix elements of the Hamiltonian with respect to the Wannier functions

$$\xi(\vec{m})=\int W^*(\vec{m},\vec{r})\mathcal{H}W(0,\vec{r})\,dv\ . \tag{21}$$

In the LCAO case the coefficients $\xi(\vec{m})$ are therefore the matrix elements with respect to the orthogonalized atomic orbitals.

III. KOSTER-SLATER METHOD

Assuming that we can define an impurity potential V, we can write the impurity problem as

$$(\mathcal{H}+V)\psi=E\psi\ , \tag{22}$$

where $\mathcal{H}$ is the one-electron Hamiltonian for the electrons in the perfect crystal [cf. (16)]. In the Koster-Slater method the unknown function ψ is expanded in the Wannier functions of the perfect crystal,

$$\psi(\vec{r})=\underline{W}\,\underline{c}=\sum_{\vec{m},\mu}W_\mu(\vec{m},\vec{r})c_\mu(\vec{m})\ , \tag{23}$$

and an equation for the coefficients $c_\mu(\vec{m})$ is obtained, which involves the Green's function (19). This equation can be derived by rewriting (22) in the form

$$\psi=-(\mathcal{H}-E)^{-1}V\psi\ . \tag{24}$$

Using (23) and the fact that the Wannier functions form a complete set, we get

$$[\underline{1}+\underline{G}\,\underline{V}]\underline{c}=\underline{0}\ , \tag{25}$$

where $\underline{G}$ is defined in (18) and $\underline{V}$ is the matrix representing the potential V in the Wannier representation.

The assumption that the impurity is somehow localized now implies that most of the matrix elements of $\underline{V}$ vanish, which reduces the size of the secular equation corresponding to (25) and makes the problem tractable. In the one-band one-site approximation all except one element of $\underline{V}$ are neglected. For a more general case Löwdin[20] has proposed an iteration procedure based on the partitioning method.

If we know explicitly a set of Wannier functions, we do not have to make any assumptions about $\underline{V}$ but we can calculate its elements directly. In the LCAO case the Wannier functions can be written as in (7) or in a more general case as

$$\underline{W}=\underline{\Phi}\,\underline{A}\ , \tag{26}$$

where

$$\underline{A}^{\dagger}\underline{\Delta}\,\underline{A}=\underline{1}\ . \tag{27}$$

Denoting the impurity matrix in the AO representation by $\underline{V}^{\Phi}$,

$$\underline{V}^{\Phi}=\langle\underline{\Phi}|\,V\,|\underline{\Phi}\rangle\ , \tag{28}$$

we get

$$\underline{V}=\langle\underline{W}|\,V\,|\underline{W}\rangle=\underline{A}^{\dagger}\underline{V}^{\Phi}\underline{A}\ . \tag{29}$$

An alternative way of evaluating the matrix elements of $\underline{V}$ is to use expansions of type (14). In any case, at most, three-center integrals have to be computed. The LCAO programs of Lafon and Lin[17] handle up to three-center integrals.

In the one-band one-site approximation, the secular equation corresponding to (25) reduces to

$$1+G(0,0;E)V_0=0, \tag{30}$$

where $V_0=V(0,0)$. As an illustration of the method described in Sec. II for the computation of the Green's function, we solve (30) for the bcc lattice. To facilitate comparison to other calculations, we make the simplifying assumption that the band under consideration can be described by

$$\begin{aligned}\epsilon(\vec{k})&=\epsilon_0+\epsilon_1\sum_{\vec{p}}^{\mathrm{nn}}e^{-2\pi i\vec{k}\cdot\vec{p}}\\&=\epsilon_0+8\epsilon_1\cos\vartheta_x\cos\vartheta_y\cos\vartheta_z\ ,\end{aligned} \tag{31}$$

where

$$\vartheta_x=\pi a k_x\ ,\quad \text{etc.}, \tag{32}$$

TABLE II. Impurity energy level E' as a function of the strength of the perturbation V_0' calculated from Eqs. (30) and (33).

E'	V_0' from (30)	V_0' from (33)
1.04	0.8355	0.8355
1.08	0.9003	0.9003
1.12	0.9568	0.9568
1.16	1.0094	1.0094
1.20	1.0595	1.0595
1.24	1.1079	1.1079
1.28	1.1551	−1.1551
1.32	1.2013	1.2013
1.36	1.2468	1.2468

TABLE III. Matrix elements $G(\vec{\mathrm{m}}, 0; E)$ of the Green's function (19) as functions of $E' = (E - \epsilon_0)/8\epsilon_1$.

$\vec{\mathrm{m}}$	$E' = 1.08$	$E' = 1.20$	$E' = 1.36$
000	1.110 78	0.943 86	0.802 03
111	0.199 64	0.132 64	0.090 77
200	0.114 03	0.063 73	0.036 84
220	0.073 91	0.038 16	0.020 91
311	0.046 67	0.020 32	0.009 44
222	0.050 32	0.023 80	0.012 26
400	0.028 10	0.010 11	0.003 92
331	0.026 29	0.009 88	0.004 13

a is the edge of the cube, and nn means nearest neighbors. With only these two parameters ϵ_0 and ϵ_1, we can calculate the impurity level E as a function of V_0 [or rather $E' = (E - \epsilon_0)/8\epsilon_1$ as a function of $V_0' = V_0/8\epsilon_1$] without introducing any actual values of ϵ_0 and ϵ_1. We want to stress, however, that the present method for calculating the Green's function works equally well in a case where a number of parameters $(\epsilon_0, \epsilon_1, \epsilon_2, \ldots, \epsilon_p, \ldots)$ are given numerically.

No one-band one-site calculation for the bcc case seems to have been published. We can get a check on our results, however, by using the analytical expression for the density of states for a band described by (31), which has recently been published by Jelitto.[21] To that end we rewrite (30) in terms of the density of states[4] $g(x)$ as

$$V_0' \int_{-1}^{1} \frac{g(x)}{E' + x}\, dx = 1. \tag{33}$$

This integral has been calculated by Gaussian quadrature.

In Table II we give E' as a function of V_0' obtained in two different ways.

A value of $V_0' = 0.722$ is needed to get the discrete level to appear (corresponding to $E' = 1$). In his variational calculation for the bcc lattice Kilby[10] obtained a value corresponding to $V_0' = 0.788$.

With the method described in Sec. II we can also calculate the nondiagonal elements $G(\vec{\mathrm{m}}, \vec{\mathrm{n}}; E)$ which are needed when more than one element of $\underline{\mathrm{V}}$ is taken into account. In Table III we show some values of the elements of the Green's function for three values of E.

IV. KOSTER-SLATER EQUATIONS IN AO REPRESENTATION

By means of (26) we can rewrite the set of equations (25) as a set of equations for the coefficients $\underline{\mathrm{b}}$ in the expansion of the impurity function ψ in terms of the AO's $\underline{\Phi}$. In the simplest case, when $\underline{A} = \underline{\Delta}^{-1/2}$, we get instead of (25)

$$[\underline{1} + \underline{\mathrm{G}}\,\underline{\Delta}^{-1}\underline{\mathrm{V}}^{\phi}]\underline{\mathrm{b}} = \underline{0}\ , \tag{34}$$

where $\psi = \underline{\Phi}\,\underline{\mathrm{b}}$ and $\underline{\mathrm{V}}^{\phi}$ is defined in (28). This provides an alternative way of solving the impurity problem in the Koster-Slater method. We should be aware though of problems connected with approximate linear dependence. The matrix $\underline{\Delta}$ can easily be inverted by the methods[16] used to calculate $\underline{\Delta}^{-1/2}$ and $\underline{\mathrm{G}}$ and the calculation of $\underline{\mathrm{V}}^{\phi}$ is more direct than that of $\underline{\mathrm{V}}$.

One can also discuss a one-site approximation in this representation. The relevant secular equation is

$$1 + G^{\phi}(0, 0; E)\, V^{\phi}(0, 0) = 0\ , \tag{35}$$

where $\underline{\mathrm{G}}^{\phi} = \underline{\mathrm{G}}\,\underline{\Delta}^{-1}$. Equation (35) has been solved in the case of an impurity in a "hydrogen metal" for four values of ηR, where η is an orbital exponent [cf. (13)] and R is the nearest-neighbor distance.

The results are given in Table IV, which shows the impurity energy level $E' = (E - \epsilon_0)/8\epsilon_1$ as a function of

$$V_0' = V(0, 0)/8\epsilon_1 = [\Delta^{-1/2}(0, 0)]^2\, V^{\phi}(0, 0)/8\epsilon_1\ .$$

The relation between $V(0, 0)$ and $V^{\phi}(0, 0)$ follows from

$$\begin{aligned} V(\vec{\mathrm{m}}, \vec{\mathrm{n}}) &= \sum_{\vec{\mathrm{m}}', \vec{\mathrm{n}}'} \Delta^{-1/2}(\vec{\mathrm{m}}, \vec{\mathrm{m}}')\, V^{\phi}(\vec{\mathrm{m}}', \vec{\mathrm{n}}')\, \Delta^{-1/2}(\vec{\mathrm{n}}', \vec{\mathrm{n}}) \\ &= V^{\phi}(0, 0)\, \Delta^{-1/2}(\vec{\mathrm{m}}, 0)\, \Delta^{-1/2}(0, \vec{\mathrm{n}})\ . \end{aligned} \tag{36}$$

A large value of ηR means that $\underline{\Delta} = \underline{1}$ and therefore $\underline{\Delta}^{-1} = \underline{1}$. Equation (35) then reduces to (30). Table IV shows that the values of V_0' approach those of Table II with increasing ηR.

The value of V_0' which corresponds to $E' = 1$, i.e., the one necessary to get a discrete level at all, has not been calculated with the same accuracy as those given in Table IV, since a rather large number of integration points was necessary to get accurate values of the elements of $\underline{\mathrm{G}}$ for this E' value. The general trend is that for smaller values of ηR larger values of V_0' are needed to get a discrete level outside the band.

TABLE IV. Impurity energy level E' as a function of the strength of the perturbation V_0' for different values of ηR.

	V_0'			
E'	$\eta R = 2\sqrt{3}$	$\eta R = 2.2\sqrt{3}$	$\eta R = 3\sqrt{3}$	$\eta R = 5\sqrt{3}$
1.04	1.0167	1.0068	0.9384	0.8448
1.08	1.0611	1.0539	0.9949	0.9090
1.12	1.1037	1.0985	1.0460	0.9652
1.16	1.1452	1.1417	1.0944	1.0174
1.20	1.1861	1.1841	1.1412	1.0673
1.24	1.2265	1.2258	1.1868	1.1155
1.28	1.2665	1.2671	1.2316	1.1626
1.32	1.3062	1.3080	1.2758	1.2087
1.36	1.3457	1.3486	1.3194	1.2541

TABLE V. Perturbation corresponding to Eq. (36) in the OAO representation $[V(\vec{m}, \vec{n})/V^{\phi}(0, 0)]$.

	$\vec{m}\backslash\vec{n}$	(000)	(111)	(200)	(220)	(311)
	(000)	1.420 22	−0.128 55	−0.049 71	0.017 59	0.008 03
	(111)		0.011 64	0.004 50	−0.001 59	−0.000 73
$\eta R = 2\sqrt{3}$	(200)			0.001 74	−0.000 62	−0.000 28
	(220)				0.000 22	0.000 10
	(311)					0.000 05
	(000)	1.000 232	−0.002 978	−0.000 953	$< 10^{-6}$	0.000 006
	(111)		0.000 009	0.000 003	$< 10^{-6}$	$< 10^{-6}$
$\eta R = 5\sqrt{3}$	(200)			0.000 001	$< 10^{-6}$	$< 10^{-6}$
	(220)				$< 10^{-6}$	$< 10^{-6}$
	(311)					$< 10^{-6}$

As shown in (36), the one-site approximation in the AO representation corresponds, at least in principle, to a many-site approximation in the Wannier representation. In Table V we show for two values of ηR the ratios $V(\vec{m},\vec{n})/V^{\phi}(0,0)$. For a relatively small value of ηR, we have a many-site OAO approximation, whereas if ηR is large, we have in practice a one-site approximation in the OAO representation also.

With a set of atomic orbitals and an impurity potential given we should of course calculate the various elements of $\underline{V}^{\phi}$. With a screened Coulomb potential

$$V(r) = (Z/r)\, e^{-\lambda r} \tag{37}$$

and the 1*s* functions (13), we can calculate the one- and two-center elements of $\underline{V}^{\phi}$ analytically. The results are

$$V^{\phi}(0,0) = Z\eta^3/(\eta + \tfrac{1}{2}\lambda)^2\ ,$$

$$V^{\phi}(\vec{m},0) = \frac{2Z\eta^3}{\lambda(\eta+\frac{1}{2}\lambda)}\, e^{-(\eta+\lambda/2)R_m} \times\left[\left(1-\frac{2\eta}{R_m\lambda(\eta+\frac{1}{2}\lambda)}\right)\sinh\frac{\lambda R_m}{2} + \cosh\frac{\lambda R_m}{2}\right]\ , \tag{38}$$

where $R_m = |\vec{m}|$. These reduce to

$$V^{\phi}(0,0) = Z\eta\ ,$$
$$V^{\phi}(\vec{m},0) = Z\eta\, e^{-\eta R_m}[1 + \eta R_m] \tag{39}$$

for the pure Coulomb potential.

In Table VI we show some numerical values of these matrix elements as functions of η and λ for the eight nearest and the six next nearest neighbors. Here we have fixed R to 3 a.u., which is the order of magnitude of the "hydrogen metal" equilibrium distance that most calculations give.[19]

Table VI indicates that even for relatively large values of the screening parameter λ it is hardly justifiable to neglect the nondiagonal elements of the impurity potential.

V. CONCLUSION

We have described how to use orthogonalized atomic orbitals as approximate Wannier functions in the Koster-Slater method for treating impurities in crystals. It is pointed out that the procedures used to compute the inverse or the inverse half-power of the overlap matrix of the atomic orbitals can also be used to calculate the Green's function for the host crystal. These procedures give not

TABLE VI. Relations between the central element $V^{\phi}(0, 0)$ and neighboring elements $V^{\phi}(\vec{m}, 0)$.

	$\eta\backslash\lambda$	0	1.0	1.5	2.0	2.5	3.0
	1	1.593	0.628	0.464	0.365	0.300	0.254
	$2/\sqrt{3}$	1.118	0.390	0.289	0.228	0.188	0.159
$\frac{8V^{\phi}(\vec{m}_{nn},0)}{V^{\phi}(0,0)}$	$3/\sqrt{3}$	0.275	0.067	0.050	0.040	0.033	0.028
	$5/\sqrt{3}$	0.013	0.002	0.002	0.001	0.001	0.001
	$10/\sqrt{3}$	4×10^{-6}	3×10^{-7}	3×10^{-7}	2×10^{-7}	2×10^{-7}	10^{-7}
	1	0.838	0.293	0.217	0.171	0.141	0.119
	$2/\sqrt{3}$	0.550	0.169	0.126	0.099	0.082	0.069
$\frac{6V^{\phi}(\vec{m}_{nnn},0)}{V^{\phi}(0,0)}$	$3/\sqrt{3}$	0.104	0.022	0.017	0.013	0.011	0.009
	$5/\sqrt{3}$	0.003	4×10^{-4}	3×10^{-4}	2×10^{-4}	2×10^{-4}	2×10^{-4}
	$10/\sqrt{3}$	3×10^{-7}	2×10^{-8}	10^{-8}	10^{-8}	10^{-8}	10^{-8}

only the diagonal element of the Green's function, which is the only one needed in the one-site approximation, but also any element. The procedures are illustrated by reference to an impurity in a "hydrogen metal." Finally, we have discussed the Koster-Slater method in terms of atomic orbitals.

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Transition-Matrix Theory of Low-Energy Electron Diffraction

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A transition-matrix formulation is presented for calculating the scattering amplitude of an elastically scattered beam from a crystal with perfect two-dimensional periodicity in the surface plane. The scattering amplitude is expressed in the transition-matrix expansion for a general potential. When applied to the muffin-tin potential model, Beeby's multiple-scattering low-energy electron diffraction (LEED) theory, Kambe's modified Korringa-Kohn-Rostoker theory, Shen's application of the Shen-Krieger variational LEED theory, and the transition-matrix LEED theory can be transformed to give the identical exact solution of this problem. In analogy to the pseudopotential formalism in the energy-band theory, the scattering amplitude can be written in Born expansions for an effective potential which is, in general, weaker than the crystal potential for the nearly-free-electron model. It is shown that the infinity of the tangent of a phase shift can result in a resonance peak in the reflectance.

I. INTRODUCTION

The diffraction of low-energy electrons (LEED) is an important subject because of its potential as a method for studying the bulk and the surface structure of a crystal. A LEED experiment is performed by allowing a beam of low-energy electrons to interact with the crystal, which is formed by bringing together 10^{22} atoms in one cubic centimeter. It is not possible to solve this entire system of complicated interacting particles exactly by many-body quantum theory. Thus, a few assumptions are essential in the LEED theory. First, no relativistic effect need be taken into account since the energies of the incident electrons are very low ($\lesssim 100$ eV). (Relativistic effects may not be