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Generalization of the Green's-functions formalism to nonorthogonal orbitals: Application to amorphous SiO_2

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It is shown that the Green's-function formalism can be extended to nonorthogonal wave functions. This new technique is illustrated on the example of amorphous SiO_2 where the calculated partial densities of states are compared to experimental data.

I. INTRODUCTION

In a previous paper we have pointed out that a good parametrized band structure of SiO_2 can be obtained in a first-nearest-neighbor approximation, provided that the corresponding overlap integrals are included.[1] A complete discussion of the band structure requires that the partial densities of states be available. For crystalline systems the matrix $(H-ES)$ (H, Hamiltonian; S, overlap; E, energy) can be factorized with respect to the wave vector $\vec{k}$, and the partial densities of states can be calculated in various ways.[2] For amorphous networks, on the other hand, the factorization breaks down and new techniques are required to perform the calculations. In this paper we intend to present a method which allows the use of nonorthogonal orbitals and which works for both crystals and glasses. Applying the Green's-function formalism to overlapping orbitals we show in the first part of the paper that the usual results[3] can be generalized in an easy-to-work way. In the second part, we calculate, as an example, the partial and total densities of states for a Bethe-lattice amorphous SiO_2 system and discuss the results.

II. GREEN'S-FUNCTION FORMALISM FOR NONORTHOGONAL WAVE FUNCTIONS

In this section we present the general frame of the method. It is based on the use of the Green's operator G:

$$G=\lim_{\eta\to 0}[(E+i\eta)I-H]^{-1}\ , \tag{1}$$

where I and H are, respectively, the identity and Hamiltonian operators. The matrix elements of G provide all the required information when working with orthonormal orbitals. With nonorthogonal wave functions, the trouble arises from the fact that three different kinds of matrix elements can be defined (this is true for any operator). These matrix elements are given by

$$\begin{aligned} &G=\sum_{ij} G^{ij}\,|\,i\,\rangle\langle\,j\,|\ ,\\ &G\,|\,i\,\rangle=\sum_{j} G_i^j\,|\,j\,\rangle\ ,\\ &G_{ij}=\langle\,i\,|\,G\,|\,j\,\rangle\ . \end{aligned} \tag{2}$$

Hereafter, we call G_k the matrix of contravariant components G^{ij}, G_m the matrix of mixed components G_i^j, and G_c the covariant matrix G_{ij}. These matrices are not independent but can be related through the representations of unity. The following result will be used:

$$G_m=G_kI_c,\quad G_k=G_mI_k\ , \tag{3}$$

where I_c is the covariant representation of the identity operator. The matrix elements of I_c, i.e., the I_{ij}, are nothing more than the overlap $\langle\,i\,|\,j\,\rangle$. I_k, the contravariant representation of the identity operator, is the inverse of the I_c matrix. Finally, I_m is the unit matrix.

An essential piece of information is given by the density of states $n(E)$ of the whole system. To derive it we write expression (1) in terms of the mixed form of G and H, i.e.,

$$G_m[(E+i\eta)I_m-H_m]=I_m\ , \tag{4}$$

where I_m, the mixed representation of unity, is simply the unit matrix. This relation has exactly the same constitutive form as in tight-binding theory, when working with orthogonal orbitals. Then G_m has exactly the same properties as the resolvent matrix of ordinary tight-binding theory. In particular, we can define a quantity

$$n(E)=-\frac{I_m}{\pi}\sum_i G_i^i(E)\ , \tag{5}$$

which turns out to be the total density of states. This follows from trace invariance, which allows us to come back to an orthogonalized basis set for which (5) defines the total density of states. The situation is somewhat more difficult for the partial densities of states. A consequence of (4) is that the quantities.

$$n_i(E) = -\frac{I_m}{\pi} G_i^i(E) \tag{6}$$

have the usual mathematical properties of partial densities of states. In particular, they are normalized to unity. However, the way they are related to experimentally observable quantities is not trivial. For instance, it is known that x-ray emission spectra reflect the local atomic character of the valence states. In Appendix A we show that their intensity is not proportional to $n_i(E)$ but rather to the unnormalized quantity

$$n_i'(E) = -\frac{I_m}{\pi} G^{ii}(E) . \tag{7}$$

In practice, the directly available terms are the covariant forms of both the identity (I) and Hamiltonian (H) operators, corresponding to the usual matrix elements $\langle i \mid j \rangle$ and $\langle i \mid H \mid j \rangle$. From the knowledge of these two matrices, G_m can be evaluated in two steps:

(i) From the definition of G and with the use of (2) one can show that

$$G_k[(E + i\eta)I - H]_c = I_m . \tag{8}$$

Thus G_k is the inverse of the covariant representation of $(E + i\eta - H)$ and can be calculated as directly as with orthogonal local orbitals.

(ii) Once G_k is known, G_m can be evaluated with the use of (3), i.e., by a simple matrix product.

This shows that only one matrix has to be inverted, as in the conventional tight-binding method. As far as G_k is concerned the calculation is exactly the same as in tight binding, provided the Hamiltonian matrix elements are replaced by the corresponding $H_{ij} - EI_{ij}$ term. This means that the usual algebra holds, with that modification. For instance, the Dyson equation for a system submitted to a perturbation is written as

$$G_k = g_k + g_k(V_c - E\Delta I_c)G_k , \tag{9}$$

where g and G are the unperturbed and perturbed Green's operators, V is the perturbative potential, and ΔI_c is the change in overlap matrix related to the perturbation. With this relation the change $\Delta N(E)$ in total number of states of energy less than E due to the perturbation can be calculated. It is found to be (Appendix B)

$$\Delta N(E) = \frac{1}{\pi}\mathrm{Im}\{\ln\det[I_m - g_k(V_c - E\Delta I_c)]\} - \frac{1}{\pi}\mathrm{Im}\{\ln\det[I_k(I_c + \Delta I_c)]\} , \tag{10}$$

where I_k is the inverse of the overlap matrix I_c for the unperturbed problem.

The significant contribution to $\Delta N(E)$ arises from the first term in (10). The second term, independent of energy, appears only to cancel the first term at large energies E.

III. APPLICATION TO SiO_2

We can now apply this formalism to SiO_2. In such a system the overlaps may be of crucial importance.[1] We extend the scheme used in Ref. 4 to nonorthogonal orbitals. As shown in Fig. 1 we consider a central SiO_4 tetrahedron coupled to a SiO_2 lattice approximated by a Bethe tree, in which the Si-O-Si angle takes its crystalline value 144°. As far as we consider the contravariant components of the Green's operator the calculations remain primarily unchanged. We have only to replace the tight-binding matrix H_{ij} by the appropriate $H_{ij} - EI_{ij}$ term (I_{ij} is the overlap matrix). This remark applies to the Bethe-lattice calculations, which thus will not be further examined. The situation is different for the study of the Green's function on the central tetrahedron since we want to calculate local densities of states and thus the mixed components of G.

For this we start from a situation where the SiO_4 tetrahedron is decoupled from the average Bethe lattice, in which case the Green's operator is g and the overlap matrix I_c. We then include the coupling between the two subsystems, which corresponds to a perturbation matrix V_c and a change in overlap matrix ΔI_c. The final Green's-function matrix G_k can then be determined with the use of Dyson's equation

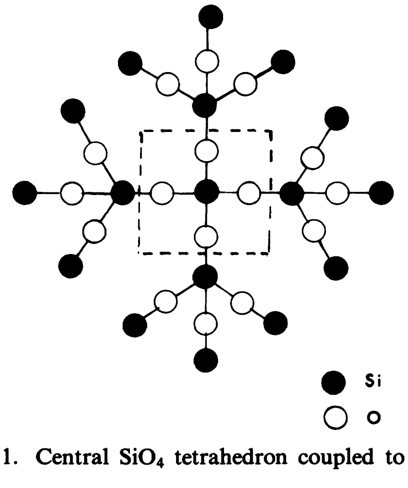

FIG. 1. Central SiO_4 tetrahedron coupled to a Bethe lattice.

[Eq. (9)] under the form

$$
\begin{aligned}
G^{ij}&=g^{ij}+\sum_{k,\alpha}g^{ik}(V_{k\alpha}-E\Delta I_{k\alpha})G^{\alpha j}\,,\\
G^{i\alpha}&=\sum_{k,\beta}g^{ik}(V_{k\beta}-E\Delta I_{k\beta})G^{\beta\alpha}\,,\\
G^{\alpha i}&=\sum_{\beta,k}g^{\alpha\beta}(V_{\beta k}-E\Delta I_{\beta k})G^{ki}\,,\\
G^{\alpha\beta}&=g^{\alpha\beta}+\sum_{\gamma,j}g^{\alpha\gamma}(V_{\gamma j}-E\Delta I_{\gamma j})G^{j\beta}\,.
\end{aligned}
\tag{11}
$$

In these equations the latin indices refer to the SiO_4 tetrahedron orbitals and the greek indices to the medium orbitals.

With the use of (3) the mixed component G_i^j can be written as

$$G_i^j=\sum_k G^{jk}I_{ki}+\sum_\alpha G^{j\alpha}\Delta I_{\alpha i}\,. \tag{12}$$

Here I_{ki} is the overlap matrix for the decoupled tetrahedron. Equation (12) shows that one needs only the G^{jk} and $G^{j\alpha}$ terms.

Eliminating $G^{\alpha j}$ and $G^{\alpha\beta}$ in (11) one finds

$$G^{ij}=g^{ij}+\sum_{k,l}g^{ik}(U_{kl}-ED_{kl})G^{lj}\,, \tag{13a}$$

$$
\begin{aligned}
G^{j\alpha}=&\sum_{k,\beta}g^{jk}(V_{k\beta}-E\Delta I_{k\beta})g^{\beta\alpha}\\
&+\sum_{k,l}g^{jk}(U_{kl}-ED_{kl})G^{l\alpha}\,,
\end{aligned}
\tag{13b}
$$

where

$$U_{kl}=\sum_{\alpha,\beta}(V_{k\alpha}-E\Delta I_{k\alpha})g^{\alpha\beta}(V_{\beta l}) \tag{14a}$$

and

$$D_{kl}=\sum_{\alpha,\beta}(V_{k\alpha}-E\Delta I_{k\alpha})g^{\alpha\beta}\Delta I_{\beta l}\,. \tag{14b}$$

Injecting Eqs. (13) in (12) leads to

$$G_j^i=g_j^i+\sum_k g^{ik}D_{kj}+\sum_{k,l}g^{ik}(U_{kl}-ED_{kl})G_j^l\,. \tag{15}$$

This equation is similar to (13) when G^{ij} has been replaced by G_j^i and g^{ij} by

$$(g_j^i)_{\text{eff}}=g_j^i+\sum_k g^{ik}D_{kj}\,. \tag{16}$$

It follows that G_j^i can be expressed in terms of G^{ij} by

$$G_j^i=\sum_k(G^{ik})(I_{kj}+D_{kj})\,. \tag{17}$$

This expression is completely similar to (3) with effective overlaps which involve only the tetrahedron orbitals. On the other hand, (13a) is similar to the Dyson equation for an effective perturbation (U,D) including both potential and overlap terms, and dealing only with tetrahedron orbitals. These two remarks show that the effective interaction method[5,6] can be extended to problems with nonorthogonal orbitals. To determine the density of states we have then first computed the contravariant components of G that cause no problems. These contravariant components are used to determine the mixed component G through Eq. (17). Finally, the density of states is calculated with the use of (5). Figure 2 illustrates the results obtained with the parameters given in Ref. 1. For numerical convenience we have used a Lorentzian to broaden the oxygen levels by 0.1 eV. The only effect of this operation is to spread out somewhat the densities of states giving rise to tails within the band gap.

We find a total density of states that is in good agreement with the results of previous calculations in Refs. 7–12. As shown in Fig. 2 it also reproduces the ultraviolet photoelectron spectroscopy (UPS) spectrum.[13,14] As concerns the x-ray emission spectra, we show in Appendix A that these are likely to reflect the local densities of states $n_i'(E)$ defined by Eq. (7). Figure 3 illustrates the results we have obtained as well as the experimental information deduced from the x-ray emission spectra. It first appears that the Si $3p$ density is very similar to the

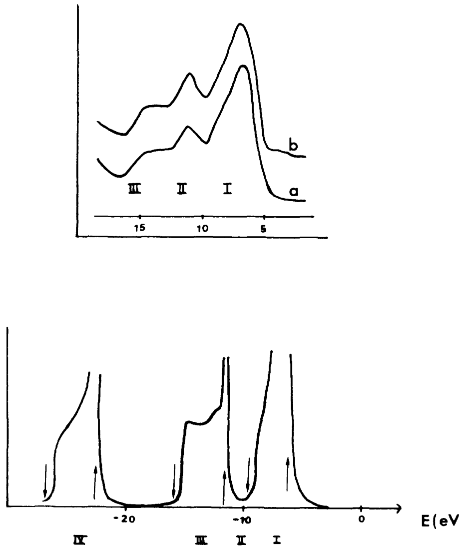

FIG. 2. Total density of states of SiO_2 with the parameters of Ref. 1. At the bottom we have plotted the UPS results of Hollinger (Ref. 14) for a thin film a and an oxydized surface b. The arrows refer to the analytic limits of the band calculated in Ref. 1. One sees that these limits are correctly reproduced with a Bethe-lattice model.

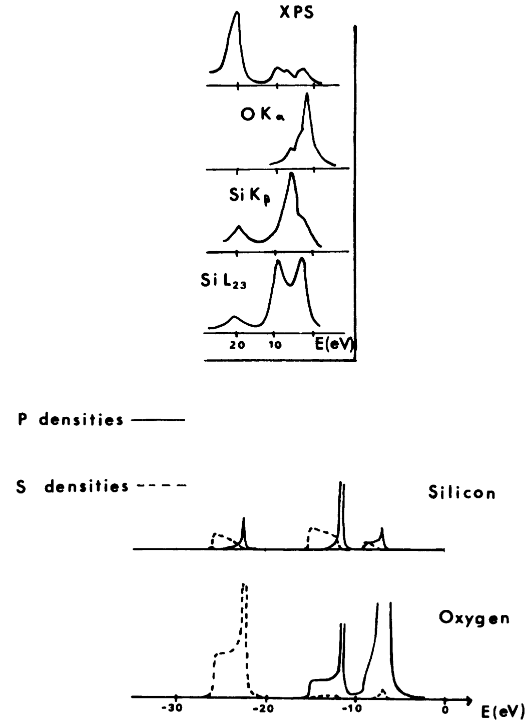

FIG. 3. Partial density of states in our model on silicon and oxygen. In the top section we have reproduced the x-ray emission spectra and XPS results as reviewed by Iguchi (Ref. 17).

shape of the Si $K\beta$ spectrum.[15] The position and the shape of the O 2s partial density of states are also in agreement with the x-ray photoelectron spectroscopy (XPS) results,[13,16] contrary to those of other calculations.[8,12] For the Si 3s and O 2p character, the agreement is not so good. Let us first consider the Si 3s density. As in the Si L_{23} spectra[15,17] three peaks are present. But while in the experiments the two upper peaks are of comparable height and width a strong dissymmetry can be seen on the calculated curves. Such a discrepancy appears in all the calculations we know. It has been suggested that it could be removed by silicon 3d electron effects;[7,18,19] we do not believe such an interpretation because d electrons are included in pseudopotential treatments. It is more plausible that correlation effects could be important as found for optical absorption[20] and Auger spectra.[21] Coming to the O 2p density, it is clear that the width of the upper band is too small. This difficulty was already found in the preliminary study[1]; the inclusion of π interactions and overlap could improve this small defect[22] so that a first-nearest-neighbor tight-binding model can provide a description of the valence band of SiO_2.

A final point of importance is to know which approximation has the more important effect on the density of states, the neglect of nonorthogonality or the use of a Bethe lattice to simulate the medium. In view of the molecular character of the bands the Bethe lattice gives practically exact position and widths for all bands, as was demonstrated by detailed calculation[10,22] (see also Fig. 2). Thus the inclusion of nonorthogonality of the atomic basic represents an important improvement in the description of the bands, as is also the case in covalent materials.

IV. CONCLUSION

We have extended the Green's-function formalism to the case of nonorthogonal orbitals. We have applied it to amorphous SiO_2 and have shown the applicability of this formalism to glasses as well as crystals. We have compared the calculated densities with experimental spectra. The results show that a nearest-neighbor model including overlaps can describe accurately the valence bands of SiO_2.

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APPENDIX A: PARTIAL DENSITIES OF STATES OBTAINED IN X-RAY EMISSION SPECTRA

The intensity of the emission at energy $E = h\nu$ is proportional to the quantity

$$I = \sum_k |\langle 0|p|k\rangle|^2 \delta(E-(E_k-E_0)) , \tag{A1}$$

where $|0\rangle$ is the core state of interest on atom 0 and E_0 its energy, while $|k\rangle$ is an eigenstate of energy E_k, p being a component of the dipole operator. It is always possible to rewrite (A1) as

$$I = -\frac{I_m}{\pi} \sum_k \langle 0|pG(E+E_0)|k\rangle\langle k|p|0\rangle , \tag{A2}$$

which, with the use of the closure relation (since $\langle 0|p|0\rangle$ vanishes), can be further simplified to

$$I = -\frac{I_m}{\pi} \langle 0|pG(E+E_0)p|0\rangle . \tag{A3}$$

When a basis of nonorthogonal atomic orbitals is used G can be expressed by the first relation (2), which gives

$$I=-\frac{I_m}{\pi}\sum_{ij}\langle 0|p\,|i\rangle G^{ij}\langle j\,|p\,|0\rangle\ . \tag{A4}$$

For the valence states of interest $|i\rangle$ has to be specified by two indices $|im\rangle$, i standing for the atom, m for the orbital. As the core state $|0\rangle$ is strongly localized on the atom the matrix elements $\langle 0|p\,|im\rangle$ will take important values only for $i=0$. Usually, from symmetry, one component p connects $|0\rangle$ with only one of the $|0m\rangle$, so that one finally gets

$$I=-\frac{I_m}{\pi}\,|\langle 0|p\,|0m\rangle|^2G^{0m,0m}\ . \tag{A5}$$

Then I does not reflect the partial density of states $n_{0m}(E)$ defined by (6), but instead the quantity $-(I_m/\pi)G^{0m,0}$, which is not normalized to unity.

APPENDIX B: CALCULATION OF $\Delta N(E)$ FOR NONORTHOGONAL ORBITALS

We start from Eq. (9), which we write

$$[I_m-g_k(V_c-E\Delta I_c)]G_k=g_k\ , \tag{B1}$$

and we use Eq. (3) to express G_k and g_k in terms of G_m and g_m, which gives

$$[I_m-g_k(V_c-E\Delta I_c)]G_m=g_mI_k(I+\Delta I)_k^{-1}\ . \tag{B2}$$

Integration of Eq. (5) leads to the well-known expression for the change $\Delta N(E)$ in the total number of states of energy smaller than E,

$$\Delta N(E)=-\frac{1}{\pi}\mathrm{Im}\ln\left[\frac{\det G_m}{\det g_m}\right], \tag{B3}$$

which, from (B2) and the fact that $(I+\Delta I)_k^{-1}$ is equal to $(I+\Delta I)_c$, can be expressed as in Eq. (10).

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