Band dispersion in the recursion method

Wang Yong-Liang

Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100 083,
People's Republic of China

(Received 11 September 1990)

The advantages of the supercell model in employing the recursion method are discussed in comparison with the cluster model. A transformation for changing complex Bloch-sum seed states to real seed states in recursion calculations is presented and band dispersion in the recursion method is extracted with use of the Lanczos algorithm. The method is illustrated by the band structure of GaAs in the empirical tight-binding parametrized model. In the supercell model, the treatment of boundary conditions is discussed for various seed-state choices. The method is useful in applying tight-binding techniques to systems with substantial deviations from periodicity.

I. INTRODUCTION

Since the recursion method[1] has been shown to be a rather stable algorithm and the rounding errors are not cumulative, many applications[2-4] have appeared in the literature. The most promising aspect of the recursion method is that it is especially suitable for studying large low-symmetry complicated systems, for example, defect complexes[5] in the presence of lattice relaxation, dislocations,[6,7] surfaces and interfaces, superlattices, and amorphous bodies. It lends itself to easy programming and does not require large storage capacity of the computer.

The link of the recursion calculation to the local density of states is straightforward. It is widely accepted that the recursion method is a real-space local environmental approach. In the case of the supercell model, a translational symmetry is artifically introduced by imposing a periodic condition on a large unit cell (supercell). The size of the supercell is chosen so that, on the one hand, physically it contains the local states interested in order to decouple the interactions of the local states between neighboring supercells and, on the other hand, computationally it will not exceed the maximum storage capacity allowed for the computer at hand.

In the case of dislocations in semiconductors, it is desirable to know the dispersion relations of the electronic states along the one-dimensional Brillouin zone, whereas in the case of surfaces and interfaces, the dispersion of the electronic states in the two-dimensional Brillouin zone is required. Then the starting states, sometimes referred to as seed states, in the recursion computation should be chosen as Bloch-sum-like complex wave functions. The recursion method is extended to **k** space and the partial density of states is expressed via Green's function as a continued fraction instead of the local density of states; the complex computation must be tackled.

When the inverse of the nonorthogonal overlap matrix cannot be avoided in the recursion computation, the complex nature of the overlap matrix increases the complication of the inverting procedure for the large sparse overlap matrix. The complex computation arising from the complex seed states can be avoided by making a unitary transformation to the seed states, Hamiltonian matrix, and overlap matrix.

In this paper we formulate the unitary transformation by connecting the **k** and −**k** basis set of seed states through the time-reversal symmetry to transform the complex Bloch-sum-like basis set into a real set. By this transformation, the Hamiltonian matrix and overlap matrix simultaneously become real matrices and the computation can be carried out in real space (with matrices 2×2 times larger). The band dispersion can be extracted from the **k**-dependent seed states in the Brillouin zone for the supercell. Thus the seed states will no longer be restricted to local atomiclike orbitals. They can be chosen as periodic Bloch-sum-type linear combinations of atomic orbitals.

The transformation is illustrated by the band-structure calculation of GaAs in the tight-binding parametrized model. The partial density of states with various Bloch-sum-like seed states was calculated by the recursion procedure and their **k** dependence was demonstrated.

In Sec. II we discuss the advantages of the supercell model as compared to the cluster model and the choice of seed states for different physical problems. The different ways for treating the boundary of the supercell in various physical system are also presented. Section III is devoted to the descriptions of the unitary transformation and its application to the band calculation for GaAs. Finally, in Sec. IV, we summarize the results and make some comments for the future application of the approach.

II. CHOICE OF THE BASIS SET AND THE BOUNDARY CONDITION

There are mainly two models in use in the application of the recursion method, namely the cluster model and the supercell model.

The recursion method can handle very large clusters (2500 atoms or more) so that the surface interactions of the cluster can be detached from the interactions in the center of the cluster. However, particular care must be taken in choosing the shape of the cluster. A regularly shaped cluster tends to add up phase-coherent boundary

corrections from all parts of the boundary at the center; thus the boundary will introduce spurious resonance peaks in the local density of states curve for the central atom, if one chooses a spherical cluster. The reason why the spurious structure in the local density of states occurs is due to the fact that the recursion procedure proceeds as the propagation of the "recursion wave." In a regularly shaped cluster the wave starting from the center of the cluster reaches the boundary of the cluster at the same time. The wave reflected from the boundary bringing with it the information of the surface interactions arrives back at the center. Though the cluster may be very large, the local density of states of the central atom will still contain peaks derived from surface states. This can be eliminated by using a cluster with a shape as irregular as possible while retaining the symmetry of the Hamiltonian. Another drawback of the cluster model is that it does not have a symmetry which can be exploited so that the dispersion relation cannot be extracted, for example, in the case of dislocations the dispersion along the dislocation line is lost.

An alternative way to deal with cluster surfaces is to impose periodic boundary conditions which correspond to an infinite crystal built up from supercells consisting of the defects or interfaces amidst a large number of host atoms. This artificially introduced periodicity allows the dispersion relations to be readily extracted by standard band-structure calculation technique. One of the advantages of the supercell model compared with the cluster model is that the perturbation on the defect coming from the surface at a distance d is removed and replaced by a perturbation at roughly a distance $2d$ coming from the surrounding defects. The surface-defect interaction is thus replaced by defect-defect interactions which result in broadening of the defect levels into a band, if the supercell is not large enough.

The choice of the seed states is problem dependent. In the case of crystal impurities, our attention is concentrated on the local density of states of the impurity and its surroundings. Thus usually we take as seed states atomic orbitals with different symmetries on the impurity sites or the surrounding atom sites in the presence of crystal relaxation. From the recursion coefficients, we can find the local density of states and deduce the bound defect levels. Here we choose as basis set and seed states real atomic orbitals or their linear combinations. The translational symmetry is exploited in the following way: For atoms near the boundary of the supercell interaction with atoms (usually first neighborings up to fourth neighborings) outside the supercell, the Hamiltonian (overlap) matrix elements will be formed with the translational equivalent atoms inside the supercell. Thus we can restrict the calculation within a supercell and the three-dimensional periodically repeated supercell structure is taken to be infinitely extended.

In Fig. 1 we illustrate the way to handle the periodic condition in a two-dimensional supercell. The supercell contains 15 atoms, the Hamiltonian and the overlap matrices are arranged by the numbering of atoms inside the supercell as demonstrated in the figure. If we take into account interactions up to the second-nearest neighbors,
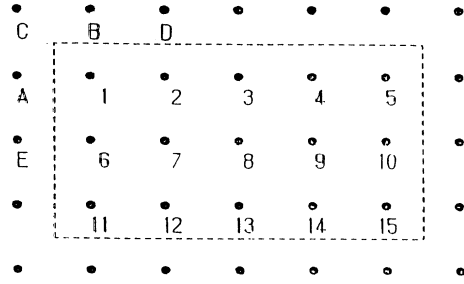

FIG. 1. The correspondence between the lattice points inside and outside a plane supercell: $A \rightarrow 15$; $B \rightarrow 11$; $C \rightarrow 15$; $D \rightarrow 12$; $E \rightarrow 10$. The dashed lines represent the boundary of the supercell.

the atom numbering 1 interacts with atoms A, B, C, D, E outside the supercell, their translational equivalents inside the supercell are atom 5,11,15,12,10, respectively. The Hamiltonian matrix element $H_{1, A}$ refers to $H_{1,5}$ in the layout of the Hamiltonian matrix for the supercell, namely,

$$H_{1,5} = H_{1, A} \; . \tag{1}$$

For the overlap matrix we have the similar relation

$$S_{1,5} = S_{1, A} \; . \tag{2}$$

All the interactions for the atoms near the boundary of the supercell are treated in this way to recover the periodicity of the supercell.

When we handle the problem of dislocations in semiconductors, because the translational symmetry along the dislocation line is retained, it is essential to know the dispersion of the bound band induced by the dislocation along the dislocation line. Thus we choose the Bloch sums of the atomic rows parallel to the dislocation line as basis set and the Bloch sums with different symmetries on the sites of dislocation core as the seed states. The basis set has only translational symmetry along the one-dimensional Brillouin zone and the translational symmetry in the plane perpendicular to the dislocation line reduces to the artificial periodicity of the supercell. For surface and interface problems in semiconductors, we deal with the translational symmetry in two-dimensional space the basis sets and seed states in the recursion computation should be taken as complex two-dimensional Bloch sums. The periodic condition of the supercell along the direction perpendicular to the surface is introduced by periodically repeated slabs with two surfaces and vacuum, the thicknesses of the slab and the vacuum layers are chosen so that the interactions between the surface states are decoupled.

III. BAND DISPERSION FOR GaAs
A. Unitary transformation

In the present section we demonstrate how to transform the complex Bloch-sum basis set to a real basis set in the recursion calculation of the band structure for

GaAs. In thé empirical tight-binding parametrized model, we employ the k-dependent Bloch sums as a basis set; it will be straightforward to deduce the partial density of states and the band dispersion from the recursion coefficients.

The recursion calculation has many advantages in that it can save very much of the storage capacity of the computer and its connection to the local density of states via Green's function expressed as a continued fraction is simple and concise. The recursion method is applicable to many physics problems, especially it is particularly powerful for large low-symmetry complicated systems such as impurity complexes with lattice relaxation, dislocations, surfaces, interfaces, and so on. From physical considerations, we choose a complex basis set, while for computational simplicity, it is usually desirable to avoid complex computations, especially when we encounter the nonorthogonality of the overlap matrix. We choose the Bloch sums formed from the quasiatomic functions $|nbR_i)$

$$|nb\mathbf{k})=N^{-1/2}\sum_i \exp(i\mathbf{k}R_i+i\mathbf{k}V_b)|nbR_i) \tag{3}$$

as basis set to construct the zinc-blende-structure tight-binding Hamiltonian. The quantum number n runs over the s, p_x, p_y, p_z, and s^* orbitals: the N wave vectors k lie in the first Brillouin zone, the site index b is either a (for anion) or c (for cation), the anion position is R_i, and in terms of the Kronecker δ, we have $V_b=\delta_{b,c}(a_l/4)(1,1,1)$. The quasiatomic functions are Löwdin orbitals: symmetrically orthogonalized atomic orbitals. The Schrödinger equation for the Bloch function $|k\lambda)$ is

$$[H-\varepsilon(\mathbf{k}\lambda)]|\mathbf{k}\lambda)=0 \tag{4}$$

or, in this basis,

$$\sum_{m,b'} [(nb\mathbf{k}|H|mb'\mathbf{k})-\epsilon(\mathbf{k}\lambda)\delta_{n,m}\delta_{b,b'}](mb'\mathbf{k}|\mathbf{k}\lambda)=0 . \tag{5}$$

The solutions are

$$|\mathbf{k}\lambda)=\sum_{n,b} |nb\mathbf{k})(nb\mathbf{k}|\mathbf{k}\lambda) . \tag{6}$$

The Hamiltonian matrix elements take the following form:

$$(nb\mathbf{k}|H|mb'\mathbf{k})=\sum_{i,b} \exp[i\mathbf{k}(R_j-R_i)+i\mathbf{k}(v_{b'}-v_b)]$$
$$\times(nbR_i|mb'R_j) . \tag{7}$$

The Hamiltonian matrix is a complex Hermitian matrix. In the case of GaAs, because in the unit cell there are only two atoms (one anion and one cation), the size of the Hamiltonian matrix is 10×10 and the structure of the Hamiltonian takes the following form:

$$H=\begin{bmatrix} H_{a,a} & H_{a,c} \\ H_{c,a} & H_{c,c} \end{bmatrix} . \tag{8}$$

The layout of the submatrix $H_{a,c}$ is as follows:

$$H_{a,c}=\begin{bmatrix} H_{s,s}^{a,c} & H_{s,p_x}^{a,c} & H_{s,p_y}^{a,c} & H_{s,p_z}^{a,c} & H_{s,s^*}^{a,c} \\ H_{p_x,s}^{ac} & H_{p_x,p_x}^{a,c} & H_{p_x,p_y}^{a,c} & H_{p_x,p_z}^{a,c} & H_{p_x,s^*}^{a,c} \\ H_{p_y,s}^{a,c} & H_{p_y,p_x}^{a,c} & H_{p_y,p_y}^{a,c} & H_{p_y,p_z}^{a,c} & H_{p_y,s^*}^{a,c} \\ H_{p_z,s}^{a,c} & H_{p_z,p_x}^{a,c} & H_{p_z,p_y}^{a,c} & H_{p_z,p_z}^{a,c} & H_{p_z,s^*}^{a,c} \\ H_{s^*,s}^{a,c} & H_{s^*,p_x}^{a,c} & H_{s^*,p_y}^{a,c} & H_{s^*,p_z}^{a,c} & H_{s^*,s^*}^{a,c} \end{bmatrix} . \tag{9}$$

We can separate the real and imaginary parts of the submatrix as

$$H_{a,c}=H_r^{a,c}+iH_i^{a,c} . \tag{10}$$

The matrices $H_r^{a,c}$ and $H_i^{a,c}$ are 5×5 matrices which are, respectively, the real and imaginary parts of matrix (9). In our case, because the quasiatomic functions are orthogonalized, the overlap matrix is a unit matrix, otherwise, it is also a complex Hermitian matrix.

In the recursion calculation, we wish to avoid complex computation, so we make a unitary transformation to the Hamiltonian matrix, so that the complex Hermitian matrix becomes a real symmetric matrix. The unitary transformation takes the following form:

$$U=\frac{1}{\sqrt{2}}\begin{bmatrix} l & l \\ -i & i \end{bmatrix} . \tag{11}$$

Because of the time-reversal symmetry, the eigenvalues of the Hamiltonians for k and $-k$ are equal, we can construct a large Hamiltonian by combining the two Hamiltonians without changing the eigenvalues of the physical problem:

$$H^b=\begin{bmatrix} H(\mathbf{k}) & 0 \\ 0 & H(-\mathbf{k}) \end{bmatrix} . \tag{12}$$

The Hamiltonian matrix after the transformation becomes

$$H'=U^{\dagger}H^bU$$
$$=\frac{1}{2}\begin{bmatrix} H(\mathbf{k})+H(-\mathbf{k}) & iH(\mathbf{k})-iH(-\mathbf{k}) \\ -iH(\mathbf{k})+iH(-\mathbf{k}) & H(\mathbf{k})+H(-\mathbf{k}) \end{bmatrix} . \tag{13}$$

After the unitary tranformation, the submatrix (9) in (13) becomes

$$H'_{a,c}=\begin{bmatrix} H_r^{a,c} & -H_i^{a,c} \\ H_i^{a,c} & H_r^{a,c} \end{bmatrix} . \tag{14}$$

The size of this submatrix is 10×10. The Hamiltonian matrix (13) is a real symmetric matrix and its size is 20×20.

In the recursion calculation we should choose a starting state. The same starting state for Hamiltonian matrices (7) and (13) differs by the unitary transformation (11).

If we choose an s-symmetric Bloch sum on the anion

position, the seed state for Hamiltonian (7) can be expressed as a column vector

$$W^\dagger = (1,0,0,0,0,0,0,0,0,0) \ . \tag{15}$$

After the unitary transformation (11) the seed state becomes

$$W'^\dagger = (1,0,0,0,0,1,0,0,0,0,0,0,0,0,0,0,0,0,0,0) \ . \tag{16}$$

Both the seed state (16) and Hamiltonian matrix (13) are real so the recursion calculation can proceed with a real computation.

B. Recursion calculation

The recursion procedure as given by Haydock, Heine, and Kelly[8] is a powerful approach for any physical system especially for the low-symmetry complicated systems. The approach is based on a tight-binding description of the systems. The recursion model is specified by a sequence of S orthonormal orbitals $\{u_0, u_1, \cdots \}$,

$$u_m^\dagger S u_n = \delta_{m,n} \ . \tag{17}$$

u_0 is the starting state for the recursion calculation and S is the overlap matrix of the local orbitals. The two sets of real recursion coefficients $\{a_0, a_1, \cdots \}$ and $\{b_1, b_2, \cdots \}$ are calculated according to the following recurrence relation:

$$b_{n+1} S u_{n+1} = H u_n - a_n S u_n - b_n S u_{n-1} \ . \tag{18}$$

The two sets of recursion coefficients are the diagonal and off-diagonal elements of the tridiagonal Hamiltonian matrix.

The calculation of the recursion coefficients can proceed as follows. First choose a suitable seed state u_0 and calculate

$$a_0 = u_0^\dagger H u_0 \ ,$$
$$b_1 = [(u_0^\dagger H - a_0 u_0^\dagger S) S^{-1} (H u_0 - a_0 H u_0)]^{1/2} \ , \tag{19}$$
$$u_1 = S^{-1}(H u_0 - a_0 S u_0)/b_1 \ .$$

For the next step we have

$$a_1 = u_1^\dagger H u_1 \ ,$$
$$b_2 = [(u_1 H - a_1 u_1^\dagger S - b_1 u_0^\dagger S)$$
$$\times S^{-1}(H u_1 - a_1 S u_1 - b_1 S u_0)]^{1/2} \ , \tag{20}$$
$$u_2 = S^{-1}(H u_1 - a_1 S u_1 - b_1 S u_0)/b_2 \ .$$

The difficult problem is the inversing of the overlap matrix, if the matrix is not a unit matrix. Usually the overlap matrix is a large sparse matrix; a specially designed algorithm is available for its inversing. The algorithm which efficiently exploits the sparseness of the overlap matrix only takes a minimum storage capacity of the computer but requires the reality of the matrix.

The diagonal element of Green's function can be expressed as a continued fraction:

$$G_0(E) = \cfrac{1}{E - a_0 - \cfrac{b_1^2}{E - a_1 - \cfrac{b_2^2}{E - a_2 \cdot \cdot \cfrac{b_{n-1}^2}{E - a_{n-1} - \cfrac{b_n^2}{E - a_n - \cdot \cdot}}}}} \tag{21}$$
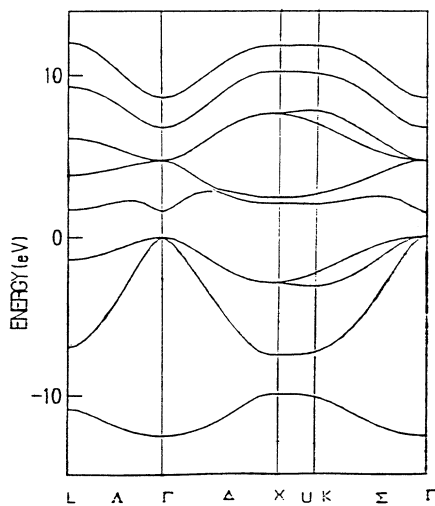

FIG. 2. The band structure of GaAs in special points and along the symmetrical lines in the Brillouin zone.
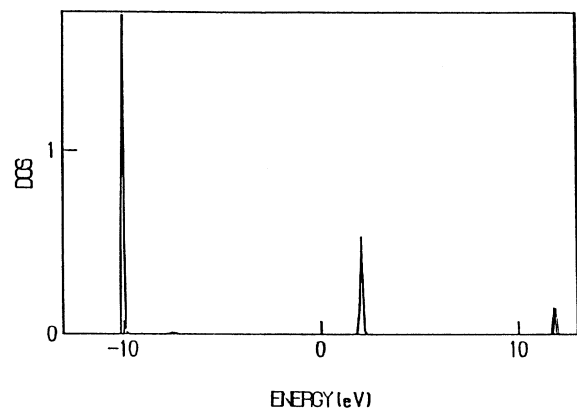

FIG. 3. The partial density of states for Bloch sum with s symmetry at anion position in the unit cell. The sharp peak at the bottom of the valence band shows a strong s character of the band level.
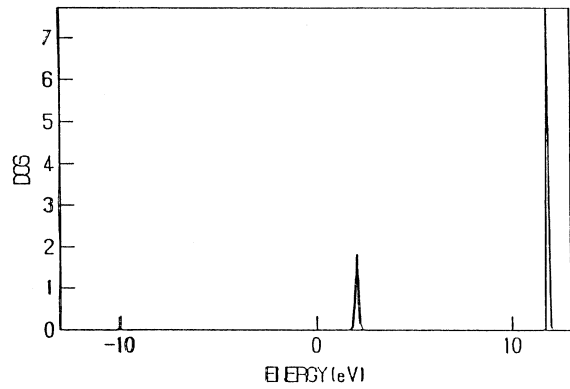
FIG. 4. The partial density of states for the Bloch sum with s^* symmetry at cation position in the unit cell. The peaks illustrate that the s^* orbital is important for the description of the conduction band.

FIG. 6. The partial density of states for bonding combination of the Bloch sums with p symmetry at anion and cation positions in the unit cell. The peak at the top of the valence band demonstrates that the top of the valence band is mainly bonding character with p symmetry.

The local density of states is

$$n_0(E) = \lim_{\epsilon \to 0} \left[-\frac{1}{\pi} \mathrm{Im} G_0(E + i\epsilon) \right] . \tag{22}$$

We carried out a diagonalization calculation for Hamiltonian (7); the Hamiltonian matrix elements are taken from Vogl et al.[9] It is an empirical tight-binding approach and the interactions are taken into account up to nearest neighbors.

In Fig. 2 we display the band-structure diagram of GaAs. Because we employ the s,p^3,s^* quasiatomic orbitals both the valence and conduction bands are well described.

Then we have performed a complex recursion calculation by using the complex Hamiltonian (7) and various seed states with the structure (15). Moreover, we have also made a real recursion calculation by using the real symmetric Hamilt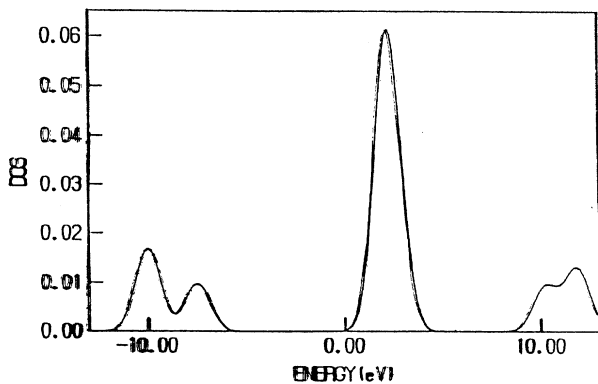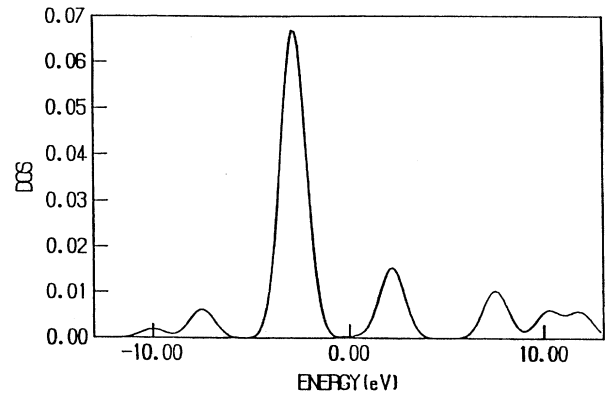onian (13) and corresponding seed states with the structure (16). The results and the computer time needed for the two calculations are the same.

In our case, because the overlap matrix is a unit matrix, the merits of the real algorithmn are not manifest. In the case of a nonorthogonal basis set, the real algorithm would be very much superior.

In Figs. 3 and 4 the partial densities of states are shown for seed states with s-symmetric and s^*-symmetric Bloch sums on the anion position, respectively. From Fig. 3 we can conclude that the bottom of the valence band is mainly s symmetric and Fig. 4 shows that the s^*-symmetric quasiatom orbital is important for the description of the conduction band. In Figs. 3 and 4, the k point is taken at the so-called Baldereschi point in the Brillouin zone, which is the average point in the Brillouin zone:

$$(2\pi/a)(0.622, 0.295, 0) ,$$

where a denotes the lattice constant.

In Fig. 5 we display the partial density of states with the seed state of antibonding combination for s- and s^*-symmetric Bloch sums on both the anion and cation positions. The sharp peak at the bottom of the conduction band means that the bottom of the conduction band is s symmetric and of antibonding character.

In Fig. 6 the partial density of states with seed states of bonding combination for p^3-symmetric Bloch sums on the anion and cation positions is displayed. The sharp peak at the top of the valence band shows that the top of the valence band is p symmetric and of bonding character.

In our recursion calculation, we choose the k-dependent Bloch sums as seed states and transform the complex Hamiltonian matrix and seed states into a real matrix and column vector; we can extract not only the band dispersion of the band structure but also the intrinsic symmetry of the band levels.

FIG. 5. The partial density of states for antibonding combination of the Bloch sums with s and s^* symmetry at anion and cation positions in the unit cell. The peak at the bottom of the conduction band shows that the band level is mainly antibonding character with s and s^* symmetry.

IV. SUMMARY

In the present paper the treatment of the supercell boundary has been discussed. When the basis set for the recursion approach is real, the periodic condition on the boundary of the supercell is taken into account by the reflection of the recursion wave on the boundary, so that we can restrict the calculation within the supercell. When the basis set for the recursion calculation is complex and **k** dependent, the periodic conditions are considered by the periocity of the Bloch sums and the reflection on the boundary of the supercell, if the Brillouin zone is less than three-dimensional.

We have extended the recursion calculation from real space to reciprocal space. Starting from the **k**-dependent Bloch-sum basis set, we can extract not only the band dispersion from the partial density of states but also the symmetric components contained in the particular band levels.

In order to avoid the complex computation, we have introduced a unitary transformation to the complex **k**-dependent Hamiltonian matrix and the basis set. By this transformation, the physical characteristic of the system is not changed, while the complex Hermitian Hamiltonian matrix become a real symmetric matrix of doubled dimensions. At the same time, the complex seed states undergo the same unitary transformation and become real column vectors.

One of the advantages of this transformation is that the calculation of the recursion coefficients can proceed within real computation so that the algorithm leads to easy programming. Especially when the basis set is nonorthogonal and the inverse of the overlap matrix is required in the calculation of recursion coefficients, the real computation can efficiently exploit the sparseness of the overlap matrix and significantly reduce the storage capacity of the computer, so that we can choose a larger supercell. For some physical problems, a larger supercell can be crucial for decoupling the interactions between defects in neighboring supercells.

The Bloch sums are no longer localized wave functions, while in the usual recursion approach, the localized atomic orbitals are taken as basis set. In the present paper, we have extended the recursion approach from real space to reciprocal space and extended the basis set in the recursion calculation from a localized orbital set to an extended wave-function set. The complex Bloch sums are taken as basis set in the recursion approach. They do not cause problems in convergence. The Bloch-sum-type basis set is based on tight-binding localized orbitals.

The convergence of the recursion coefficients depends on the degree of localization of the tight-binding orbitals (how many neighbors the interaction extends up to). For the supercell model it turns out that the larger the supercell, the more rapidly the recursion coefficients converge. In fact, the essential factor for the convergence of the recursion coefficients is the sparseness of the overlap and Hamiltonian matrices. Sparser overlap and Hamiltonian matrices results in a faster converging of the recursion coefficients.

[1] R. Haydock, in *Solid State Physics; Advances in Research and Applications,* edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35, p. 215.

[2] P. J. Lin-Chung and T. L. Reinecke, Phys. Rev. B **27**, 1101 (1983).

[3] Wang Yong-Liang and U. Lindefelt, Phys. Rev. B **37**, 1320 (1988).

[4] Wang Yong-Liang, Phys. Rev. B **40**, 5669 (1989).

[5] U. Lindefelt and Wang Yong-Liang, Phys. Rev. B **38**, 4107 (1988).

(1988).

[6] H. Veth and H. Teichler, Philos. Mag. B **49**, 371 (1984).

[7] Yong-Liang Wang and H. Teichler, Phys. Status Solidi B **154**, 649 (1989).

[8] R. Haydock, V. Heine, and M. J. Kelly, J. Phys. C **8**, 2591 (1975).

[9] P. Vogl, Harold P. Hjalmarson, and John D. Dow, J. Phys. Chem. Solids **44**, 365 (1983).