Calculation of defect states in semiconductor crystals by recursion method

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The termination method of recursion coefficients (continued-fraction technique) for semiconductor crystals is carefully examined using model density of states (DOS) and exact recursion coefficients. It is shown that the linear prediction method tends to produce spurious peaks in the DOS when a δ-function-like band-gap state appears or when a band-edge singularity exists. We point out that further improvement of the termination method is required for such calculations (if gap states exist). We propose an efficient termination method based on perturbation theory and an averaging procedure.

Recently there has been considerable interest in the study of electronic structure of lattice defects in semiconductor crystals.[1] Particular attention has been focused on the determination of band-gap states associated with the defects in the semiconductors.[2] This is due to the fact that the gap states play an essential role in determining the various physical (e.g., electrical and mechanical) properties of the semiconductor crystals.

For simple lattice defects such as impurities or point defects in the semiconductors, the theoretical calculations are usually successful and helpful in interpreting the corresponding experimental results.[3-5] For the complex extended defects (e.g., dislocations and grain boundaries), however, theoretical schemes are very limited and fully quantitative results have not been obtained. The supercell method[6] or linear combination of atomic orbitals (LCAO) recursion method[7-9] can be applicable to the electronic-structure calculation of these extended defects, but both methods have certain drawbacks and calculational difficulties. In the former method, supercells are usually too small to obtain the accurate result of the lattice defects, while in the latter method it is not possible to calculate infinite numbers of the recursion coefficients (a_n, b_n) and it is required to use an appropriate termination method.

Recently, the termination method based on first-order perturbation (FOP) theory[10,11] has been used to calculate the electronic structure of various lattice defects in semiconductor crystal. The explicit expression of the termination function is derived from FOP theory

$$G_{ll}=g+(1/b)\exp(-2i\phi)\sum_{n=0}^{\infty}\exp(-in\phi)\alpha_{n+2l-1}\ , \tag{1}$$

where

$$g=\{(E-a)-i[4b^2-(E-a)^2]^{1/2}\}/2b^2\ , \tag{2}$$

$$\phi=\cos^{-1}[(E-a)/2b]\ , \tag{3}$$

$$\alpha_{2n-1}=(a_n-a)/b\ , \tag{4}$$

$$\alpha_{2n}=2(b_n-b)/b\ . \tag{5}$$

In the above Eqs. (2)–(5), a and b are the asymptotic coefficients (or center of the undamped oscillation of the recursion coefficients) of a_n and b_n, respectively. In addition, some modifications must be made so that real problems can be treated: The termination function G_{ll} is fitted to the first known recursion coefficients (a_n, b_n), $n \lesssim 20$. It is generally believed that the procedure allows the detection of any peak in the DOS associated with the defect. However, in the present paper we point out that such a linear termination (perturbative) method tends to produce spurious structure in the DOS when a δ-function-like band-gap state appears or band-edge singularity exists. To show this, we consider several examples for the electronic DOS with δ-function-like peak or band-edge singularity.

First, let us consider the linear atomic chain composed of A and B atoms, with atomic energy levels E_A and E_B, alternatively. For this semi-infinite linear system the electronic Green's function can be given exactly as

$$G_{AA}=\frac{(E-E_A)(E-E_B)-i[4t^2(E-E_A)(E-E_B)-(E-E_A)^2(E-E_B)^2]^{1/2}}{2t^2(E-E_A)}\ , \tag{6}$$

where the surface is terminated by A atom and t denotes the transfer integral between atoms A and B. A similar expression is also given for the surface Green's function G_{BB}. The local DOS on the surface atom A $\rho_A(E)$, can be calculated straightforwardly from the imaginary part of the Green's function G_{AA}. We present in Fig. 1 the $\rho_A(E)$ curve for the parameter values $E_A=-E_B=1.0$ and $|t|=4.0$ (energies are given in units of one-fourth of the hopping integral t). The exact $\rho_A(E)$ curve in Fig. 1(c) shows the band gap for the energy region $E_B \le E \le E_A$.

In Fig. 1 we also present the approximate local DOS for the surface atom A, calculated by using the recursion method: Figs. 1(a) and 1(b) are obtained with the use of the so-called constant (square-root) termination method and the linear termination method based on the FOP theory,[10,11] respectively. The exact recursion coefficients (a_n, b_n) are taken into account up to $n=30$ in both DOS curves. For the $\rho_A(E)$ calculation in Fig. 1(b), the termination function $G_{ll}(l=31)$ is given by

$$G_{ll}=g+(1/t)^2\exp(-2i\phi)[E_A+E_B\exp(-2i\phi)]/[1-\exp(-4i\phi)] . \quad (7)$$

For the constant termination scheme, the termination function G_{ll} simply becomes g.

In Fig. 1(a), one can observe the prominent oscillations in the DOS curve. This oscillation is a direct consequence of using the constant termination method for the DOS with band gaps: Physically it is due to the abrupt matching between the known coefficients and the constant ones.[11] It is known that this type of oscillation in the DOS can be removed almost completely by using the better approximation for the termination method.[12-14] However, it is noted that the oscillations cannot be avoided within the theoretical scheme using the FOP theory, as shown in Fig. 1(b). This is because the FOP theory does not work well for the electronic DOS with the band-edge (Van Hove) singularity.

Second, we consider the electronic DOS having a δ-function-like band-gap state. For this example we take a linear atomic chain with adsorbed atoms at the surface. In Fig. 2 we present the electronic DOS on the atom B adsorbed on the surface of $BABA\cdots$ linear chain (i.e., B atom in the configuration of $\underline{B}BABA\cdots$). We now have a band-gap state at $E=0.66$, without the band-edge singularity.

Figures 2(a) and 2(b) are calculated by using the constant termination method and the linear termination method based on the FOP theory, respectively; Fig. 2(c) gives the exact DOS. In these DOS calculations exact recursion coefficients (a_n, b_n) up to $n=30$ level (30 pairs of the coefficients) are taken into account. The DOS $\rho_B(E)$ obtained by using the constant termination method shows the unphysical oscillations again, which are absent in the exact DOS curve in Fig. 2(c). These marked oscillations in the DOS are not removed when we use the linear termination method based on the FOP theory, as shown in Fig. 2(b).

In order to investigate the DOS behavior with increasing number of exact recursion coefficients, we have also calculated the local DOS $\rho_B(E)$ on site B in the configuration of $\underline{B}BABA\cdots$, by systematically changing the number of levels n in the continued fraction. The electronic DOS $\rho_B(E)$ thus calculated for $n=25$, 60, and 200 is presented in Figs. 3(a)–3(c), respectively. One can see in Fig. 3 that the unphysical oscillations in the DOS are suppressed gradually with increasing the number of levels n. However, it should be noted that the spurious oscillations or peaks survive even in the DOS obtained for $n=200$ (for real problems it is usually not possible to calculate the exact coefficients up to this level).

The DOS calculations presented in Fig. 3 also give us the information regarding the separation of the gap states from the band edge (band region). In fact as shown in Fig. 3(a) ($n=16$) or in Fig. 2(b) ($n=30$), the gap state (located near the center of the gap region) is not separated from the band edge of the upper "conduction" band, if we terminate the continued fraction at the level $n \lesssim 30$. In order to separate the δ-function-like gap state from the band region, it is required at least to calculate exact recursion coefficients up to the $n \simeq 50$ level; DOS calculations with the $n \simeq 30$ level would be insufficient for the detection of the defect states (gap states) in the semiconductor crystals.

We now discuss the convergence of the perturbation expansion for the electronic Green's function. For this purpose, we take into account the second-order perturbation (SOP) contributions $G_{ll}^{(2)}$ to the termination function G_{ll}, and calculate the local DOS using the same model as in Fig. 3. The termination function $G_{ll}^{(2)}$ based on the

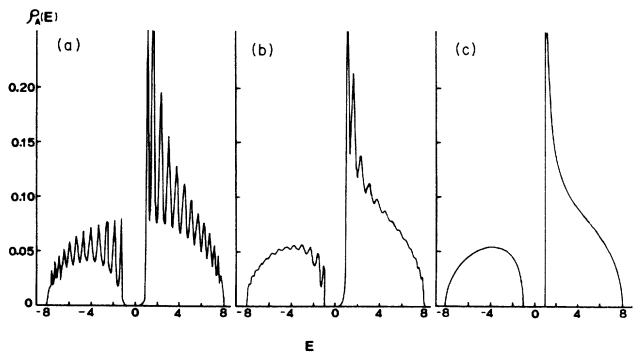

FIG. 1. Local DOS $\rho_A(E)$ for surface atom A of the linear chain $ABAB\cdots$. DOS curve (a) and (b) are obtained by using the constant termination method and the linear termination method, respectively. Curve (c) shows the exact DOS. Exact recursion coefficients are calculated up to $n=30$ level.

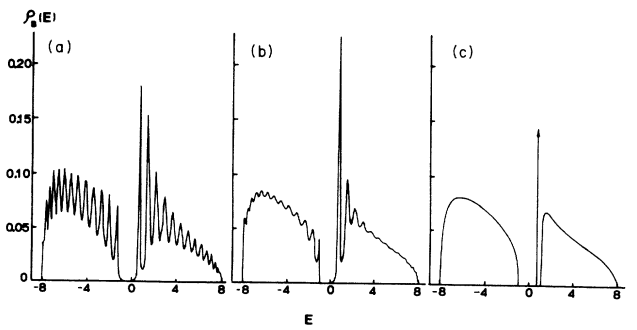

FIG. 2. Local DOS $\rho_B(E)$ for adsorbed atom B on the surface $BABA\cdots$ ($\underline{B}BABA\cdots$). DOS curves (a), (b) and (c) are the same as in Fig. 1.

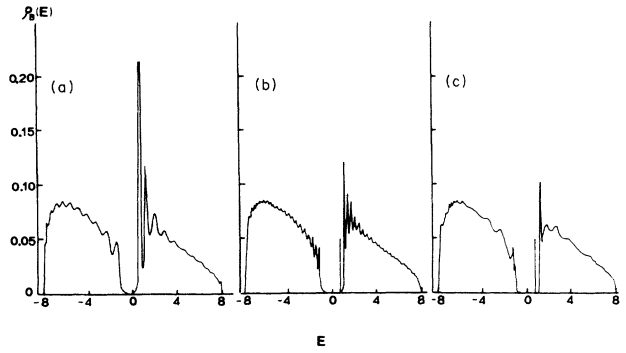

FIG. 3. Local DOS $\rho_B(E)$ for adsorbed atom B on the surface $BABA\cdots$ ($\underline{B}BABA\cdots$), calculated by using the linear termination method. Exact recursion coefficients are taken into account up to (a) $n=16$, (b) $n=60$, and (c) $n=200$ levels.

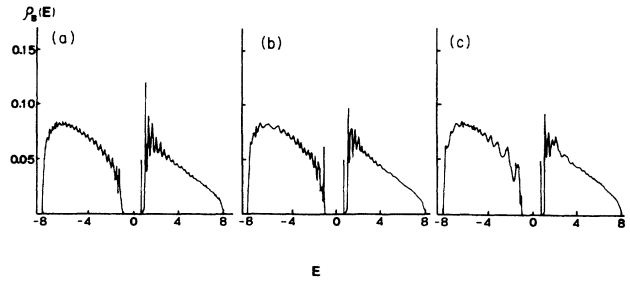

FIG. 4. Local DOS $\rho_B(E)$ for adsorbed atom B on the surface $BABA\cdots$ ($\underline{B}BABA\cdots$) calculated by using the exact recursion coefficients of $(a_n, b_n;\ n \leq 60)$. $G_{ll}^{(2)}$ functions are taken into account for curves (b) and (c), while curve (a) is calculated without $G_{ll}^{(2)}$ contribution.

SOP theory is given as

$$G_{ll}=g+G_{ll}^{(1)}+G_{ll}^{(2)}\ , \tag{8}$$

where

$$G_{ll}^{(2)}=(1/t^3)\sum_{m=1}^{\infty}E_{l+m-1}e^{-(2m+1)\phi i}\left[\sum_{p=1}^{m-1}E_{l+p-1}e^{-(p-1)\phi i}D_p(\phi)\right.$$
$$\left.+D_m(\phi)(E_{l+m-1}e^{-(m-1)\phi i}+E_{l+m}e^{-(m+1)\phi i})/(1-e^{-4\phi i})\right] \tag{9}$$

with

$$D_p(\phi)=\begin{cases}2\sum_{q=1}^{p/2}\cos[(2q-1)\phi], & \text{for even } p \quad (10a)\\ 1+2\sum_{q=1}^{(p-1)/2}\cos(2q\phi), & \text{for odd } p\ . \quad (10b)\end{cases}$$

In the above Equation (5), E_i takes either E_A or E_B, and m, p, and q are positive integers. $G_{ll}^{(1)}$ is the termination function of the FOP theory, and given by the second term of Eq. (7).

In Fig. 4 we present the local DOS for the adsorbed B atom on the $BABA\cdots$ surface (same adsorption geometry as in Fig. 3), calculated by using the exact recursion coefficients of $(a_n, b_n;\ n \leq 60)$. The second-order $G_{ll}^{(2)}$ functions are taken into account for curves b and c, in the range of recursion levels of (l to $l+100$) and (l to $l+200$), respectively: the DOS curve a is calculated without the $G_{ll}^{(2)}$ contribution. Though the inclusion of the second-order $G_{ll}^{(2)}$ function suppresses, to some extent, the spurious structure in the DOS, it is still insufficient to detect correctly the characteristic peaks or gap states of the lattice defects (indicating the slow convergence of perturbation expansion).

In order to investigate more general defect states (two δ functions) in covalent semiconductors, we adopt the more realistic sp-hybrid orbital model.[15] The Hamiltonian of the sp-hybrid linear chain can be described by the intra-atomic overlap integral V_1 and the interatomic hopping integral V_2. The model interface (grain) boundary is introduced in the lattice by changing the hopping integral from V_2 to $\tilde{V}_2$ between the hybrid orbitals on the atomic sites at $i=0$ and $i=1$, as shown by the inset of Fig. 5(d). For this sp-hybrid lattice the first-order termination functions $G_{ll}^{(1)}$ can be given by

$$G_{ll}^{(1)}=(1/h^2)\exp(-3i\phi)[X_A+X_B\exp(-2i\phi)]/[1-\exp(-4i\phi)]\ , \tag{11}$$

where

$$h=(V_1+V_2)/2\ , \tag{12}$$

$$X_A=2(V_1-V_2)/(V_1+V_2)\ , \tag{13a}$$

and

$$X_B=2(V_2-V_1)/(V_1+V_2)\ . \tag{13b}$$

The second-order Green's function is also given in an explicit expression

$$G_{ll}^{(2)}=(1/h^3)\sum_{n=1}^{\infty} e^{-(2n+2)\phi i}X_n\left[2\sum_{p=1}^{n-1}D_p(\phi)e^{-p\phi i}(X_{p-1}e^{2\phi i}+X_p)+(X_{n-1}e^{2\phi i}+X_n)D_n(\phi)e^{-n\phi i}\right.$$
$$+(X_{n-1}e^{2\phi i}+2X_n+X_{n+1}e^{-2\phi i})D_n(\phi)e^{-n\phi i}/(1-e^{-4\phi i})$$
$$\left.+(X_ne^{2\phi i}+2X_{n+1}+X_{n+2}e^{-2\phi i})D_{n+1}(\phi)e^{-(n+1)\phi i}/(1-e^{-4\phi i})\right], \quad (14)$$

where X_n takes either X_A or X_B depending on the atomic orbitals.

In Fig. 5 we present the electronic structure on the α orbital ($i=0$) at the interface boundary with $V_1=2.0$, $V_2=2.185$, and $\tilde{V}_2/V_2=0.25$. For this set of parameters the band-gap-to-bandwidth ratio becomes 0.044, less than 0.05. The DOS curves (b) and (c) are obtained by using the FOP and SOP termination functions, respectively: The exact recursion coefficients are taken into account up to the $n=61$ level. Curve (c) is obtained by using the SOP termination function $G_{ll}^{(2)}$, which is calculated by Eq. (14) as a contribution of 180 atomic sites. Also shown in Fig. 5(d) is the exact local DOS. One can see in Fig. 5 that Shockley interface states (two δ functions) appear in the band gap due to the reduced hopping integral across the boundary layer. Here, it must be noted that in spite of small band-gap-to-bandwidth ratio (~ 0.04), many spurious peaks survive in the DOS curves (b) and (c) calculated by using the perturbative termination functions.

It is also possible to examine the applicability of perturbative termination method in the limit of zero gap width. For this purpose, we use the Hubbard model with a δ-function impurity state.[16] The model DOS is given by

$$\rho_{\rm im}(E)=C_1(2/\pi B^2)(B^2-E^2)^{1/2}+C_2\delta(E-E_0)\ , \quad (15)$$

where the band region extends over the energy range $-B\le E\le B$, and the coefficients C_1 and C_2 satisfy the condition $C_1+C_2=1$. For simplicity, we assume the symmetric case $C_1=C_2=\frac{1}{2}$ and $E_0=0$. For this case recursion coefficients (a_n,b_n) are analytically given as

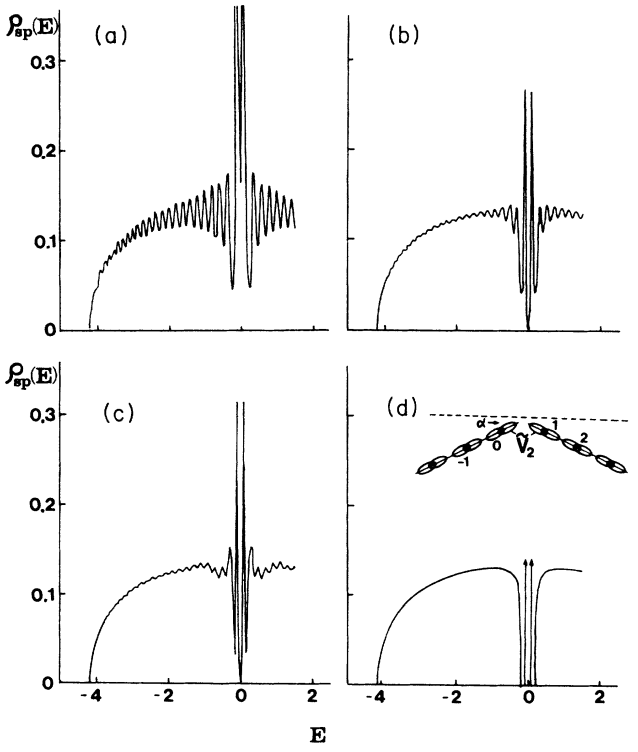

FIG. 5. Local DOS on α orbital of site 0 at the interface boundary, calculated by using (a) the constant, (b) FOP, and (c) SOP termination functions. The exact recursion coefficients are taken into account up to $n=61$ level. Curve (d) is the exact DOS. $\tilde{V}_2=V_2/4$ is used.

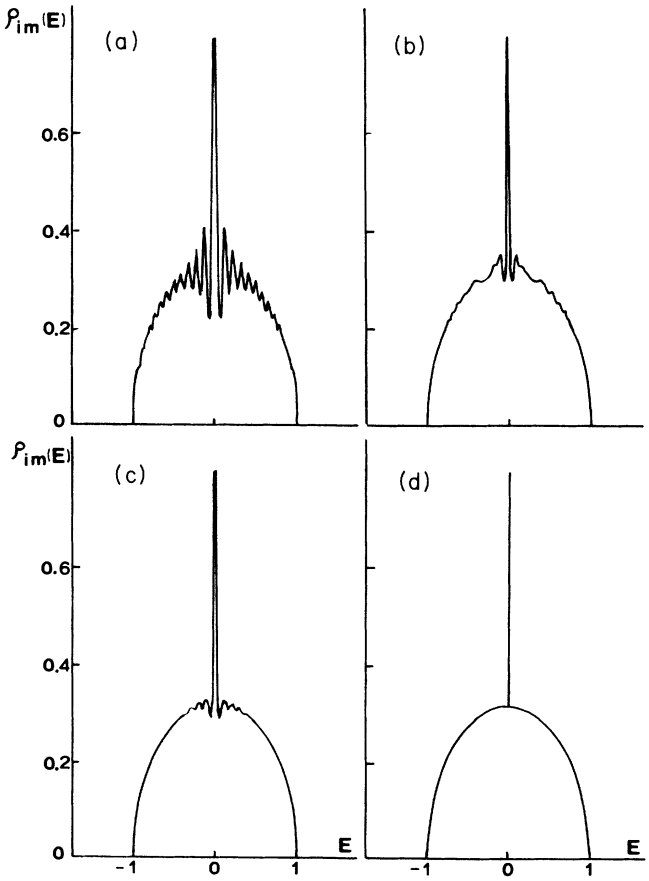

FIG. 6. Local DOS $\rho_{\rm im}(E)$ of Hubbard model with an impurity state: Approximate DOS by (a) constant termination and (b) and (c) linear termination method. (d) is the exact DOS.

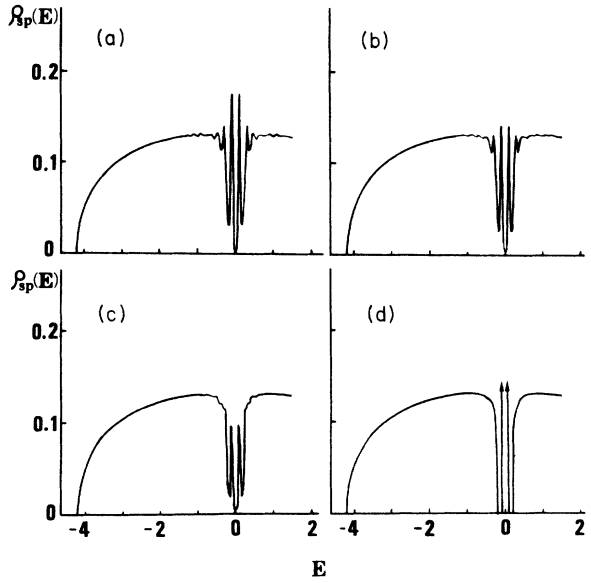

FIG. 7. Local DOS on α orbital of site 0 at the interface boundary, calculated by using the FOP terminating function and averaging procedure. Curves (a), (b), and (c) are calculated from 10, 15, and 25 successive DOS. (d) is the exact DOS. $\tilde{V}_2 = V_2/4$ is used.

$$b_n^2 = \begin{cases} (B^2/4)(n+1)/(n+3), & n=1,3,5,\ldots \quad (16a) \\ (B^2/4)(n+4)/(n+2), & n=2,4,6,\ldots, \quad (16b) \end{cases}$$

with $a_n = 0$. The coefficients b_n exhibit the damped oscillation and the asymptotic limit is $B^2/4$.

In Fig. 6 we present the approximate DOS curves calculated by using the constant termination method (a) and linear termination method based on the FOP theory (b) and (c), respectively; Fig. 6(d) shows the exact DOS. The energies are given in units of B. The DOS curves in Figs. 6(b) and 6(c) are obtained by using the approximate termination functions G_{ll}: The correction terms proportional to δb_n [Eq. (1)] are taken into account only in the finite region of n, i.e., $l+1 \le n \le l+N$. Specifically, N values are chosen to be 100 and 300 in Figs. 6(b) and 6(c), respectively. For damped oscillation of the recursion coefficients, these approximate termination functions are expected to work fairly well (compared to the exact termination function G_{ll} or fitted termination function as used by Mauger *et al.*[9]). In Figs. 6(b) and 6(c) one notices the unphysical oscillation around the δ-function peak. It is noted that the oscillation near the δ-function peak does not disappear even when we use the value of $N=300$ (or much larger N value). These oscillations in the DOS are considered to arise from the insufficient termination function of the perturbation theory.

Finally, we propose an efficient termination method to eliminate (or further suppress) spurious peaks in the DOS without extensive numerical computations. In view of the complexities of the higher-order perturbative terminating functions, we have tried to calculate the local DOS using the FOP theory and the averaging procedure. In Fig. 7 we present the averaged local DOS on the α orbital of site $i=0$ at the interface boundary, using the same parameter values as in Fig. 5. The DOS curves (a), (b), and (c) are averaged over 10, 15, and 25 successive DOS curves with recursion level $n \ge 61$, respectively; curve (d) being the exact DOS. One can see in Fig. 7 that spurious peaks disappear almost completely by using the FOP termination function and averaging procedure over a small number (~ 25) of successive DOS. This is due to the fact that the positions of the spurious peaks in the DOS vary systematically with varying the number of the recursion coefficients. The present termination procedure is found to be much more effective compared to that based on the constant termination method plus averaging procedure.[8] Using the latter method, it is difficult to remove the unphysical oscillations near the band edges. We have also found that the smoothed DOS structure is insensitive to the details of the averaging procedure.

In conclusion, we have presented several examples for the electronic DOS and examined the utility of the termination method using the exact recursion coefficients. The approximate DOS curves calculated by using the constant termination method and the perturbative termination method are compared to the exact ones. We have demonstrated that the linear termination method based on the FOP theory is unsatisfactory and leads to spurious structure in the DOS when a δ-function-like band-gap state appears or when band-edge singularity exists. To suppress the spurious structure in the DOS, it would be required to go beyond the FOP theory: It has been pointed out that the perturbative termination method coupled to the averaging procedure is very successful for the calculation of the defect energy levels. Calculations taking into account high-n-level coefficients are not always satisfactory and usually not practical.

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