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Density-of-states calculations within the recursion method

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We investigate methods to calculate projected density of states from a finite set of recursion coefficients. We consider tight-binding Hamiltonians describing the diamond-structure semiconductors α-Sn, Ge, Si, and C. Coefficients for about 110 levels of recursion are available for these Hamiltonians. Thus, we have coefficients for a sufficient number of recursion levels so that their asymptotic behavior is apparent. We first extrapolate the calculated coefficients using a linear predictive analysis suggested by Allan. This extrapolation is based on a perturbation theory that assumes that band gaps are small compared to the bandwidth. For α-Sn, Ge, and Si, which have band gap to bandwidth ratios (for the model Hamiltonians) of less than 0.05, the extrapolation procedure is found to be very successful. For C, however, with a band gap to bandwidth ratio of 0.106, large spurious features, which can be clearly associated with second-order perturbation terms, appear in the calculated density of states. We modify the extrapolation procedure using nonperturbative results for the asymptotic behavior of the recursion coefficients. The new extrapolation procedure gives good densities of states for C. Also, the calculated Green's function has the correct analytic structure.

I. INTRODUCTION

The recursion method[1,2] is an approach to calculate projected densities of states for one-electron Hamiltonians. An initial-state vector, on whose projection one wishes to calculate a density of states, is selected. Starting with this state, a new basis set and a series of recursion coefficients are generated by a three-term recursion relation. The Hamiltonian is tridiagonal in this new basis set and the recursion coefficients are the matrix elements of the Hamiltonian. From these matrix elements, the projected density of states is generated as a continued fraction. For an infinite system, the new basis set will, in general, have an infinite number of elements. In practice, of course, only a finite number of recursion levels can be calculated. Typically, the initially chosen state is localized in R space and as the recursion proceeds, the generated state functions spread out in R space. If the recursion calculation is performed in an R-space representation, the number of recursion levels that can be calculated in practice is limited by the size of the cluster of atoms that can be treated. In a typical calculation with a realistic model Hamiltonian, a cluster of a few thousand atoms may be considered, which allows about 10–20 recursion levels to be exactly determined. Recently, an approach to perform recursion calculations for translationally invariant systems in a K-space representation has been developed.[3] (Similar ideas had previously been discussed in the context of moment calculations.[4]) This approach allows a larger number of recursion levels to be evaluated. Calculations were performed[3] on realistic tight-binding Hamiltonians[5] describing diamond- and zinc-blende-structure semiconductors. For these Hamiltonians, 63 recursion levels were calculated exactly and ~ 110 recursion levels were accurately determined. Asymptotic behavior of the recursion coefficients set in after about 30–40 recursion levels.

For an infinite system, the projected density of states is expressed as an infinite continued fraction that contains the coefficients for an infinite number of recursion levels. Because only a finite number of recursion levels can be evaluated, the question of how to approximately calculate the projected density of states from a finite number of known recursion coefficients arises.[6–9] There have been two basic approaches to this problem.[8] The first is to terminate the continued fraction with an analytic expression that is based on the suspected asymptotic behavior of the recursion coefficients. Sometimes the calculated recursion coefficients are extrapolated in some way before the continued fraction is terminated. The second approach, usually called the quadrature method,[6] is best suited for evaluating integrals over the projected density of states. Here, we will concentrate on the termination approach.

Previous discussions of the termination approach can be divided into two general classes. In the first class, idealized model densities of states are considered.[8] This approach has the advantage that the asymptotic region of the recursion coefficients can be reached in the calculation and theorems concerning their asymptotic behavior are directly applicable. The disadvantage is that complexities that occur in physically realistic densities of states are not addressed. In the second class of discussions, realistic model Hamiltonians are used[9] and the complexities that occur in physically realistic densities of states are faced. However, the asymptotic behavior of the recursion coefficients is not reached in these calculations, and theorems concerning their behavior are, therefore, not directly applicable. In this paper, we take advantage of the recently developed K-space representation approach to recursion calculations,[3] which allows a large number of recursion levels to be calculated for realistic model Hamiltonians, to discuss the termination of continued fractions in recursion-method density-of-states calculations. A principal difference between the results presented here and previous results is that here we consider realistic model Hamiltonians *and* can calculate enough levels of recursion accurately so that the asymptotic behavior of the recursion coefficients is reached. Thus, complexities inherent in physically realistic densities of states (band gaps, internal Van Hove singularities, etc.) are faced and theorems describing the asymptotic behavior of the recursion coefficients are applicable.

We specifically consider model Hamiltonians, proposed by Vogl *et al.*,[5] to describe the group-IV semiconductors α-Sn, Ge, Si, and C (diamond phase). These materials are listed in order of increasing band gap. We apply a linear prediction analysis, first suggested by Allan,[9] which is based on perturbation theory to extrapolate the calculated recursion coefficients. The perturbation parameter in this analysis is the band gap divided by the bandwidth. We find that this approach is very suitable for α-Sn, Ge, and Si. For C, however, spurious features are introduced by this approach that can be clearly associated with second-order perturbation terms. We then describe a modification of Allan's approach,[9] which is based on nonperturbative results of Turchi *et al.*[10] for the asymptotic behavior of the recursion coefficients. We show that this approach eliminates the spurious features originally produced in the C density of states.

The paper is organized in the following way: in Sec. II, we apply linear predictive analysis to extrapolate the calculated recursion coefficients; in Sec. III, we present calculated density of states based on these extrapolated coefficients; in Sec. IV, we modify the extrapolation procedure and present density-of-states calculations based on this modified approach; and in Sec. V, we summarize our conclusions.

II. LINEAR PREDICTIVE EXTRAPOLATION OF RECURSION COEFFICIENTS

In the recursion method one starts with a one-electron Hamiltonian and a normalized state function U_0 and generates an orthonormal series of state functions U_n and recursion coefficients a_n and b_n by

$$\tilde{U}_{n+1}=(H-a_n)U_n-b_nU_{n-1}\ , \tag{1a}$$

$$a_n=\langle U_n\,|\,H\,|\,U_n\rangle\ , \tag{1b}$$

$$b_n=(\langle \tilde{U}_n\,|\,\tilde{U}_n\rangle)^{1/2}\ , \tag{1c}$$

$$U_n=\frac{\tilde{U}_n}{b_n}\ , \tag{1d}$$

with the initial condition

$$U_{-1}=0\ . \tag{1e}$$

Within the basis $\{U_n\}$, the Hamiltonian is tridiagonal with matrix elements given by Eq. (1b), and

$$\langle U_n\,|H\,|\,U_{n+1}\rangle=\langle U_{n+1}\,|H\,|\,U_n\rangle=b_{n+1}\ . \tag{2}$$

The U_0 diagonal matrix element of the Green's function,

$$G_0(E)=\langle U_0\,|\,(H-E)^{-1}\,|\,U_0\rangle\ , \tag{3}$$

can be expressed as a continued fraction involving the recursion coefficients

$$G_0(E)=\cfrac{1}{E-a_0-\cfrac{b_1^2}{\cfrac{\vdots}{E-a_{l-1}-b_l^2t_l(E)}}}\ . \tag{4}$$

Here, $t_{l(E)}$ represents a termination of the continued fraction after l levels of recursion. The projected density of states is found from $G_0(E)$,

$$\begin{aligned} n_0(E)&\equiv\sum_j\,|\,\langle U_0\,|\,\Psi_j\rangle\,|^2\delta(E-\varepsilon_j)\\ &=\frac{-1}{\pi}\mathrm{Im}G_0(E+i\delta)\ , \end{aligned} \tag{5}$$

where Ψ_j is an eigenstate of H with eigenvalue ε_j. Here, we are concerned with practical methods of terminating the continued fraction when about 100 levels of recursion coefficients are known. Our basic approach is to extrapolate the known coefficients based on an assumed asymptotic behavior. The extrapolated form is chosen so that after a large number of recursion levels, the coefficients reduce to a form for which an analytic terminating function is known.

Considerable effort has been spent in describing the asymptotic behavior of the recursion coefficients.[10–15] Using perturbation arguments, Hodges[11] has shown that internal Van Hove singularities in the projected density of states cause the recursion coefficients to oscillate sinusoidally with algebraically decaying amplitude ($l^{-3/2}$), about limiting values. Using similar perturbation arguments, Bylander and Rehr[13] and Turchi *et al.*[10] have shown that band gaps in the projected density of states cause the recursion coefficients to oscillate sinusoidally with undamped amplitude about average values. The oscillation frequency is related to the energy position of the feature that produced it. For internal Van Hove singularities, the oscillations decay with increasing recursion number, and the perturbation analysis must eventually (large enough recursion number) be valid. For band gaps, the oscillations do not decay with recursion number. The perturbation parameter is the band gap divided by the bandwidth. Higher than first-order terms in the perturbation parameter lead to additional oscillations, at different frequencies and smaller amplitude, in the recursion coefficients.

Based on the perturbation analyses[10,11,13] described above and following the work of Allan,[9] we write the recursion coefficients in the asymptotic region as

$$a_{l+l_0}=a+\sum_i |r_i|^{2l+1}4C_i\cos[(2l+1)\gamma_i+\phi_i]\ , \tag{6a}$$

$$b_{l+l_0}=b+\sum_i |r_i|^{2l}2C_i\cos[(2l)\gamma_i+\phi_i]\ , \tag{6b}$$

where l_0 is the smallest recursion level considered to be in the asymptotic region, $|r_i|$ is a number between zero and one, i labels the features (internal Van Hove singularities and band gaps) in the density of states, C_i gives the amplitude and γ_i the frequency of the oscillations, and a and b are the averaged values of a_n and b_n, respectively. On the basis of the perturbation analyses,[10,13]

$$M=a\ , \tag{7a}$$

$$B=4b\ , \tag{7b}$$

$$g_i=a+2b\cos(\gamma_i)\ , \tag{7c}$$

and

$$\Delta E_i=8C_i\ , \tag{7d}$$

where M is the energy center of the projected density of states, B is the bandwidth, g_i is the energy of an internal Van Hove singularity or the midgap energy of a bandgap, and ΔE_i is the magnitude of the band gap (does not apply for internal Van Hove singularities). Equation (6) does not exactly describe the asymptotic behavior for two reasons. First, and most important, it is based on a first-order perturbation analysis that assumes that band gaps are small. Second, the damping described by $|r_i|$ is exponential. The perturbation analyses argue that band gaps should lead to undamped oscillations, and internal Van Hove singularities should lead to algebraically damped oscillations. Operationally, however, the form of Eq. (6) is very convenient to use. The parameters contained in this equation can be extracted from a finite number of calculated recursion coefficients through linear predictive analysis.[9,16] The oscillations are damped so that the extrapolated recursion coefficients eventually approach constant values and the terminating functions for constant recursion coefficients are well known.[1] The undamped oscillations from band gaps can be modeled by taking a very slow damping rate ($|r_g|\lesssim 1$). In practice, strong oscillations in the recursion coefficients can be clearly associated either with band gaps or with deep dips in the density of states. Internal Van Hove singularities themselves, except to the extent that they are associated with gaps or dips, do not appear to have a strong influence on the recursion coefficients in the asymptotic region.

Given a finite set of calculated recursion coefficients, we extrapolate this set by fitting the form of Eq. (6) to the calculated coefficients of high recursion number. We consider the recursion coefficients and for α-Sn, Ge, Si, and C (diamond phase) calculated by the K-space method and presented in Ref. 3. These coefficients are exact through $l=63$ and are accurate through $l\sim 110$. We determine the parameters in Eq. (6) by the method of Allan.[9] First define

$$X_{2l+1}=\tfrac{1}{2}a_{l+l_0}\ , \tag{8a}$$

$$X_{2l}=b_{l+l_0}\ . \tag{8b}$$

Then, Eq. (6) can be written as

$$X_n=[\tfrac{1}{4}(2b+a)]+[\tfrac{1}{4}(2b-a)](-1)^n+\sum_j[C_je^{i\phi_j}(|r_j|e^{i\gamma_j})^n+\text{c.c.}]\ . \tag{9}$$

For a fixed set of X_n's, constructed from the calculated recursion coefficients, we invert the sum to find the basis functions $\{1,(-1),|r_j|e^{i\gamma_j},|r_j|e^{-i\gamma_j}\}$, and then the corresponding expansion coefficients $\{\tfrac{1}{4}(2b+a),\tfrac{1}{4}(2b-a),C_je^{i\phi_j},C_je^{-i\phi}\}$ as described in Ref. 9. The number of basis functions used is an input to the extrapolation procedure. It is possible to get real basis functions ($\gamma_i=0$) in addition to the conjugate pairs indicated in Eq. (9). Such functions do not have an interpretation of the perturbation theory analyses. We have always found the coefficients of such functions, when they do appear, to be very small.

In Tables I and II we show the basis functions and coefficients for the S-orbital and P-orbital recursion coefficients of Si, respectively. Also listed are the energies at which density-of-state features leading to the basis function's oscillation frequency should occur from Eq. (7c). In both cases the number of basis functions (including the fixed ones 1 and -1) was taken to be 16. For the S orbitals the fitting range was 48–99 and for the P orbitals it was 60–120. (There is a weak dependence of the results on the fitting range.) For the model Hamiltonian used here, Si has two band gaps: The main band gap of 1.16 eV centered at 0.58 eV (the valence-band maximum defines the energy zero for these Hamiltonians) and a small gap (an artifact of the model Hamiltonian) of 0.17 eV centered at 6.58 eV. There is also a cusp (zero) in the density of states at -8.27 eV. The coefficients of the fixed basis functions $(1,-1)$ give the bandwidth from Eqs. (9), (7a), and (7b). Because the bandwidth is the same for the S and P orbitals, one expects the coefficients of the

TABLE I. Silicon S-orbital basis functions.

$\lvert C_m\rvert$ (eV)	$\lvert r_m\rvert$	γ	g_m (eV)
2.83	1.00	0.00	
3.12	1.00	3.14	
0.159	0.999	−1.47	0.562
0.159	0.999	1.47	
0.001 11	0.877	−2.74	−11.5
0.001 11	0.877	2.74	
0.0158	0.993	−2.26	−8.19
0.0158	0.993	2.26	
0.004 83	0.936	−1.85	−3.92
0.004 83	0.936	1.85	
0.0381	0.968	−1.17	4.04
0.0381	0.968	1.17	
0.0689	0.993	−0.927	6.56
0.0689	0.993	0.927	
0.004 93	0.866	−0.456	10.1
0.004 93	0.866	0.456	

TABLE II. Silicon *P*-orbital basis functions.

$\|C_m\|$ (eV)	$\|r_m\|$	γ_m	g_m (eV)
2.83	1.00	0.00	
3.12	1.00	3.14	
0.152	0.9995	−1.47	0.588
0.152	0.9995	1.47	
0.001 71	0.955	−2.76	−11.6
0.001 71	0.955	2.76	
0.0185	0.987	−2.27	−8.22
0.0185	0.987	2.27	
0.0267	0.992	−1.78	−3.09
0.0267	0.992	1.78	
0.0654	0.627	−1.23	3.41
0.0654	0.627	1.23	
0.0530	0.997	−0.917	6.66
0.0530	0.997	0.917	
0.006 01	0.956	−0.571	9.44
0.006 01	0.956	0.571	

fixed basis functions to be the same for the two orbitals. From the first two rows of Tables I and II we see that this is indeed the case. For both orbitals, a large-amplitude very slowly damped pair[17] of functions can be clearly associated with the main band gap. These functions are listed in the third and fourth rows of Tables I and II. Pairs of functions clearly associated with the small second gap at 6.58 eV and the cusp at −8.27 eV occur for both orbitals. When the Si densities of states for these orbitals are shown, it will be seen that the pairs of functions with $g_m = -3.92$ and 4.04 eV for the *S* orbital and $g_m = -3.09$ and 3.41 eV for the *P* orbital can be associated with dips in the projected density of states for these orbitals. The other two pairs of basis functions ($g_m = -11.5$ and 10.1 eV for the *S* orbital and $g_m = -11.6$ and 9.44 eV for the *P* orbitals), which have rather small coefficients, cannot clearly be associated with density-of-states features. Note that it is gaps or dips in the density of states that show up in the asymptotic oscillations of the recursion coefficients. Internal Van Hove singularities, except to the extent that they are associated with gaps or dips, do not show up in the basis functions in this analysis.

The band edges can be determined from the coefficients of the fixed and the gap basis functions. We define E_1 and E_2 as the low- and high-energy edges of the density of states and G_1 and G_2 as the low- and high-energy edges of the main band gap. In Table III, we compare these energies for α-Sn, Ge, Si, and C determined by the coefficients of the basis functions[18] and by diagonalizing the Hamiltonian (essentially exact values). α-Sn does not have a band gap. Here, the value of $|r_m|$ for the gap function was set to unity before finding the coefficients. Thus, they differ slightly (~5%) from the values in Tables I and II for Si. This procedure improves slightly the description of the band-gap edges. From Table III, one sees that the band edges are accurately determined from the basis-function coefficients.

The number of basis functions is an input to the extrapolation method. Empirically, we have found the best results using between 14 and 18 functions (including the two fixed functions). This allowed the calculated recursion coefficients to be fit to within about 1% of the asymptotic oscillation amplitude. Using more basis functions, of course, allows a better fit over a finite range of coefficients. However, the extraction of the band edge parameters becomes less good and the extrapolation of the coefficients appears less satisfactory.

III. DENSITY-OF-STATES CALCULATIONS

The extrapolated recursion coefficients, described by Eq. (6), decay to constant values. From Tables I and II (and comparable results for the other materials considered), we see that oscillations from the basis functions describing the main band-gap decay rather slowly, whereas oscillations from the other basis functions decay much more rapidly. The termination function describing a continued fraction for constant recursion coefficients is well known:

$$t(E)=\frac{(E-a)-[(E-a)^2-4b^2]^{1/2}}{2b^2} . \qquad (10)$$

TABLE III. Band and gap parameters.

		E_1 (eV)	E_2 (eV)	G_1 (eV)	G_2 (eV)
Sn	*S*	−11.34	10.62		
	P	−11.34	10.62		
Theor.		−11.34	10.63		
Ge	*S*	−12.66	11.11	−0.09	0.78
	P	−12.65	11.12	−0.10	0.80
Theor.		−12.66	11.13	0.00	0.76
Si	*S*	−12.49	11.32	−0.05	1.18
	P	−12.49	11.33	−0.01	1.18
Theor.		−12.50	11.34	0.00	1.16
C	*S*	−27.22	22.49	−0.05	5.33
	P	−27.21	22.49	−0.05	5.32
Theor.		−27.27	22.61	0.00	5.31

In constructing projected densities of states from recursion coefficients, it is important that the nature of the coefficients not be abruptly changed. We therefore smooth between the calculated coefficients and the extrapolated coefficients and between the extrapolated coefficients and the constant values implied by Eq. (10). Let a_n (b_n) be the calculated coefficients, a_n^* (b_n^*) be the extrapolated coefficients [i.e., Eq. (6)], a (b) be the constant values, and $\tilde{a}_n$ ($\tilde{b}_n$) be the coefficients actually used in the density-of-states calculation. We take

$$\begin{aligned}\tilde{a}_n &= a_n, \quad n \le n_1\\ &= \frac{a_n(n_1+l_1-n)+a_n^*(n-n_1)}{l_1}, \quad n_1 \le n \le n_1+l_1\\ &= a_n^*, \quad n_1+l_1 \le n \le n_2\\ &= \frac{a_n^*(n_2+l_2-n)+a(n-n_2)}{l_2}, \quad n_2 \le n \le n_2+l_2\\ &= a, \quad n \ge n_2+l_2\ . \end{aligned} \tag{11}$$

The constant coefficients are included by the analytic expression in Eq. (10). Throughout the calculations we take $n_2=1500$ and $l_2=300$. There is virtually no dependence of the results on these choices. The values of n_1 and l_1 were chosen separately in each density-of-states calculation. There is a weak dependence of the results on the choice of n_1 and l_1.

Using these recursion coefficients, we calculate the projected densities of states using standard methods.[7] In Figs. 1 and 2, we compare the recursion density-of-states calculation for S and P orbitals of α-Sn with the results of Gilat-Raubenheimer (GR) integration.[19,20] The values $n_1=90$ and $l_1=20$ were used for both the S- and P-orbital calculations. The calculations using the recursion coefficients are very satisfactory. All features in the GR integration are reproduced. No spurious features occur. The only flaws are that the sharpest features in the GR integration are broadened a bit, and a little noise is introduced on smoothly varying parts of the spectrum. α-Sn is a favorable example for the extrapolation procedure described above. It has no band gaps, and the perturbation analyses, which suggest Eq. (6), are valid.

For materials with band gaps, the perturbation parameter in the analyses suggesting Eq. (6) is the ratio of band gap divided by bandwidth. We have performed calculations on Ge, Si, and C for which these numbers are 0.032, 0.049, and 0.106, respectively. In Figs. 3 and 4, we compare the recursion density-of-states calculation for S and P orbitals of Si with the results of GR integration. The values $n_1=90$, $l_1=20$, and $n_1=80$, $l_1=50$ were used for the S orbital and the P orbital, respectively. The calculations using the recursion coefficients are very satisfactory. The overall quality is about as good as for a α-Sn. All features of the GR integration are reproduced. The density of states does not go exactly to zero in the gap region. However, it does get extremely small and the band-gap edges are quite sharp and well defined. We performed

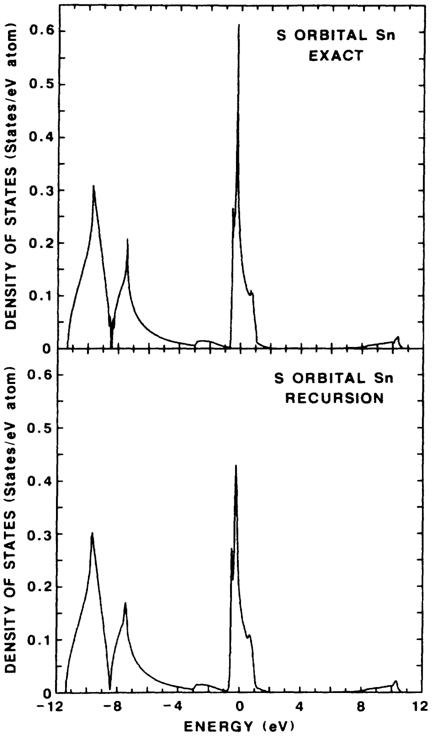

FIG. 1. S-orbital projected density of states in α-Sn calculated with the recursion method (lower panel) and by Gilat-Raubenheimer integration (upper panel).

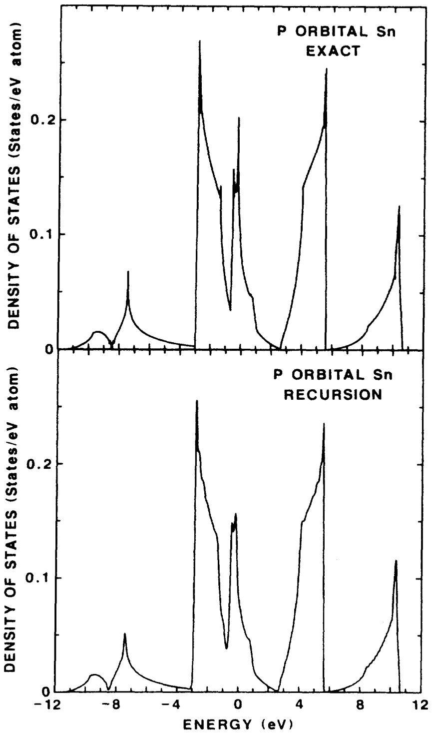

FIG. 2. P-orbital projected density of states in α-Sn calculated with the recursion method (lower panel) and by Gilat-Raubenheimer integration (upper panel).

similar calculations for Ge, and the overall quality is about as good as that for α-Sn and Si.

Upon close inspection of Figs. 3 and 4, one can detect *very* small, spurious features that can be associated with second-order perturbation terms. The model Hamiltonian describing Si has two band gaps: the main gap and a small secondary gap (artifact of the model Hamiltonian) at 6.58 eV. Each of these gaps leads to weakly damped sinusoidal oscillation in the asymptotic form of Eq. (6) (see Tables I and II). From perturbation theory,[10,13] two sinusoidal oscillations in the recursion coefficients, of frequency γ_1 and γ_2, should produce second-order features at

$$\varepsilon = a + 2b\cos(k) \ , \tag{12a}$$

where

$$k = 2\gamma_i, \ \ \pi - 2\gamma_i, \ \ \gamma_i \pm \gamma_2, \ \ \pi - (\gamma_1 \pm \gamma_2) \ . \tag{12b}$$

Neglecting the two terms that are second order in the secondary gap, the corresponding energies are -12.3 eV ($2\gamma_g$), 11.1 eV ($\pi - 2\gamma_g$), -9.4 eV ($\gamma_g + \gamma_s$), 8.2 eV ($\pi - \gamma_g - \gamma_s$), 9.6 eV ($\gamma_g - \gamma_s$), and -10.8 eV ($\pi - \gamma_g + \gamma_s$). Here γ_g (γ_s) refers to the frequency corresponding to the main (secondary) gap. Very weak spurious features can be seen in the recursion calculations at about -12.2 eV (S orbital only), -10.7 eV (S orbital only), -9.3 eV (S and P orbitals), and 9.6 eV (S and P orbitals). These features are very weak but occur at almost exactly the expected energies for second-order terms. At energies where a feature is expected but not seen, the density of states is, in all cases, very small. The small value of the density of states at these energies presumably accounts for the lack of an observed feature. Analogous features are not seen in the γ-Sn densities of states.

In Figs. 5 and 6, we compare the recursion density-of-states calculations for S and P orbitals of C with the results of GR integration. The values $n_1 = 50$, $l_1 = 60$, and $n_1 = 40$, $l_1 = 70$ were used for the S and P orbitals, respectively. The recursion calculations now show two very prominent, spurious features at -25.1 and 20.5 eV. (The feature at -25.1 eV is not clearly seen in the P-orbital calculation owing to the small density of states at that energy.) The expected energies of spurious second-order features from Eq. (12) are -25.2 and 20.6 eV. (Because C has only one band gap, only two features, corresponding to $k = 2\gamma_g$ and $\pi - 2\gamma_g$, are expected.) Thus, one can clearly attribute the observed features to second-order effects that result from the assumed sinusoidal behavior of the recursion coefficients in Eq. (6). The spurious features seen in Figs. 5 and 6 cannot be removed by changing fitting or smoothing ranges (n_1, l_1, etc.). Except for these two features, however, the recursion density-of-states calculation for C is fairly good.

IV. NONPERTURBATIVE TREATMENT OF ONE-BAND-GAP HAMILTONIANS

The extrapolation procedure described in the previous section is based on perturbation theory and assumes that the band-gap is small compared to the bandwidth. The results of that section suggest that the procedure is ade-

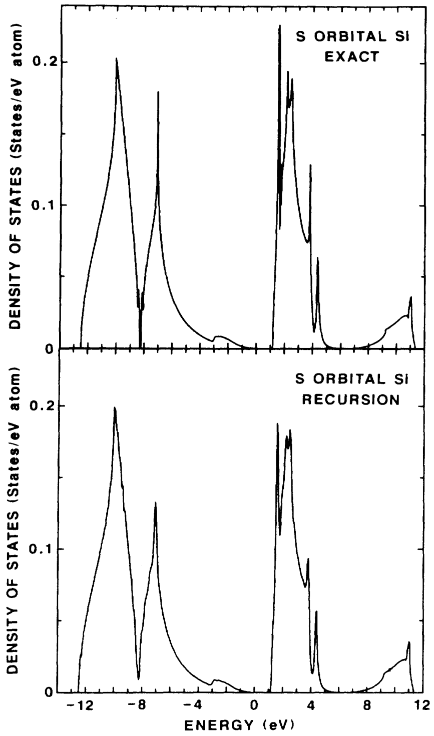

FIG. 3. S-orbital projected density of states in Si calculated with the recursion method (lower panel) and by Gilat-Raubenheimer integration (upper panel).

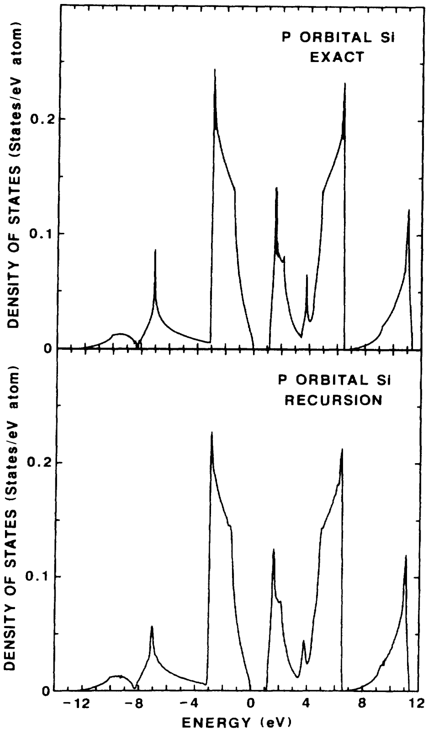

FIG. 4. P-orbital projected density of states in Si calculated with the recursion method (lower panel) and by Gilat-Raubenheimer integration (upper panel).

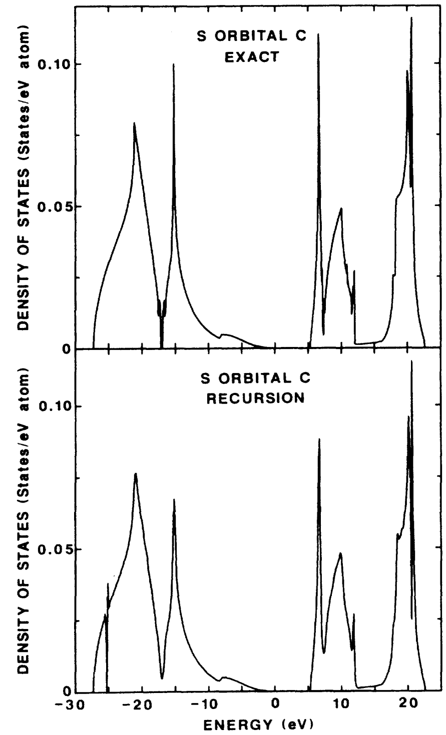

FIG. 5. *S*-orbital projected density of states in diamond calculated with the recursion method (lower panel) and by Gilat-Raubenheimer integration (upper panel).

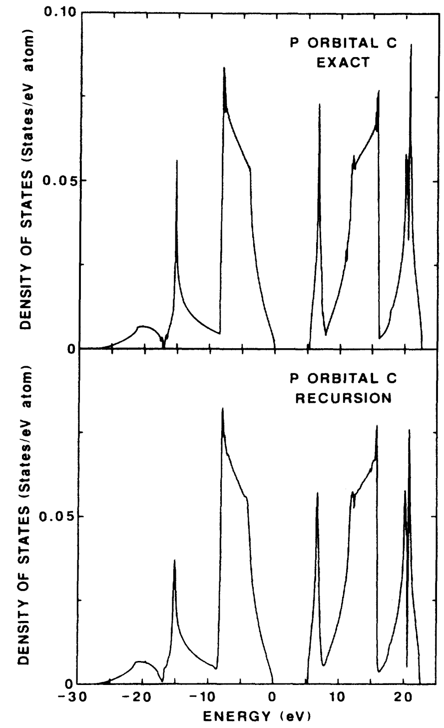

FIG. 6. *P*-orbital projected density of states in diamond calculated with the recursion method (lower panel) and by Gilat-Raubenheimer integration (upper panel).

quate for band-gap to bandwidth ratios less than or equal to about 0.05. For the ratio of about 0.1, spurious features are introduced into the calculated density of states that can be clearly associated with second-order terms. The extrapolation procedure slowly damps oscillations in the recursion coefficients that result from band gaps and, after a large number of extrapolated coefficients, terminates the continued fraction with a function appropriate for constant recursion coefficients (i.e., no band gaps). For most practical purposes, this is an acceptable procedure. Because the damping rate of the recursion coefficients is quite slow, the band-gap edges are sharp and the calculated density of states in the band gap is extremely small. From a rigorous point of view, however, the calculated density of states in the band-gap region is not zero and the analytic structure of the calculated Green's function is not, strictly speaking, correct. Nonperturbative treatments of the asymptotic behavior of the recursion coefficients for Hamiltonians with band gaps have been presented.[10,14,15] In this section, we use these nonperturbative results to modify the previous extrapolation procedure. This modified procedure eliminates the spurious feature in the calculation of C density of states and leads to a correct analytic structure for the calculated Green's function.

For a Hamiltonian with one band gap and for large enough recursion level, the behavior of the recursion coefficients will be determined completely by the band gap. The influence of internal Van Hove singularities, dips in the density of states, etc., will have been damped out. For l in this region, Turchi *et al.*[10] have shown that the terminating function [see Eq. (4)] is

$$t_l(E)=\frac{E^2+A_1E+A_2+2b_l^2\mp[Y(E)]^{1/2}}{2b_l^2(E+A_1+a_{l-1})}\ , \tag{13}$$

and the recursion coefficients satisfy

$$a_l+a_{l-1}+A_1+A_3/2b_l^2=0\ , \tag{14a}$$

$$2b_{l+1}^2b_l^2=A_3a_l-A_4\ , \tag{14b}$$

where

$$Y(E)=(E-E_1)(E-G_1)(E-G_2)(E-E_2)\ , \tag{14c}$$

$$A_1=-(E_1+G_1+G_2+E_2)/2\ , \tag{14d}$$

$$A_2=\frac{(G_1+G_2)(E_1+E_2)}{4}-\frac{(E_1-E_2)^2+(G_2-G_1)^2}{8}\ , \tag{14e}$$

$$A_3=\frac{G_1+G_2-E_1-E_2}{16}[(E_2-E_1)^2-(G_2-G_1)^2]\ , \tag{14f}$$

and

$$A_4=\frac{G_2+G_1-E_2-E_1}{32}[(E_1+E_2)(E_2-E_1)^2-(G_1+G_2)(G_2-G_1)^2]-\tfrac{1}{128}[(E_2-E_1)^2-(G_2-G_1)^2]^2\ . \tag{14g}$$

The sign in Eq. (13) is chosen so that $\mathrm{Im}t_l(E)$ is negative.

The results of Eqs. (13) and (14) apply for values of l large enough so that only the band gap influences the recursion coefficients. The calculated recursion coefficients used here do not satisfy this condition because the influence of density-of-states features other than the band gap has not yet completely decayed. To overcome this problem, we first select a fixed range of recursion levels for which the calculated coefficients display asymptotic behavior. We assume that over this range of recursion levels, the coefficients can be written as the sum of two terms, one of which is due to the main band gap and satisfies Eq. (14); the other term is due to dips and internal Van Hove singularities, and decays with increasing recursion level. We fit each of these two parts over the selected range of recursion levels and extrapolate them separately to large recursion number. These two extrapolated terms are added to form the complete extrapolated recursion coefficients. The extrapolated coefficients asymptotically approach the result for the single band-gap density of states.

In particular, we use the following prescription to extrapolate the calculated coefficients. First, the calculated coefficients are fit to Eq. (6) as in the previous section. (The value of $|r_g|$ is set to unity before the coefficients are found.) This allows one to determine E_1, E_2, G_1, and G_2. The calculated recursion coefficients are assumed to satisfy

$$a_n = a'_n + \alpha_n \ , \tag{15a}$$

$$b_n = b'_n + \beta_n \ , \tag{15b}$$

where a'_n and b'_n describe the contribution from the band gap and satisfy the iteration conditions of Eq. (14), and α_n and β_n describe the contribution from other density-of-states features and decay with increasing recursion level. To determine the set (a'_n, b'_n), we choose a value n_0, within the selected range of recursion levels, and define a'_{n_0-1} and b'_{n_0} (required inputs to the iteration condition) as

$$a'_{n_0-1} = a + G_{A_{n_0-1}} \ , \tag{16a}$$

$$b'_{n_0} = b + G_{B_{n_0}} \ , \tag{16b}$$

where G_A (G_B) is the contribution to Eq. (6) from the gap basis functions. The other values of a'_n and b'_n are determined by the iteration condition. The set (α_n, β_n) for n in the selected range of recursion levels is found from the calculated values (a_n, b_n) by subtraction [Eq. (15)]. α_n and β_n outside of the selected range are extrapolated from those in the selected range as in the previous section. When this extrapolation was performed we did not fix the basis functions 1 and -1. However, such functions (with $|r| \sim 1$) were always found. The extrapolated recursion coefficients are then constructed by adding the extrapolated forms for a'_n (b'_n) and α_n (β_n). The extrapolated recursion coefficients are smoothly adjoined to the calculated coefficients as in Eq. (11). The extrapolated forms for α_n (β_n) decay fairly rapidly with increasing n. For large n the recursion coefficients simply become (a'_n, b'_n), which satisfy the iteration relation [Eqs. (14)] and give the termination function [Eq. (13)]. After the (α_n, β_n) have decayed, the continued fraction is terminated with Eq. (13).

In Tables IV and V, we compare the basis functions and coefficients for the diamond S-orbital extrapolation of the calculated recursion coefficients (a_n, b_n) (Table IV) and the reduced coefficients[21] (α_n, β_n) (Table V). We used 16 basis functions for the recursion coefficient extrapolation and 12 basis functions for the reduced coefficient extrapolation. The basis functions for the calculated recursion coefficients show the fixed functions, gap functions at $g_m = 2.64$ eV, and functions corresponding to strong dips in the density of states at $g_m = -16.9$ and 11.7 eV. The functions at $g_m = -25.2$ eV can clearly be associated with second-order contributions from the band gap. They can be viewed as an attempt of the fitting scheme to correct

TABLE IV. Carbon S-orbital basis functions.

$\lvert C_m \rvert$ (eV)	$\lvert r_m \rvert$	γ_m	g_m (eV)
5.62	1.00	0.00	
6.81	1.00	3.14	
0.680	0.9998	−1.37	2.64
0.680	0.9998	1.37	
0.0171	0.995	−2.73	−25.2
0.0171	0.995	2.73	
0.0477	0.986	−2.19	−16.9
0.0477	0.986	2.19	
0.0119	0.925	−1.96	−11.9
0.0119	0.925	1.96	
0.0874	0.804	−1.15	7.88
0.0874	0.804	1.15	
0.0920	0.977	−0.969	11.7
0.0920	0.977	0.969	
0.0110	0.959	−0.531	19.1
0.0110	0.959	0.531	

TABLE V. Carbon S-orbital basis functions: asymptotic method.

$\lvert C_m \rvert$ (eV)	$\lvert r_m \rvert$	γ_m	g_m (eV)
0.0404	0.991	0.00	
0.0195	0.991	3.14	
0.0427	0.980	−1.37	2.53
0.0427	0.980	1.37	
0.0188	0.752	−2.28	−18.6
0.0188	0.752	2.28	
0.0546	0.981	−2.18	−16.7
0.0546	0.981	2.18	
0.0797	0.980	−0.977	11.5
0.0797	0.980	0.977	
0.0203	0.799	−0.620	17.9
0.0203	0.799	0.620	

for the first-order form of Eq. (6). Removing these functions by hand from the extrapolation makes the spurious features seen in Fig. 5 worse. The basis functions for the reduced coefficients also show the fixed basis functions (1 and -1) and the gap functions, but with much smaller amplitude coefficients. The appearance of these basis functions can be veiwed as slight corrections to the bandwidth and band-gap description in the (a_n', b_n') coefficients. Basis functions corresponding to the dips at -16.7 and 11.5 eV show up as they did in the extrapolation of the calculated recursion coefficients. There are no basis functions corresponding to second-order terms.

In Fig. 7 we compare the analytic termination function of Eq. (13) with the extrapolated termination function calculated as described in Sec. III for the S orbital of C. [The extrapolated function is calculated as a continued fraction terminated with Eq. (10).] In particular, we plot

$$-\frac{1}{\pi}\operatorname{Im} t_{502}(E)$$

in units of states/(eV atom). For the extrapolation terminator, only the fixed and gap basis functions remain. (All others are thoroughly damped out; see Table IV.) These two terminating functions are similar except for the two spurious features associated with second-order terms in the extrapolation terminator. The band gap has also closed up a bit in the extrapolation terminator.

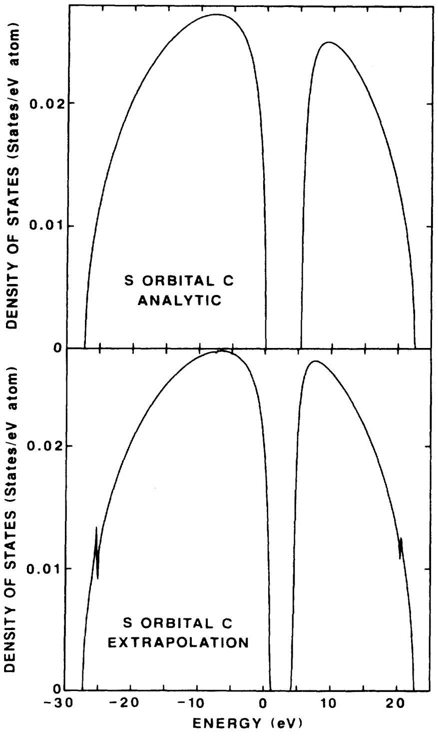

FIG. 7. Imaginary part of the terminating function for $l=502$ and the S orbital in diamond calculated using the perturbative extrapolation (lower panel) and the one-band-gap analytical result (upper panel).

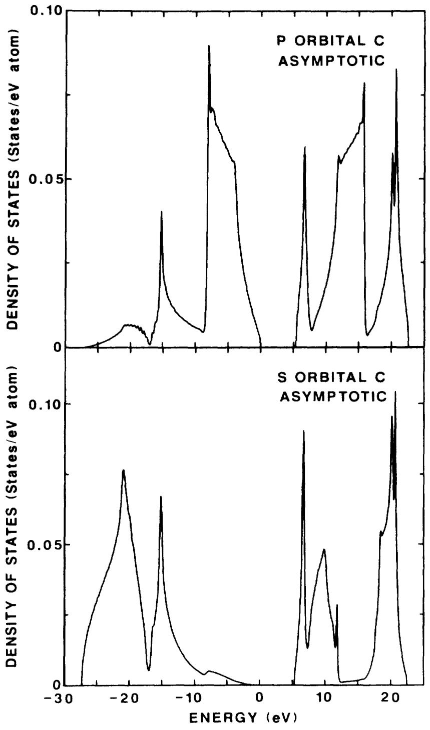

FIG. 8. S-orbital (lower panel) and P-orbital (upper panel) density of states in diamond calculated using the recursion method and the nonperturbative asymptotic extrapolation of the recursion coefficients.

In Fig. 8, we show the calculated S- and P-orbital densities of states for C using the nonperturbative termination scheme described here. The values $n_0=79$, $n_1=50$, $l_1=60$, and $n_0=79$, $n_1=65$, $l_1=65$ were used for the S and P orbitals, respectively. The spurious features are clearly removed by this procedure and the calculated densities of states are quite satisfactory. The overall quality of the calculation is about as good as the earlier results for α-Sn, which does not have a band gap. The calculated density of states in the band gap is exactly zero, and the analytic structure of the Green's function is correct. We have also performed the nonperturbative calculation on Si. As for C, the spurious features from second-order effects were removed. However, these features were very small to start with so the improvement in the calculated density of states was minor in this case.

V. SUMMARY AND CONCLUSIONS

We have investigated methods to calculate projected density of states from a finite set of recursion coefficients. Our basic approach was to extrapolate the known coefficients based on an assumed asymptotic behavior. The extrapolated form was chosen so that after a large number of recursion levels, the extrapolated coefficients have a form for which an analytic terminating function is known. We specifically considered model Hamiltonians describing the diamond structure semiconductors α-Sn, Ge, Si, and C. Coefficients for about 110 levels of recursion had been previously calculated accurately for these Hamiltonians. A feature that distinguishes this discussion from previous work is that here we have coefficients for a sufficient number of recursion levels so that their asymptotic behavior is apparent.

We first extrapolate the calculated coefficients using a linear predictive analysis originally suggested by Allan. This extrapolation procedure is based on a perturbation analysis that assumes all band gaps are small compared to the bandwidth. We found that band-gap and bandwidth parameters can be accurately determined from the linear predictive analysis. For α-Sn, Ge, and Si, which all have main band gap to bandwidth ratios of less than 0.05, this extrapolation procedure was found to be very successful. For C, however, with a band gap to bandwidth ratio of 0.106, large spurious features, which could be clearly associated with second-order perturbation terms, appeared in the calculated density of states. We then modified the extrapolation procedure using nonperturbative results for the assumed asymptotic behavior. The new extrapolation procedure gave good densities of states for C that did not have any spurious features. It also has the virtue that the calculated density of states is exactly zero in the band-gap region, or to say the same thing, the calculated Green's function has the correct analytic structure.

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[17] The damping rate $|r_g|$ of the main gap functions can be adjusted. (It must be less than unity.)

[18] The fitting ranges were as follows: *S*-orbital Sn, 48–99; *P*-orbital Sn, 60–100; *S*-orbital Ge, 48–99; *P*-orbital Ge, 40–90; *S*-orbital C, 48–99; *P*-orbital C, 40–100. Sixteen basis functions were used in all cases except for the *S* orbital of Sn, in which case 14 were used.

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[20] The slight retrograde structure near the dip at -8.46 eV in the GR calculation of Fig. 1 and analogous features in the other GR results are artifacts. They are reduced by using a tighter integration mesh.

[21] The value of $|r_g|$ was adjusted down from 1.0068 to 0.98 before the coefficients were calculated.