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Effects of overlap and next-nearest-neighbor interactions in tight-binding calculations

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Effects due to overlap between orbitals on neighboring atoms and to next-nearest-neighbor interactions, on the electronic structure, are investigated. As an illustration of their importance, analytic results are obtained for the density of states of a Bethe lattice and numerical calculations are carried out to obtain the band structure of a diamond lattice, starting from a realistic Hamiltonian. We show that overlap and next-nearest-neighbor interactions have important effects which are of opposite sign and tend to cancel each other in the valence band, but they are additive in the conduction band. The implications of our results for transition metals and surfaces are briefly discussed.

I. INTRODUCTION

Calculations of the electronic-energy-band structure of solids, using the linear-combination-of-atomic-orbitals (LCAO) method are usually carried out under the assumption that effects due to overlap between the basis wave functions are negligible.[1-3] On the other hand, when overlap effects are included they yield energy-dependent matrix elements in the secular equation which considerably complicate the computation.[4,5]

Several attempts have already been made to include the nonorthogonality of the basis set in band-structure calculations. Löwdin[6] has developed a scheme in which the matrix elements of the Hamiltonian are developed in a power series in the overlap; this method is quite general, but approximate. More recently Tejeda and Shevchik[5] have included the overlap in a simple manner, but their method is exact only in the limit of degenerate atomic orbitals: the application to the bond-orbital model[7,8] assumes orthogonality between sp^3 orbitals on adjacent atoms.

In this contribution we develop a method to study overlap effects on the electronic band structure and density of states which is simple, exact, and valid for any Hamiltonian and any crystal structure.

In addition, the usual procedure is to keep interactions only up to nearest neighbors; also in this respect we go further and include in our calculations interactions between orbitals on atoms which are next-nearest neighbors (NNN). We show below that the electronic band structure and the density of states are very sensitive functions of both overlap and NNN interactions, and the inclusion of them in the calculation leads to remarkable qualitative changes in the computed results.

In fact, for a simple s-state Hamiltonian, overlap and NNN interaction effects can be quite large. As they have opposite signs, for an appropriate set of parameters almost total cancellation between them can be achieved. However, for covalent semiconductors the situation is more striking: while in the valence band again a partial cancellation of effects does occur, in the conduction band, overlap and NNN contributions are additive.

We would like to point out, right from the beginning, that our aim and purpose in this work is to analyze and study the importance of including overlap and distant-neighbor interactions in the calculation. For the time being we are not attempting to fit a certain band structure with a set of parameters, but rather we are trying to provide an estimate of the magnitude of contributions usually neglected in computations of the electronic structure of solids.

The organization of this paper is as follows: in Sec. II a detailed discussion of a simple s-state Hamiltonian is given, and the density of states for a Bethe lattice and the band structure of a diamond lattice are studied with the inclusion of overlap and NNN effects. In Sec. III, the band structure of the diamond lattice is studied for two sp^3 Hamiltonians: (i) a simple one similar to the Weaire-Thorpe[9,10] Hamiltonian, and (ii) a realistic sp^3 one, which includes all possible interactions between orbitals on nearest-neighbor (NN) atoms and an interaction between sp^3 orbitals on NNN atoms. In the first case (i) there is an analytical transformation between the eigenvalues of an s-state Hamiltonian and our sp^3 one. Finally, we conclude the paper with Sec. IV where a summary of our most relevant results, some important comments, and an outline of related work which is in progress are provided.

II. OVERLAP AND NEXT-NEAREST-NEIGHBOR INTERACTION EFFECTS FOR AN *s*-STATE HAMILTONIAN

The simplest of all possible Hamiltonians, which allows an understanding of overlap and NNN interaction effects on the electronic structure, is an s-state Hamiltonian with only one s orbital per atom. Analytically it can be written as

$$h = v_1 \sum_{\langle i', j' \rangle} |i'\rangle\langle j'| + v_2 \sum_{\langle i'', j'' \rangle} |i''\rangle\langle j''| \,, \tag{2.1}$$

where $|i\rangle$ represents the s-orbital wave function on atom i, v_1 and v_2 are the interaction parameters between NN and NNN, and the primed and double-primed summations in Eq. (2.1) are restricted as well to NN and NNN, respectively.

Focusing our attention on overlap effects, we set $v_2 = 0$ for the time being. If we normalize the s states to unity on the same lattice site

$$\langle i|j\rangle = \delta_{ij} \,, \tag{2.2a}$$

and define

$$S_{ij} \equiv \delta_{ij} + S_1 \delta_{i, j+|\vec\delta|} \,, \tag{2.2b}$$

where $\vec\delta$ is a vector connecting two NN atoms, we obtain a secular equation for the eigenvalues of the Hamiltonian h which reads

$$h|\phi\rangle = \epsilon S|\phi\rangle \,. \tag{2.3}$$

Here ϵ is the energy and the overlap operator S was defined in Eq. (2.2b).

In our study we treat in detail two different situations; they are: (a) the Bethe lattice, and (b) the diamond lattice. The former[11,12] provides us with a simple approximation to the density of states of a real crystal, whereas for the diamond lattice we do obtain exact numerical results for the electronic band structure.

A. Bethe lattice ($v_2 = 0$)

Under the assumption of orthogonality of the basis set a Bethe lattice of coordination c has a density of states given by[12]

$$D(\epsilon) = \frac{-1}{\pi} \operatorname{Im}\left(\epsilon - \frac{c}{2(c-1)} |\epsilon - [\epsilon^2 - 4(c-1)v_1^2]^{1/2}|\right)^{-1} . \tag{2.4}$$

Nonorthogonality of the basis set can be included exactly, as seen from inspection of Eqs. (2.1) and (2.3), introducing the transformation

$$v_1 \to v_1 - \epsilon S_1 \tag{2.5}$$

in Eq. (2.4).

In addition, once the transformation (2.5) is introduced in Eq. (2.4), it becomes clear that the density of states with overlap included ($S_1 \neq 0$) and the one with overlap neglected ($S_1 = 0$) are related through the following analytic transformation of the energy:

$$\epsilon' = [1 - (S_1/v_1)\epsilon]^{-1}\epsilon \,. \tag{2.6}$$

Here ϵ' labels the case when $S_1 \neq 0$ and ϵ stands for $S_1 = 0$. The transformation (2.6) was already obtained by Tejeda and Shevchik.[5]

Another interesting piece of information is the position of the band edges, which are given by the zeros of the square root of Eq. (2.4), i.e., by the solutions of

$$\epsilon^2 - 4(c-1)v_1^2 = 0 \,. \tag{2.7}$$

The generalized form of the above equation to the case $S_1 \neq 0$ is

$$\epsilon^2 - 4(c-1)(v_1 - \epsilon S_1)^2 = 0 \,, \tag{2.8}$$

according to the transformation (2.5). The band edges are thus given by

$$\epsilon = \pm 2(c-1)^{1/2} v_1 / [1 \mp 2(c-1)^{1/2} S_1] \,. \tag{2.9}$$

An important direct consequence of the above expression is the existence of a *critical value* of the overlap, which we shall denote by S_1^c. In fact, when

$$S_1 \geqslant S_1^c \equiv 1/2(c-1)^{1/2} \,, \tag{2.10}$$

the tight-binding picture in the NN approximation breaks down altogether.

In order to illustrate overlap effects on the densities of states of a Bethe lattice we have plotted several of them, corresponding to different values of S_1 in Fig. 1(a). We observe that as S_1 becomes larger a portion of the density of states is pushed towards lower energies while the band edges are shifted upwards in energy.

B. Diamond lattice ($v_2 = 0$)

We now turn our attention to actual crystal structures and, while our discussion is qualitatively valid for any of them, we take the diamond structure as an illustrative example in the following calculation. In this case the solution of Eq. (2.3) is obtained from

$$\det \begin{vmatrix} -\epsilon & (v_1 - \epsilon S_1)T(\vec k) \\ (v_1 - \epsilon S_1)T^*(\vec k) & -\epsilon \end{vmatrix} = 0 \,, \tag{2.11}$$

where $T(\vec k)$ is the structure factor given by

$$T(\vec k) = 4(\cos\tfrac14 k_x a \cos\tfrac14 k_y a \cos\tfrac14 k_z a - i \sin\tfrac14 k_x a \sin\tfrac14 k_y a \sin\tfrac14 k_z a) \,, \tag{2.12}$$

a being the lattice constant. The solution of Eq. (2.11) is

$$\epsilon_{\vec k}^{\pm} = \pm v_1 |T| / (1 \pm S_1 |T|) \tag{2.13}$$

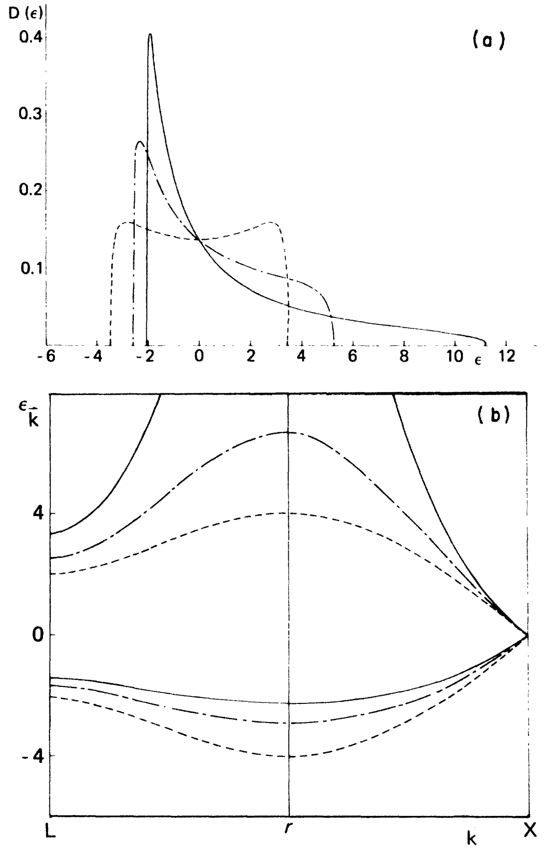

FIG. 1. Density of electron states $D(\epsilon)$ vs ϵ [Fig. 1(a)] and $\epsilon_{\vec{k}}$ vs $\vec{k}$ [Fig. 1(b)] obtained for an s-state Hamiltonian, for a Bethe lattice and a diamond lattice, respectively. The energy is measured in units of $|v_1|$ (i.e., $v_1=-1$). The dashed lines correspond to the case when overlap is neglected ($S_1=0$), while for the dash-dot lines $S_1=0.1$, and for the solid lines $S_1=0.2$.

and thus, as in the Bethe-lattice case there is a critical value of S_1, now given by

$$S_1^c=\tfrac{1}{4}\,. \tag{2.14}$$

In Fig. 1(b) we have drawn curves of $\epsilon_{\vec{k}}$ vs $\vec{k}$, for $S_1=0$, 0.1, and 0.2 which clearly display the effects of including overlap in the calculations. In fact, these simple examples show that the electronic structure is a highly sensitive function of the overlap and in consequence it cannot be simply neglected. Certainly, a way of avoiding the overlap problem altogether is to orthogonalize the basis set; however, this implies the necessity of including distant-neighbor interactions which again complicate the calculation considerably.

Having discussed overlap effects by themselves, we now also include in our treatment next-nearest-neighbor interactions for the same two cases considered before, the Bethe and diamond lattices.

C. Bethe lattice ($v_2\neq 0$)

We focus on an atom, labeled by 0, which we choose as the origin of a Bethe lattice. The integers 1, 2, ... label the different shells of atoms as we go outwards from the origin (atom 0). Following a standard procedure,[13] we do obtain an infinite chain of linear self-consistent equations for the matrix elements $g_{i,j}\equiv\langle i|g|j\rangle$ of the Green's function g defined by the Hamiltonian h of Eq. (2.1). This chain of equations reads:

$$\begin{aligned}
\epsilon g_{0,0}&=+cv_1g_{1,0}+c(c-1)v_2g_{2,0}\,,\\
\epsilon g_{1,0}&=v_1[g_{0,0}+(c-1)g_{2,0}]+v_2[(c-1)g_{1,0}\\
&\qquad+(c-1)^2g_{3,0}]\,,\\
&\;\;\vdots\\
\epsilon g_{n,0}&=v_1[g_{n-1,0}+(c-1)g_{n+1,0}]\\
&\qquad+v_2[g_{n-2,0}+(c-2)g_{n,0}+(c-1)^2g_{n+2,0}]\,,\\
&\qquad\qquad n\geqslant 2\,.
\end{aligned}\tag{2.15}$$

The solution of (2.15) can be obtained using standard techniques for finite difference equations. Once the pertinent boundary conditions are invoked, a closed analytic form for the density of states is obtained, which has the form

$$D(\epsilon)=2(c-1)/\pi\left|\frac{d\epsilon}{dx}\right|\frac{(1-x^2)^{1/2}}{c-[4(c-1)/c]x^2}\,, \tag{2.16}$$

and where the relation between ϵ and the variable $x\,(-1\leqslant x\leqslant 1)$ is given by

$$\epsilon(x)=4v_2(c-1)x^2+2v_1(c-1)^{1/2}x-cv_2\,. \tag{2.17}$$

It is understood that when taking the derivative $(d\epsilon/dx)$ in (2.16) the transformation (2.5) can be used to include overlap effects. Moreover, this derivative can vanish and thus again a critical value v_2^c comes into sight, limiting the range of the NNN interaction parameter v_2. It turns out that the value of v_2^c is the solution of

$$\mp(5c-4)S_1v_2^c+4(c-1)^{1/2}v_2^c\pm v_1=0\,. \tag{2.18}$$

When $S_1=0$ we obtain

$$v_2^c=\pm v_1/4(c-1)^{1/2}\,, \tag{2.19}$$

which sets an upper limit on the strength of v_2 compared to v_1. In other words, when the NNN interaction v_2 becomes larger than a certain fraction of the NN parameter v_1, the lattice becomes unstable.

In Fig. 2(a) we have plotted the density of states vs ϵ for different values of v_2/v_1. It is interesting to compare Figs. 1(a) and 2(a) to notice that including v_2 and neglecting S_1 has qualitatively a similar effect to keeping S_1 and neglecting v_2, the difference being that the shift of the densities of states

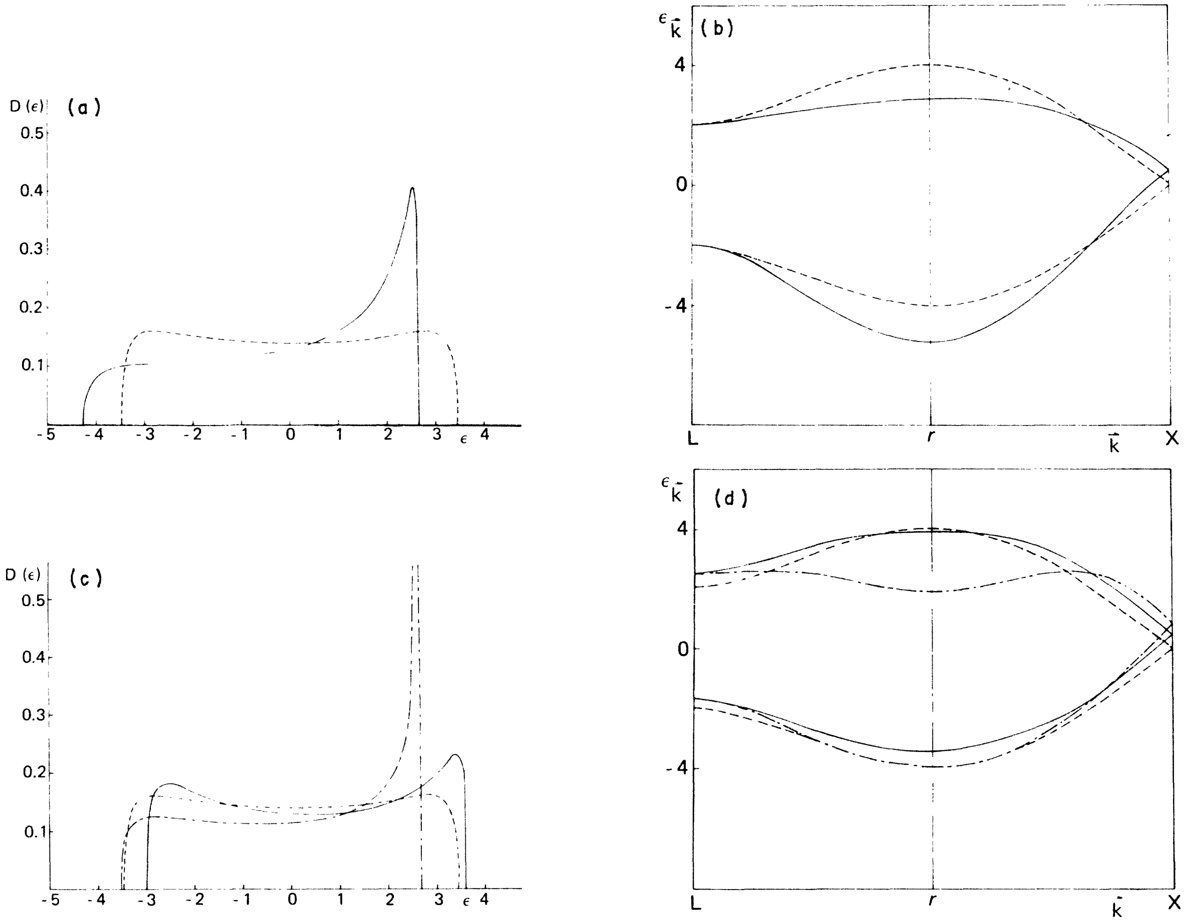

FIG. 2. Density of electron states $D(\epsilon)$ vs ϵ [Figs. 2(a) and 2(c)] and $\epsilon_{\vec{k}}$ vs $\vec{k}$ [Figs. 2(b) and 2(d)] obtained for an s-state Hamiltonian, for a Bethe lattice and a diamond lattice, respectively. Both overlap and NNN interaction effects are illustrated. The dashed lines correspond to the case when overlap and NNN interactions are neglected ($S_1 = v_2 = 0$). In Figs. 2(a) and 2(b) the solid lines correspond to $v_2/v_1 = 0.1$ and $S_1 = S_2 = 0$. In Figs. 2(c) and (d) the dot-dash line corresponds to $v_2/v_1 = 0.2$ and $S_1 = 0.1$, and the solid line to $v_2/v_1 = 0.1$, $S_1 = 0.1$, and $S_2 = 0.01$. The maxima and minima of the "conduction" band of Fig. 2(d), with nonzero k, are related to singularities in the density of states.

occurs in opposite directions. In effect, for an adequate choice of parameters it is feasible to obtain almost total cancellation of overlap and NNN interaction effects on the density of states of a Bethe lattice. Illustrated in Fig. 2(c) are the results for a couple of typical examples.

D. Diamond lattice ($v_2 \neq 0$)

The dispersion relation (2.13) can be generalized to incorporate NNN interactions, in which case it is given by

$$\epsilon_{\vec{k}} = (\pm v_1 |T| + v_2 R)/(1 \pm S_1 |T|), \tag{2.20}$$

where T was defined in Eq. (2.12) and $R(\vec{k})$ is a structure factor of the form

$$R(\vec{k}) = |T(\vec{k})|^2 - 4. \tag{2.21}$$

Plots of ϵ vs $\vec{k}$, for different values of v_2/v_1 and S_1 are given in Fig. 2(d). The general features obtained in Sec. II C for the Bethe lattice are present also now, i.e., the opposite signs of overlap and NNN interaction effects and the existence of a critical value of v_2, such that for $v_2 \geq v_2^c$ tight-binding results become meaningless. In fact, when $v_2 \geq v_2^c$ the energy of the Γ point $[\vec{k} = (0,0,0)]$ is not the lowest energy level as required by symmetry arguments. v_2^c is the solution of

$$\pm 20 v_2^c S_1 + 8 v_2^c \pm v_1 = 0, \tag{2.22}$$

which is similar to (2.18) for $c = 4$. For $S_1 = 0$ we obtain

$$v_2^c = \pm \tfrac{1}{8} v_1. \tag{2.23}$$

We conclude this section by stressing our main results. The effect of both NNN interactions and overlap of the basis wave functions on the electronic structure are important. We also would like to stress that the inclusion or the omission of overlaps and higher-order interaction would lead to very different sets of the fitting parameters to the band structure.

III. sp^3 HAMILTONIANS

In Sec. II several simple cases were discussed in order to display the relevant physical consequences of overlap and NNN interactions with a minimum of algebra. Now we carry out more realistic calculations for the diamond lattice, first evaluating the density of states of a simple sp^3 Hamiltonian, similar to the Weaire and Thorpe[10] one, and next computing numerically the electronic band structure of Si including overlap and NNN effects.

Our Weaire-Thorpe-type Hamiltonian has the form

$$H=\Delta \sum_{\substack{i,j,j' \\ j\neq j'}} |ij\rangle\langle ij'| + V_1 \sum_{\substack{i,i',j \\ i\neq i'}} |ij\rangle\langle i'j| + V_2 \sum_{\langle i,j,i',j'\rangle} |i'j'\rangle\langle ij| , \tag{3.1}$$

where $|ij\rangle$ represents the sp^3 orbital wave function with i labeling the atoms ($i=1,2,\ldots,\infty$) and j the bonds of the system ($j=1,2,3,4$). Δ measures the strength of the interaction between sp^3 orbitals on the same atom. V_1 describes the interaction between sp^3 orbitals on NN atoms which are pointing towards each other. V_2 represents the interaction between the sp^3 orbitals on NNN atoms pointing towards one common NN atom.

It is easy to obtain an analytic transformation between the eigenvalues of the s-state Hamiltonian of Eq. (2.1) and the eigenvalues of the sp^3 Hamiltonian of Eq. (3.1). A particularly simple way to obtain this transformation is to write a set of equations analogous to (2.15); now they read

$$\begin{aligned} (E-2V_2)G_{n,0} &= V_1 G_{n-1,0} + 3\Delta G_{n+1,0} + V_2 G_{n-3,0} , \\ (E-2\Delta)G_{n+1,0} &= \Delta G_{n,0} + V_1 G_{n+2,0} + 3V_2 G_{n+4,0} , \end{aligned} \tag{3.2}$$

where $G_{n,0}$ is the matrix element $\langle n|G|0\rangle$ of the Green's function G of the Hamiltonian H of Eq. (3.1), which has energy eigenvalues E. These two generic equations can be reduced to one of the form:

$$\left(E-2V_2-\frac{V_1^2-3\Delta^2-3V_2^2}{E-2\Delta}\right)G_{n,0} = \frac{V_1(V_2+\Delta)}{E-2\Delta}(G_{n-2,0}+3G_{n+2,0}) + \frac{V_2\Delta}{E-2\Delta}(G_{n-4,0}+9G_{n+4,0}) . \tag{3.3}$$

Setting $c=4$ in Eq. (2.15), we obtain by direct comparison between (2.15) and (3.3) the $s \leftrightarrow sp^3$ analytic transformation which follows:

$$\begin{aligned} &\epsilon - 2v_2 \leftrightarrow E-2V_2-(V_1^2-3\Delta^2-3V_2^2)/E-2\Delta , \\ &v_1 \leftrightarrow [V_1(V_2+\Delta)]/(E-2\Delta) , \\ &v_2 \leftrightarrow V_2\Delta/(E-2\Delta) . \end{aligned} \tag{3.4}$$

As a consequence of the above transformation, the density of states of the sp^3 Hamiltonian (3.1) is constituted by two bands separated by a gap and, in addition, by two δ-function contributions corresponding to the p bonding and antibonding states.

In order to calculate the band structure with Hamiltonian (3.1), we use the transformation (3.4) in conjunction with Eq. (2.21) and obtain

$$E_{\vec{k}} - 2V_2 - \frac{3V_2^2+V_1^2+3\Delta^2-2V_2\Delta}{E_{\vec{k}}-2\Delta} = \frac{V_2\Delta}{E_{\vec{k}}-2\Delta} R \pm \frac{V_1(V_2+\Delta)}{E_{\vec{k}}-2\Delta}|T| . \tag{3.5}$$

To include overlap effects we can use the transformations

$$\begin{aligned} V_1 &\to V_1 - ES_1 , \\ V_2 &\to V_2 - ES_2 . \end{aligned} \tag{3.6}$$

Combination of (3.5) and (3.6) yields a quadratic equation for the energy $E_{\vec{k}}$.

Choosing silicon as a prototype in our calculations, we use the parameters $V_1=-6.13$ eV and $\Delta=-1.8$ eV given by Chadi and Cohen.[1] The choice of V_2, S_1, and S_2 is based on the following assumptions. (a) The sp^3 orbital wave functions decay exponentially, as a function of the distance to atom 0, according to the same law which is valid for s states. (b) The overlap between sp^3 orbitals and the corresponding matrix elements of the Hamiltonian, between the same orbitals, are linearly proportional.

Under these assumptions we choose $S_1=0.15$ and thus $S_2=0.02$ and $V_2=-0.817$ eV. In Figs. 3(a) and (b) we show the corresponding band structure; first $S_1=S_2=V_2=0$ is given as a reference. Next S_1 is made nonzero and finally in Fig. 3(b) all the above given values are used. We note that overlap has a similar effect as for the s-state Hamiltonian of Sec. II, i.e., S_1 induces the energy levels both of the valence and conduction bands to rise. In Fig. 3(b) we observe that the inclusion of V_2 partially cancels the effect of S_1 in the valence band, but the consequences of including V_2 and S_1 are *additive* in the conduction band. Moreover, V_2 also dramatically reduces the band gap from approximately 5 eV ($S_1=S_2=V_2=0$) to around 1.4 eV when the above given values ($S_1=0.15$, $S_2=0.02$, and $V_2=-0.817$ eV) are included.

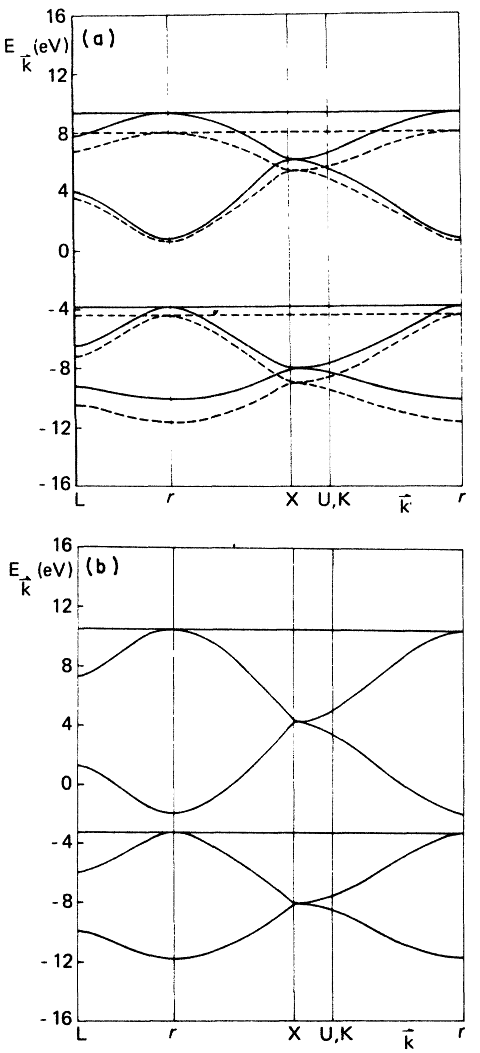

FIG. 3. Band structure $E_{\vec{k}}$ vs $\vec{k}$ for a Weaire-Thorpe-type Hamiltonian. The dashed line corresponds to the case when overlap and NNN interaction effects are neglected ($S_1 = V_2 = 0$). The solid line of Fig. 3(a) includes overlap effects; Fig. 3(b) corresponds to the case where both overlap and NNN interactions are incorporated.

As a final check of these results we carry out a numerical computation with the more realistic Hamiltonian described in detail in Ref. 1, which considers all possible interactions between sp^3 orbitals on NN atoms and some important NNN ones. In addition to the values of $V_1 = -6.13$ eV and $\Delta = 1.8$ eV already used above, we take from Ref. 1 the parameters $\gamma_3 = -0.11$ eV, $\gamma_5 = -0.51$ eV, and $\gamma_6 = 0.57$ eV also using their notation. To incorporate overlap we have to solve

$$\det(\underline{H} - E\underline{S}) = 0\,, \tag{3.7}$$

where $\underline{H}$ is the Hamiltonian of Ref. 1, and $\underline{S}$ is the overlap operator defined in Eq. (2.2b).

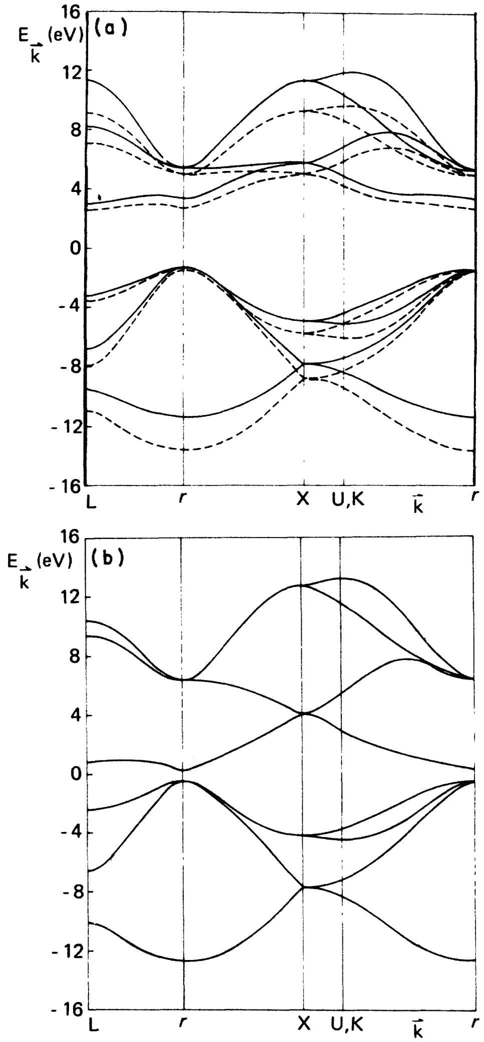

FIG. 4. Band structure $E_{\vec{k}}$ vs $\vec{k}$ for the Hamiltonian of Ref. 1. The dashed line in Fig. 4(a) corresponds to the results of Ref. 1. The solid line of Fig. 4(a) includes overlap effects; in Fig. 4(b) both overlap and NNN interactions are incorporated.

Since $\det\underline{S} \neq 0$ (recall that when overlap is neglected $\underline{S} = \underline{1}$) the problem is reduced to the evaluation of the eigenvalues of the operator $\underline{S}^{-1}\cdot\underline{H}$.

We have calculated the band structure for the set of parameters given above; the corresponding overlaps are $S_1 = 0.15$, $S_2 = 0.02$; $S_3 = 0.0027$, $S_5 = 0.0125$, and $S_6 = -0.0139$. The value of S_1 is arbitrarily chosen and the other overlaps are determined according to the assumptions made above.

The results of our computation are given in Fig. 4 and Table I. We again observe the same general features: not much change in the valence band, while a drastic qualitative modification of the conduction band does take place when overlap and NNN interactions are included in the calculations.

TABLE I. Comparison of the energy eigenvalues of Si. The energies (in eV) are measured relative to the top of the valence band at $\Gamma_{25'}$.

	Reference 1	NN without overlap	NN with overlap	NNN with overlap
$\Gamma_{25'}$	0	0	0	0
Γ_1	−12.16	−12.16	−10.01	−12.16
$L_{2'}$	−9.44	−9.49	−8.21	−9.44
L_1	−7.11	−6.63	−5.57	−6.07
$L_{3'}$	−1.44	−2.16	−1.35	−1.82
X_1	−7.70	−7.33	−6.50	−7.22
X_4	−2.87	−4.32	−3.54	−3.66

IV. CONCLUDING REMARKS

In closing this paper we want to summarize our most important results, outline their implications, and mention several aspects which deserve further investigation.

Our main conclusion is that the electronic structure of a regular solid is a very sensitive function of: (a) the overlap between atomic orbitals on different atoms, and (b) the interactions between orbitals which are further apart than nearest neighbors. While these effects are similar in order of magnitude, they tend to cancel each other in the valence band, but are additive in the conduction band. Therefore, a good deal of caution should be exercised when carrying out or using LCAO calculations; in fact, it is advisable to restrict them to core states or at most to obtain a qualitative picture of the valence band. Similar conclusions, based on a completely different line of reasoning, have recently been reached by Fry *et al.*[14]

In addition, there are critical values which the overlap S_1 [defined in Eq. (2.2b)] and the NNN interaction parameter v_2 of Eq. (2.1) cannot exceed; beyond these critical values the calculation scheme breaks down completely. When approaching these critical values of S_1^c and v_2^c from below, the numerical solutions become unstable; this could be the cause for numerical instabilities reported in the literature,[5] in connection with previous calculations of the type described in this paper.

We wish to emphasize that it is neither our intention nor our purpose in the present contribution to fit a specific band structure. In fact, the introduction of a whole set of new parameters make such endeavor meaningless; with quite different sets of parameters one could obtain very similar valence bands.[1,2] Instead, we have tried to shed light on the relative importance of including effects usually neglected in LCAO-type electronic structure calculations and which we find to be quite important.

In this paper we have restricted our examples to diamond structure semiconductors; certainly the line of reasoning we have followed could have important consequences for transition metals. In particular it would be interesting to test the implications of including overlap effects in electronic structure calculations of transition metals, paying attention to the role played by screening.

Finally, surface density-of-states computations of transition metals are usually carried out[15] within a tight-binding scheme. Here the anisotropy of the overlap between orbitals of surface atoms is expected to have important consequences which should be interesting to explore.

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