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Brief Reports

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Effects of orbital nonorthogonality on band structure within the tight-binding scheme

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Within the tight-binding approximation, the consequences on the band spectrum of the lack of orthogonality between orbitals are fully investigated for a one-dimensional monoatomic crystal with one orbital per atom. The limitations of the nearest-neighbor approximation are first exposed and then, through a set of reasonable assumptions, a general analytical result is obtained for this system. It is seen that orbital nonorthogonality destroys the symmetry of the band spectrum with respect to the corrected atomic level, decreasing the effective mass at the top of the band and increasing it at its bottom. As an application, the errors involved in neglecting the multicenter integrals in the interaction matrix elements are evaluated.

I. INTRODUCTION

In the extensively used tight-binding approach, extended one-electron states can be approximated (in the variational sense) as linear combinations of atomic orbitals of the constituent atoms. The coefficients are the matrix elements of the self-consistent-field Hamiltonian for one electron in the crystal between basis states, and involve the calculation of one-, two-, and three-center integrals corresponding to on-site energies and hopping terms. For a perfect crystal these coefficients contain Bloch phase factors, so that the resulting band spectrum is essentially a Fourier series in the wave vector $\mathbf{k}$ in which successively higher terms correspond to interactions with farther atoms.

The immense difficulties connected with the calculation of the multicenter integrals led Slater and Koster to put the scheme forward not as a primary method of calculation, but as an interpolation procedure in connection with more accurate calculations made with other methods.[1] The Hamiltonian matrix elements, rather than being directly computed, were treated as convenient constants chosen to fit computations made somehow else at restricted-symmetry points of the Brillouin zone.

A standard *assumption,* which greatly simplifies single-particle and many-body calculations, is to consider that the basis set is orthogonal (whereas atomic orbitals belonging to the same atom are granted to be orthogonal to each other, this is not necessarily true for orbitals belonging to different atoms once they interact). It is true that an orthogonal basis set can always be built up from a nonorthogonal one using, for instance, Löwdin's procedure;[2] however, the resulting orthogonal orbitals have long tails, which require more-distant-neighbor interactions be considered. An often resorted to alternative is to absorb orbital-nonorthogonality effects altogether by modifying the corrected atomic level and hopping terms.[3]

The purpose of this paper is to investigate the effects of orbital nonorthogonality (ONO) on a band spectrum, within the framework of a simple model consisting of a one-dimensional monoatomic crystal with one orbital per atom. As a consequence of ONO the band spectrum becomes *asymmetric* with respect to the corrected atomic level, so that the effective masses at the top of the band decrease whereas those at the bottom increase. These features cannot be adequately reproduced by a cosine spectrum with modified parameters.

Section II is devoted to nearest-neighbor orbital nonorthogonality (NNONO): it is shown that the resulting band spectrum is analogous to that of a crystal with more-distant-neighbor interactions in an orthogonal basis.[4,5] As mentioned above, more-distant-neighbor interactions are an unavoidable consequence or orthogonalization. The interaction strengths are found to be functions of the NNONO parameter $S=\langle n|n+1\rangle$. However, it will be shown that the NNONO approximation gives a systematic way to account for ONO effects only for small values of S,[6] since not only the bandwidth tends to infinity for $S=z^{-1}$ (z being the coordination number of the lattice, $z=2$ in our case), but the second derivative of the energy spectrum shows an oscillatory behavior fo S as small as 0.125, which directly affects the effective mass.

In Sec. III it is shown how this trouble can be overcome by taking into account the nonorthogonalities between orbitals other than those corresponding to nearest neighbors. In order to perform the calculation analytically, a basis set of exponential functions are chosen, together with δ-function atomic potentials, which allow us to compute explicitly all the multicenter integrals involved.

II. NEAREST-NEIGHBOR ORBITAL-NONORTHOGONALITY EFFECTS ON THE BAND STRUCTURE

In this section we review and discuss some of the emerging features of the nearest-neighbor nonorthogonality approximation.[5] The model we work on is an infinite monoatomic chain with one s-like orbital per atom (one-band model), and interactions restricted to nearest neighbors. The effective one-electron Hamiltonian for such a system can be written in site representation as

$$H=\alpha\sum_n|n\rangle\langle n|-\gamma\sum_n(|n+1\rangle\langle n|+|n\rangle\langle n+1|)\ , \tag{1}$$

where α and γ represent the correction to the atomic level and the nearest-neighbor hopping term, respectively (γ negative for s-like orbitals).

When $|\Psi\rangle$ is expressed as a linear combination of atomic orbitals and the NNONO parameter S is taken into account, the eigenvalue problem $(E-H)\Psi\rangle=0$ yields an infinite set of coupled difference equations of the form

$$(ES+\gamma_{n,n+1})C_{n+1}+(E-\alpha)C_n+(ES+\gamma_{n,n-1})C_{n-1}=0\ . \tag{2}$$

As can be easily seen from Eq. (2), orbital nonorthogonality introduces energy-dependent off-diagonal terms into the secular equation. Using translational invariance the coefficients acquire the usual Bloch form $C_n=\exp(inKa)$, where a denotes the lattice spacing, so that the band spectrum becomes

$$E=(\alpha=2\gamma\cos ka)/(1+2s\cos ka)\ . \tag{3}$$

Equation (3) clearly reduces to the familiar cosine spectrum as $S\rightarrow 0$.

Figure 1 shows how, even for small values of S, the NNONO approximation leads not only to a wider band, by a factor $1/(1-4S^2)$, but to a clearly asymmetric band with respect to the corrected atomic level. (Although one could attempt to hide the nonorthogonality effects in the Hamiltonian matrix elements, the resulting cosine spectrum will not reproduce these features.) As S increases, the band moves upwards by flattening the bottom and sharpening its top [but without changing the value of the spectrum at the middle of the Brillouin zone, i.e., $E(\pi/2)=\alpha$], so that the effective masses are changed by a factor $1/(1\pm 2S)^2$. (See Ref. 5 for some enlightening examples.)

By means of a formal Taylor expansion of the denominator of Eq. (3), we can gain understanding about the effects of the NNONO approximation. The resulting band spectrum is formally analogous to that of a crystal with more-distant-neighbor interactions in an orthogonal basis. For instance, to first order in S we obtain

$$E=(\alpha+2\gamma S)-2(\gamma+\alpha S)\cos ka+2\gamma S\cos 2Ka\ . \tag{4}$$

Equation (4) can be obtained by defining an effective Hamiltonian acting on a new basis set in which each atomic orbital has been orthogonalized with respect to its neighbors to first order in S, i.e., $|N\rangle=|n\rangle-(S/2)(|n+1\rangle+|n-1\rangle)$ (all terms of higher order than the first are neglected in the eigenvalue problem). It should be mentioned, however, that this approximation not only becomes poor as S increases, but the spectrum becomes unstable for $S\geq 0.25$. Such an instability arises because the resulting interactions between *even* and *odd* neighbors are competitive. Interestingly, instabilities emerge only when an even number of interactions are taken into account. It was found that interaction strengths tend to the Fourier coefficients corresponding to Eq. (3) when an infinite number of neighbors are considered, i.e.,

$$a_n=\frac{2(\alpha S+\gamma)}{S(1-4S^2)^{1/2}}\left[\frac{(1-4S^2)^{1/2}-1}{2S}\right]^n\ , \tag{5}$$

$$a_0/2=\frac{2(\alpha S+\gamma)-2\gamma(1-4S^2)^{1/2}}{S(1-4S^2)^{1/2}}\ . \tag{6}$$

The term a_0 shows how the NNONO affects the electronic part of the total energy.

As can be seen for Eq. (3), the NNONO approximation is valid only for $S<0.5$, since for $S=0.5$ the bandwidth tends to infinity. Even worse, already for $S>0.125$ there is trouble with this approximation, since the second derivative of the dispersion relation ceases to have a single minimum, which leads to an artificial value of the effective mass at the bottom of the band. This behavior

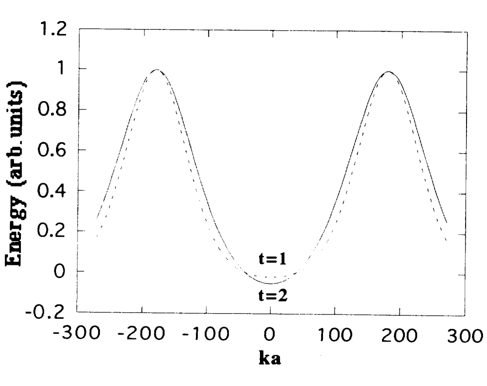

FIG. 1. Band structure for two values of the nonorthogonality parameter t [Eq. (12) in the test]. As t decreases (S_n increases) the effective mass at the bottom of the band increases, whereas the one at the top decreases. (ka is given in degrees, and the bands have been normalized to the same height.)

arises as a consequence of neglecting the nonorthogonalities between neighbors other than the first ones. For $S \geq 0.5$ it is unavoidable to consider overlap between more-distant neighbors. That is done in the next section, in the framework of a specific model.

III. EFFECTS OF INTERACTION AND NONORTHOGONALITY BETWEEN NON-NEAREST-NEIGHBOR ORBITALS

In what follows, the effects of ONO are extended to all neighbors. When interactions and nonorthogonalities between any neighbors are considered, the tight-binding one-electron spectrum for an s-type band becomes

$$E(k)=[\alpha-2\sum_n \Gamma_n \cos(nka)][1+2\sum_n S_n \cos(nka)]^{-1} . \tag{7}$$

In order to analytically compute the multicenter integrals involved in the overlap- and interaction-matrix elements between any orbitals in the crystals, we assign to each atom an s-type orbital of the form

$$\Phi(x)=(x_0)^{-1/2}\exp[-(|x|/x_0)] . \tag{8}$$

We also assume that the crystal potential U can be expressed as a sum of individual atomic potentials, which we choose to be Dirac's δ functions, that is, $U(x)=\sum_n V_n(x)$, with $V_n(x)=-A\delta(x-na)$. If we call $t=a/x_0$, we obtain the following expressions for the normalized Hamiltonian matrix elements:

$$S_n=[1-t(d/dt)]e^{-nt} , \tag{9}$$

$$\alpha=e^{-t}/\sinh t , \tag{10}$$

$$\Gamma_n=(n+\alpha)e^{-nt} . \tag{11}$$

As expected, the successive S_n and Γ_n decrease rapidly for a given value of the parameter t. By substituting these expressions in Eq. (3) we obtain

$$\lambda(ka,t)=\frac{A_0+A_1\cos ka+A_2\cos 2ka}{1+2\sigma\cos ka} , \tag{12}$$

where $\lambda=Ex_0/A$ represents the reduced energy and the coefficients A_0, A_1, A_2, and σ are given by

$$A_0=\coth t\{[1+e^{-t}(\cosh t+e^{-t})]/(\cosh t\sinh t-t)\} , \tag{13}$$

$$A_1=-\coth t\{(3e^{-t}+e^{-2t}\operatorname{sech} t+\sinh t)/(\sinh t\cosh t-t)\} , \tag{14}$$

$$A_2=e^{-t}/[\sinh t(\sinh t\cosh t-t)] , \tag{15}$$

$$\sigma=[(t\cosh t-\sinh t)/(\sinh t\cosh t-t)] . \tag{16}$$

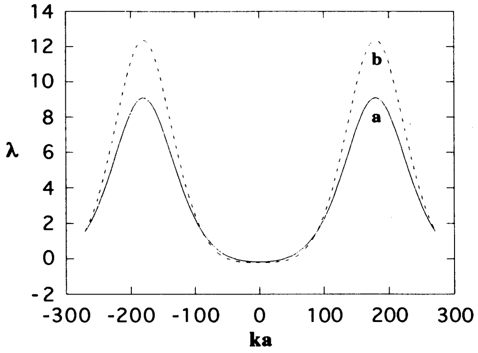

FIG. 2. Comparison of two spectra for $t=1$: a, the exact one, Eq. (12), and b, the one obtained by neglecting three-center integrals, Eq. (17). The approximate spectrum appears to be wider than the exact one. (ka is given in degrees.)

As a remarkable feature, the resulting band of this model looks like the band corresponding to a problem with interactions up to second-nearest neighbors, with an effective NNONO given by σ.

Figure 1 shows the form of the spectrum of Eq. (12) for two values of t. As t decreases, S_n, T_n, and α increase, and the band sharpens at the top and flattens at its bottom. These results are in qualitative agreement with the ones obtained in the NNONO approximation. It is worth noting, however, that in the present case the effective masses do not show the oscillatory behavior, which in the NNONO approximation was present for $S>0.125$, nor does the spectrum diverge for $S=0.5$. Interestingly, the bandwidth grows monotonically with S and becomes infinite only for $S=1$ (i.e., $t=0$). This shows that limiting the ranges of overlaps and interactions can be misleading, even when they mean an improvement over the orthogonal case.

We can exploit this analytical model to evaluate the differences between the exact spectrum and one in which the three-center integrals are neglected, namely,

$$\lambda(ka,t)=\frac{(\cosh t-\cos ka)(1-\cosh t\cos ka)}{\sinh t[\sinh t(\cosh t-\cos ka)-t(1-\cosh t\cos ka)]} . \tag{17}$$

We have found that by neglecting three-center integrals a wider spectrum is generated for $t>1$ (i.e., for $S<0.74$), such that the effective masses at the top appear to be smaller than in the exact model (see Fig. 2).

IV. CONCLUSIONS

(1) When the lack of orthogonality between orbitals is explicitly taken into account, the band structure becomes

asymmetric, decreasing the effective mass at the top and increasing it at the bottom.

(2) The effective masses are extremely sensible to the range of the interactions and overlaps. This means that one could possibly be misled when interpreting correctly calculated band structures, if overlaps between different orbitals were not properly taken into account.

(3) The effects of nearest-neighbor orbital nonorthogonality can be simulated by considering more-distant-neighbor interactions in a Slater-Koster scheme.

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