

Orthogonalized-moment method and the study of the electronic structure of heterostructures: Application to CdTe/ZnTe superlattices

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We present an approach that uses power moments of the Hamiltonian to calculate the electronic states in low-dimensional structures, such as quantum wells or superlattices. From a microscopic tight-binding description of the crystals, the orthogonalized moments of the Hamiltonian are used to obtain the coefficients of the continued fraction representing the density of the electronic states. This method allows us to calculate quite efficiently the electronic states of large-period systems and clusters. Application to a one-dimensional quantum-well model shows the ability of the method to determine the localized states with good accuracy. Then, we calculate the electronic structure of a strained CdTe/ZnTe superlattice and we study the dependence of the highest valence states at the center of the Brillouin zone, with respect to the valence-band offset. Existence of type-I–type-II transition for a critical value of the valence-band offset is brought out.

I. INTRODUCTION

The electronic structure of semiconductor systems has become a subject of increasing importance. These systems are artificially grown layered structures such as quantum wells, multiquantum wells, or superlattices.¹ In the first two cases, there is a break of the translational symmetry in the growth direction and only two-dimensional translation symmetry in the plane of the interfaces is retained. Superlattices have three-dimensional translation symmetry with a large period along the growth axis. Recently, substantial progress has been realized in epitaxial growth and nanostructure techniques and new structures, quasi-one-dimensional-like quantum wires, or zero-dimensional-like quantum dots have been produced with good quality.² These systems are very promising for making electronic devices and knowing their electronic structure is important for the understanding of their physical properties. All the band calculation methods can be *a priori* used to obtain the electronic structure of these systems. However, their implementation can lead to a very large amount of calculations, which requires more efficient computational procedures. The tight-binding approximation based on an empirical description of the bulk states has often been applied to the heterostructure studies.³ The interest of this method is to give a microscopic description of the material which allows the full symmetry of the system to be taken into account. This avoids the assumption that there is the absence of mixing between the light- and heavy-hole states at the Brillouin-zone center and the presence of inversion symmetry. Moreover, the tight-binding method describes the states of the whole of the Brillouin zone which is necessary when states both near and far from the zone center must be considered at the same time as, for instance, in the case of an indirect band gap. In the tight-

binding method, the electronic wave function is expanded in terms of atomic orbitals. A basis set often used for the study of semiconductors consists of *s* and *p* states of each atom. For bulk systems, there are two atoms in the unit cell and energy band calculations require diagonalization of 20×20 matrices when spin-orbit and *s** orbitals⁴ are included. In the case of superlattices, the number of atoms in the unit cell is large and the direct diagonalization becomes intractable for large-period heterostructures. Calculations of the electronic structure of quantum wells, quantum wires, and quantum dots is still more cumbersome because of the lack of translation invariance. In these cases, the very large size of the unit cell to be considered prevents even any direct diagonalization of the Hamiltonian matrix.

Several methods have been developed to determine the electronic properties of such systems. The recursion method⁵ gives one way to solve the problem, providing a procedure to determine the Green's function of the Hamiltonian operator. Starting from an initial basis state, a new basis set is constructed by a three-term recursion relation in such a way that the Hamiltonian is tridiagonal in this basis set. From the matrix elements so obtained, the density of states projected on the initial state is generated as a continued fraction. This approach has been used to perform calculations in real space for semiconductor clusters⁶ and quantum wells.⁷ It has also proved its efficiency when the recursion is performed in the *k* space as for the study of translationally invariant systems.⁸ A second method to enable the handling of systems leading to large-dimensional Hamiltonian matrix is based on the renormalization techniques.^{9–11} In this method, the Green's function projected on a given layer is calculated by successive elimination of all the other layers. At each step, a renormalized energy-dependent Hamiltonian of lower dimension is obtained and the pro-

cess is repeated until only the layer concerned remains. The renormalization method is closely related to the recursion method.¹² Recently, it has been applied to study the electronic band structure of large-period systems in order to interpret the intrinsic origin of the semiconductor-semimetal transition of InAs/GaAs superlattices.¹³ However, these methods can only be used for renormalizable systems. An alternative way to obtain the Green's function is to expand it in power moments.¹⁴ However, the calculation of these moments presents great difficulties. The use of generalized moments^{15,16} which seek to keep the linearity of the moments in the Green's function leads to numerical instabilities. A particular form of the generalized moments, called the orthogonalized moments, was proposed.¹⁷ They can be calculated exactly by a numerically stable procedure and this method is equivalent to the recursion method. Recently, this orthogonalized-moment method (OMM), called spectral moment method in lattice dynamics, has been applied to the direct determination of the infrared absorption, Raman or Brillouin scattering of light, and inelastic scattering of neutrons.^{18,19} This method has been revealed to be a powerful tool to obtain the spectral densities of systems such as perfect crystals or those with impurities and disordered systems.^{20,21} The purpose of this paper is the extension of this new approach to the study of the electronic properties of superlattices or multilayer heterostructures. This constitutes, to our knowledge, the first application of the OMM to the calculation of electronic states of these systems. In Sec. II we give a brief outline of the method and we describe the algorithm which allows us to obtain the orthogonalized moments and to deduce from these the projected density of states. In Sec. III we apply the method on a simple one-dimensional model superlattice in order to verify the precision and the convergence of procedure. In Sec. IV an application of the OMM to the calculation of the electronic structure of a realistic CdTe/ZnTe superlattice is presented. From a semiempirical tight-binding description of the microscopic interactions, we show the great precision obtained by using the OMM and we discuss the existence of a type-I-type-II transition when the valence-band offset varies.

II. ORTHOGONALIZED-MOMENT METHOD

We consider a Hamiltonian represented on an orthogonal local basis such as, for instance, a tight-binding model Hamiltonian, and define $n_0(E)$ the local density of states (LDOS) on local orbital $|u_0\rangle$ as

$$n_0(E) = \langle u_0 | \delta(E - \mathbf{H}) | u_0 \rangle = -\frac{1}{\pi} \lim_{\epsilon \rightarrow 0^+} \text{Im} G_0(E + i\epsilon), \quad (1)$$

where $G_0(E)$ is the diagonal matrix element of the Green's function which is given in the eigenbasis by

$$G(z) = (z - \mathbf{H})^{-1} = \sum_{n,k} \frac{|nk\rangle \langle nk|}{z - E_{nk}}, \quad (2)$$

where E_{nk} is the energy of the eigenstate $|nk\rangle$. In this

basis, $n_0(E)$ can be written as

$$n_0(E) = \sum_{n,k} |\langle u_0 | nk \rangle|^2 \delta(E - E_{nk}). \quad (3)$$

The main interest of the Green's functions is that they allow one to obtain the relevant physical information while avoiding the direct diagonalization of the Hamiltonian matrix. The poles of the Green's function are the energies of the eigenstates and the residues at these poles give the local contribution to the eigenstates. The matrix elements of the Green's function can be expressed as a continued fraction

$$G_0(z) = \frac{1}{z - a_1 - \frac{b_1}{z - a_2 - \frac{b_2}{z - a_3 - \frac{b_3}{z - a_4 - \dots}}}}. \quad (4)$$

The recursion coefficients a_n and b_n are real and positive. On the other hand, the Green's function can be expanded in Laurent set

$$G(z) = \sum_{n=0}^{\infty} \frac{\mu^n}{z^{n+1}}, \quad (5)$$

where the power moments are defined as

$$\mu_n = \langle u_0 | \mathbf{H}^n | u_0 \rangle = \int E^n n_0(E) dE. \quad (6)$$

The two expressions (4) and (5) are formally equivalent, however, the expansion (4) is convergent as n goes to infinity while (5) is not. The coefficients of the continued fraction are related to the moments by the ratios of Hankel determinants Δ_n and Δ_{n-1} . These determinants are obtained from the Hankel matrices, the elements of which are the power moments. However, it is not easy to compute the coefficients a_n and b_n in this way because the calculation is ill conditioned. To overcome this difficulty, Gaspard and Lambin^{15,16} have defined generalized moments μ_n from a sequence of polynomials $\{p_n(E)\}$,

$$\begin{aligned} \mu_{2n} &= \int_{-\infty}^{\infty} n_0(E) p_n(E) p_n(E) dE, \\ \mu_{2n-1} &= \int_{-\infty}^{\infty} n_0(E) p_n(E) p_{n-1}(E) dE, \end{aligned} \quad (7)$$

where $p_n(E)$ is a polynomial of degree n in energy which satisfies a three-term recurrence

$$p_{n+1}(E) = E p_n(E) - c_{n+1} p_n(E) - d_n p_{n-1}(E). \quad (8)$$

The coefficients c_n and d_n must be defined *a priori* and their choice determines the success of this method. This one is tricky to work because it requires the knowledge of a sequence of polynomials close enough to the sequence of the polynomials which are orthogonal to the function *a priori* unknown $n_0(E)$. In fact, the recurrence process is led with a set which is not rigorously orthogonal. The accuracy of results is very sensitive to input parameters and small changes in their values can give large variation in the results. An important improvement recently supplied by Jurczek¹⁷ has shown that it was possible to gen-

erate a sequence of polynomials which is *a priori* orthogonal to an unknown function. This method provides an exact determination of the continued fraction coefficients by making use of a particular form of generalized moments. These orthogonalized moments v_n are obtained from another recurrence relation for $\overline{\Delta}_n$, in which the input coefficients do not appear. If one defines the new elements

$$\begin{aligned} v_n &= \int_{-\infty}^{\infty} n_0(E) p_n^2(E) dE, \\ \overline{v}_n &= \int_{-\infty}^{\infty} n_0(E) p_n^2(E) E dE, \end{aligned} \quad (9)$$

the continued fraction coefficients are given by

$$a_{n+1} = \frac{\overline{v}_n}{v_n}, \quad b_n = \frac{v_n}{v_{n-1}} \quad \text{for } n \geq 1. \quad (10)$$

These equations together with Eq. (8) allow us to determine all the v_n and \overline{v}_n coefficients from the initial values $v_0 = 1$, $p_{-1} = 0$, and $p_0 = 1$, by the following algorithm:

$$p_n \rightarrow (v_n, \overline{v}_n) \rightarrow (a_{n+1}, b_n) \rightarrow p_{n+1}. \quad (11)$$

With the relations (11), the orthogonalized-moment method is equivalent to the recursion method.

For an infinite system, the basis set contains an infinite number of atoms and the development in continued fraction requires an infinite number of recurrence levels. As only one limited number of terms can be considered, the expansion must be truncated to a given level. Several approaches have been proposed to cut off the development and to include the asymptotic form of the continued fraction coefficients. As discussed in previous works,^{14,22} their asymptotic variation depends both on the occurrence of Van Hove singularities in the density of states which give damped oscillations in the recursion coefficients and on the existence of band gaps which produce undamped oscillations. However, a large part of these results is conjectured²³ and the precise behavior of the coefficients a_n and b_n for large physical systems is often more complicated. On the other hand, the convergence of the continued fraction increases with the number of calculated moments and the precise choice of the infinite tail is not very crucial when considering a large number of a_n and b_n coefficients.²¹ If necessary, the accuracy of the method can be increased by developing the coefficients in Fourier series and taking a periodic tail. By this procedure, the densities of states of very large harmonic systems have been determined with good precision.

For materials with a periodic structure, such as crystals or superlattices, it is possible to take into account the periodicity of the system and to build a new basis of Bloch functions $\Phi_\alpha(\mathbf{k}, \mathbf{r})$ from a localized basis $u_\alpha(\mathbf{r} - \mathbf{R}_n)$ by the relation

$$\Phi_\alpha(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{n=1}^N e^{i\mathbf{k} \cdot \mathbf{R}_n} u_\alpha(\mathbf{r} - \mathbf{R}_n), \quad (12)$$

where N is the number of unit cells of the crystal and α denotes one of the p different basis functions centered on the lattice site \mathbf{R}_n . In this new basis, the Hamiltonian is

block diagonal because all the matrix elements between Bloch functions with different \mathbf{k} vectors are equal to zero. Then, the Hamiltonian matrix is expressed as a set of N matrices $\mathbf{H}(\mathbf{k})$ each of them with a dimension equal to p ; and consequently the N \mathbf{k} points in the Brillouin zone must be considered. However, as usual, only a limited number of \mathbf{k} points is included in the calculations such as, for instance, when a special \mathbf{k} -point method²⁴ is used. The Green's function can be obtained in the Bloch basis and the recurrence equations can be applied to the Hamiltonian matrices directly in the \mathbf{k} -space representation.⁸ To find the local density of states, one starts from a given state $|u_0\rangle$ which is usually localized in the direct space. When the recurrence is implemented in the \mathbf{k} space, the $|u_0\rangle$ state is decomposed in contributions originating from different \mathbf{k} points and the recursion must be performed in each orthogonal subspace.

It is important to note that it is equivalent to proceed to the calculation of moments in the direct space or in the \mathbf{k} space because the relation between the basis functions given by Eq. (12) is unitary. However, the manner to implement calculations is different. In the real space, only a finite cluster is considered and, after some recurrence level, the state vector is no longer contained in the initial cluster and some approximations must be made. In the \mathbf{k} space, each submatrix is finite. Usually, its dimension is much weaker and the moment calculation is performed without the choice of an asymptotic form being necessary. On the other hand, the moments must be calculated for all the \mathbf{k} points. As only a finite number of these points can be considered, special \mathbf{k} -point method is often used.²⁴

III. APPLICATION TO THE QUANTUM WELLS

To illustrate how the orthogonalized-moment method can be applied to electronic band-structure calculations, we first consider an infinite one-dimensional lattice formed by two kinds of atoms with one s state, for instance, an anion A and a cation C , alternatively distributed on the chain with a spacing between two successive sites equal to a . A model Hamiltonian in the tight-binding approximation, retaining only the nearest-neighbor interactions, is

$$\mathbf{H} = \sum_n (-1)^n \varepsilon c_n^\dagger c_n + \sum_n t_{n,n+1} (c_{n+1}^\dagger c_n + c_n^\dagger c_{n+1}) + \overline{E}, \quad (13)$$

where c_n^\dagger and c_n are, respectively, the creation and annihilation operators for one electron on the n th site, $\varepsilon = (E_A - E_C)/2$ is the half difference between the anion and cation one-site energies, $\overline{E} = (E_A + E_C)/2$ the mean energy, and $t_{n,n+1}$ the hopping integral assumed constant with t value. This system is periodic with a period $2a$ and it is easy to obtain the total density of states by atom (DOS) as

$$n_0(E + \bar{E}) = \begin{cases} \frac{1}{\pi} \frac{|E|}{[(E^2 - \varepsilon^2)(\varepsilon^2 + 4t^2 - E^2)]^{1/2}} & \text{if } \varepsilon^2 \leq |E| \leq (\varepsilon^2 + 4t^2)^{1/2} \\ 0 & \text{otherwise} . \end{cases} \quad (14)$$

As a test case, we shall consider a biatomic chain composed of 100 atoms with the parameters $E_A = 0.5$ eV, $E_C = 1.5$ eV, and $t = -4$ eV. Figure 1 shows the local density of states on an anion site and the DOS calculated by OMM. We have obtained these densities from the contribution of the first ten moments with the usual square-root termination which accounts for the oscillations originating from the energy gap $E_g = 2\varepsilon$. To evaluate the precision of the method, we have also reported, in Fig. 1, the DOS calculated from Eq. (14). The agreement with the DOS obtained by OMM is very good and the comparison clearly shows that OMM allows one to obtain the features of the DOS with only a few moments. We have also calculated the DOS by direct diagonalization of the Hamiltonian matrix. For a chain with 160 atoms, the computation time for the DOS determination with 12 moments is 15 s as compared with only 2 s with OMM, all the calculations being performed on an IBM 3081 computer.

The study of the electronic structure of semiconductor quantum wells and superlattices has recently known a large development because the quantum size effect leads to a spatial localization of the electrons and holes into layers. The confinement of these carriers leads to the appearance of states which are localized in the direction

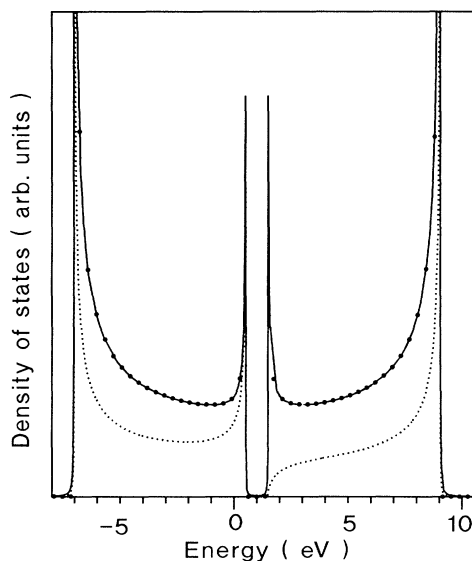


FIG. 1. Densities of states for a biatomic one-dimensional chain. Solid and dotted curves, respectively, refer to the DOS and to the LDOS on an anion site obtained from the first ten moments by the OMM. Black circles give the exact total DOS calculated from Eq. (14).

perpendicular to the layers and the calculation of the corresponding energy states must be implemented with a great precision whatever the well size, in order to be used in the interpretation of optical spectra. It was interesting to check how the OMM can be applied to obtain the localized state energy of large systems. We have considered a quantum well formed by 20 layers of a new material surrounded with 50 layers of the previous material on each side. The two materials, described in the same way as before, are supposed to have a common anion ($E_A = E_{A'}$) and the same hopping integral t . We take $E_C = 2.5$ eV so that the offset appearing between the highest (conduction) bands of each compound is 1 eV. To test the accuracy of the OMM, we have first calculated the quantum-well state energies by numerical direct diagonalization of the Hamiltonian which, in theory, gives the exact eigenvalues. On the other hand, we have determined these values from the OMM as the maxima of the LDOS calculated on the layer at the center of the well, varying the number of moments which are included in the evaluation of the LDOS. The calculations have been performed to obtain the energy values with a given precision and require a larger number of moments than those needed to calculate the main features of the LDOS. Considering 20 moments, we obtained the localized state energy within 5 meV of that given by the direct diagonalization. When 40 moments are included in the calculation, the agreement between the energies is better than 1 meV. These calculations of the eigenstates using the

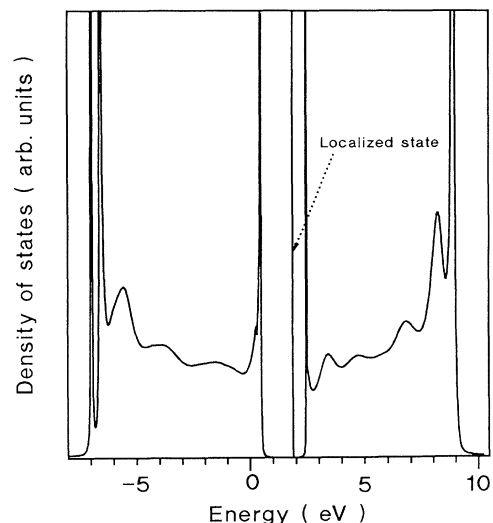


FIG. 2. LDOS on the layer lying at the well center, at $\mathbf{k}=0$, for a one-dimensional quantum well.

OMM method do not require much computer time. Moreover, the great advantage of the method is that the computation time varies linearly with the moment number and matrix order. We have shown, in Fig. 2, the LDOS at the center of the well determined by OMM when 20 moments are included in the calculation. As expected, a localized state appears in the gap under the bottom of the conduction band. The great advantage of the OMM lies in the high speed of the calculation with respect to the direct diagonalization, which is very important for the application of the OMM method to systems with a large number of atoms.

IV. CdTe/ZnTe SUPERLATTICES

Our purpose is the study of semiconductor superlattices by the OMM. Therefore, after this preliminary study of a very simple one-dimensional model, we will consider more realistic semiconductor heterostructures and we will study as an example the case of strained CdTe/ZnTe superlattices. This system presents an interesting property according to the heterostructure characteristics. It is possible to find the two kinds of carriers in the same semiconductor layer or in two neighboring layers. In the first case, the superlattice is type I and the optical transitions are intense because of the large overlap of the electronic states localized in the same layer. Otherwise, hole and electrons are in neighboring layers, the superlattice is type II, and the oscillator strengths are weaker. To describe the bulk crystals, we use a tight-binding approach. The interest of this method lies in the microscopic description of the materials from the atomic interactions between anions and cations. It retains the full symmetry of the crystal. We use a modified sp^3s^* basis⁴ including spin-orbit interactions. In order to analyze more easily how the superlattice valence states are formed from the bulklike hole states of the two composing materials, we have taken as basis functions the linear combinations of the Bloch states which are the eigenstates of the total angular momentum and of its components along the z direction. Only interactions up to first neighbors are retained. However, these limitations are not necessary to use our method, which can be applied to more general situations. Consideration of spin-orbit coupling leads to a basis of ten orbitals per atom which gives a Hamiltonian matrix in \mathbf{k} space with the dimension $(M+N) \times 20$. All the matrix elements are fitted to bulk band structures of the two semiconductors. Two sorts of requirements can be imposed for the parametrization. One can try to reproduce the energy bands at the high symmetry points of the Brillouin zone; this way is well adapted to a description of overall properties of the crystals. On the other hand, if we are interested in the optical properties, only states near the fundamental band gap of the crystals are concerned, and it is important to have an accurate description of the band dispersion into this region. We have proceeded in this latter manner in order to describe precisely the energy bands near the Γ and X extreme.

CdTe and ZnTe materials present a lattice mismatch of about 6%. This results in heavy biaxial stress which

deeply modifies the electronic structure of materials, shifting the conduction band and splitting the valence band, in a superlattice built with two mismatched semiconductors, two neighboring layers experience antagonistic stresses. This gives a contribution to the band offset which mainly depends on the thicknesses of the layers. This component adds to the band offset which exists if the two semiconductors are unstrained. The lattice mismatch of the two compounds causes the cations and anions to move from the perfect lattice sites. This entails changes in the length and the orientation of the bonds and consequently, modifies the Hamiltonian. The off-diagonal matrix elements $V_{\alpha,\beta}(d)$ between two atomic orbitals α and β , centered on adjacent sites at a distance d are assumed to vary according to the law

$$V_{\alpha,\beta}(d) = V_{\alpha,\beta}(d_0) \left(\frac{d_0}{d} \right)^{\eta_{\alpha,\beta}}, \quad (15)$$

where d and d_0 are the nearest-neighbor distances for the strained and unstrained cases, respectively. The exponents $\eta_{\alpha,\beta}$ are determined by fitting to the experimental pressure variations of bulk energy states of the semiconductors. So, to obtain accurate results for strained superlattice energy states, we must require our parameter set to reproduce, at the same time, the experimental values of the effective masses and the deformation potentials of each compound. As the main scope of this paper is to show the great interest of the OMM in the electronic structure calculations, we do not detail the parametrization method for such strained superlattices. Only the values of effective masses and deformation potentials obtained from tight-binding parameters are compared with experimental data in Table I.

We now present some results obtained with the OMM on [001] CdTe/ZnTe superlattices in order to illustrate the ability of the method to calculate the electronic band structure of realistic systems. We consider a superlattice in a free-standing configuration. In this case, the lattice mismatch constant is determined by minimizing the strain energy density in the superlattice, assuming complete relaxation with respect to the buffer, and forcing the in-plane lattice constant to be equal on the two sides of

TABLE I. Effective masses (in units of electron masses) and deformation potentials (in eV) calculated from our tight-binding approximation and compared with experimental values. a and b are, respectively, the hydrostatic and the uniaxial deformation potentials. $m_{hh}[100]$ and $m_{lh}[100]$ are the heavy- and light-hole effective masses in the [001] direction.

		a	b	$m_{hh}[100]$	$m_{lh}[100]$
CdTe	Theory	-3.17	-1.2	0.5128	0.1597
	Expt.	-3.17 ^a	-1.17 ^a	0.5128 ^b	0.1595 ^b
ZnTe	Theory	-5.19	-1.2	0.3985	0.1778
	Expt.	-5.19 ^c	-1.3 ^d	0.3984 ^b	0.1776 ^b

^aReference 31.

^bReference 32.

^cReference 33.

^dReference 34.

the interfaces. For superlattices made up of two semiconductors having the same number of layers N , the in-plane lattice constant is independent of N , like the strain effects. Varying N only changes the confinement. The valence-band offset at the CdTe/ZnTe interfaces in the absence of the strain V_0 is defined as the valence-band energy difference $E_{V_2} - E_{V_1}$ where E_{V_1} is the valence-band energy of the semiconductor of a larger gap, here ZnTe. So, V_0 positive value corresponds to an upward step in going from the valence band of the wide gap compound ZnTe to the valence band of the narrow gap compound CdTe. The V_0 value is not known with great precision. Most of the valence-band offset estimations are deduced from a comparison between optical studies and calculations based on the envelope function approximation.²⁵⁻²⁷ The precision of these determinations is limited by the accuracy with which exciton binding energies and strain effects are known. Optical studies give small values for V_0 . However, a larger value of V_0 has recently been obtained.²⁸ Because of the large range of these determinations, we have first studied the influence of the offset of the electronic states. Figure 3 shows the dependence of the highest valence states at the center of the Brillouin zone H_1 and L_1 , upon the valence-band offset value V_0 for a ZnTe(10)/CdTe(10) superlattice. H and L denote the nature of the superlattice states at the zone center according to whether, mainly or wholly, they originate from the bulk heavy- or from light-hole states. The valence states strongly depend on V_0 . For the considered offset values, the electrons are always localized in CdTe layers. When $V_0=0$, CdTe is the well material for the heavy-hole states and the superlattice is type I. For posi-

tive offset values, the localization of heavy-hole state H_1 in CdTe layers increases and the band gap is reduced. The light-hole state L_1 becomes more extended and is always less energetic than the heavy-hole state H_1 . The case of negative values of V_0 presents a more interesting feature and gives evidence of a superlattice type-I-to-type-II transition. V_0 decreasing has two effects. It lowers the barrier height for the heavy-hole states which delocalize in all the superlattice and increases the localization of the light-hole state which becomes the hole ground state. So, $V_0 = -60$ meV appears as the value of the valence-band offset for which the transition from a type-I to a type-II superlattice occurs. For weaker V_0 values, light-hole state L_1 lies lower than the heavy-hole state H_1 and the superlattice is type II. The excitonic transition becomes indirect in the real space with weak oscillator strength. Similar trends have been obtained by previous tight-binding approaches^{29,30} using a different parametrization of the Hamiltonian.

We now continue our study of the ZnTe(10)/CdTe(10) superlattice assuming a zero valence-band offset. Figure 4 shows the electronic band structure of such a sample along the growth direction Γ -Z [001] and the in-plane direction Γ - Δ [100]. The highest-energy band H_1 is strongly bound in the CdTe layers which constitute wells of depth 102 meV and consequently shows little dispersion. The H_2 and H_3 bands lie in the continuum and possess a strongly marked character of folded bands. The ZnTe layers form a deeper well (199 meV) for the light-hole states and all these states except $L_1(\Gamma)$ are in the continuum and show a nearly parabolic dispersion. It is

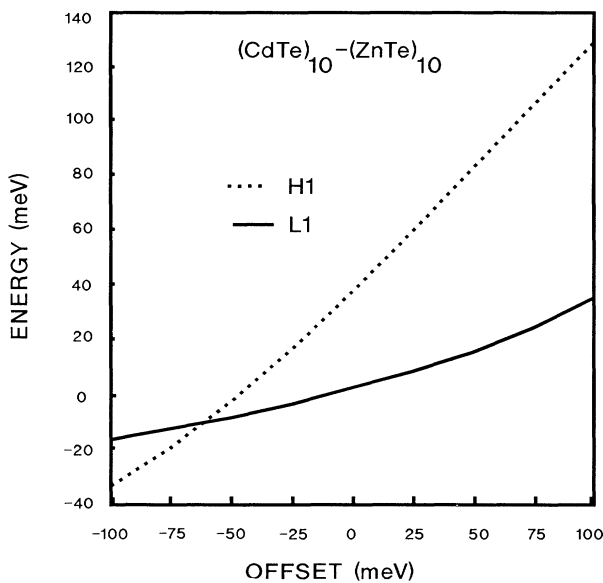


FIG. 3. Dependence of the two highest-energy valence states at the center of the Brillouin zone, upon the valence-band offset V_0 for ZnTe₁₀/CdTe₁₀ superlattice. The energy origin is taken on the top of the valence band of the wider gap semiconductor (ZnTe).

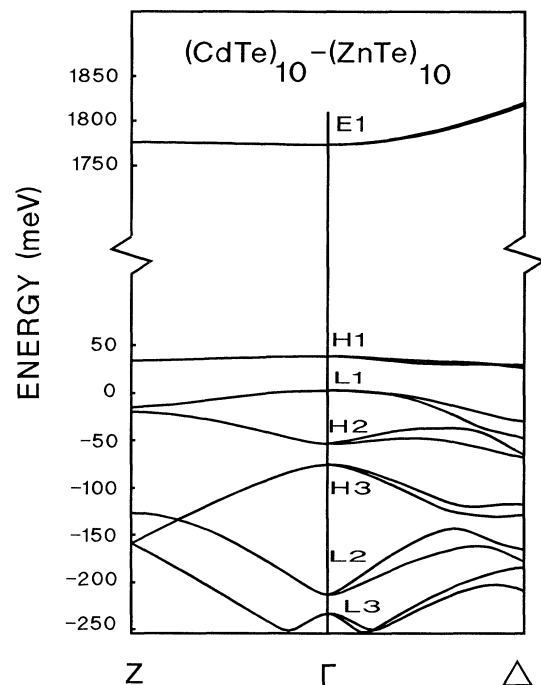


FIG. 4. Electronic band structure for ZnTe₁₀/CdTe₁₀ superlattice calculated with a valence-band offset $V_0 = 0$ meV.

interesting to discuss the anticrossings which appear in the two considered directions. For superlattice wave vectors directed along the [001] direction, there is only one two-dimensional irreducible representation. All the bands are twofold degenerate and cannot cross each other. However, the energy difference between the two states is weak and cannot be seen in Fig. 4. For superlattice wave vectors directed along the [100] direction, there are two one-dimensional irreducible representations which entail a splitting of the superlattice bands. In this case, crossing is only forbidden for subbands belonging to the same irreducible representation. This explains the anticrossing which occurs between the L_1 and H_2 bands.

V. CONCLUSION

We have shown that the orthogonalized-moment method is a very efficient method to determine the electronic band structure of superlattices and multilayer heterostructures. This method presents great ability to deal with systems having a unit cell of large size and to successfully describe systems with low-dimensional translation symmetry. We have used this approach to perform two applications concerning tight-binding Hamiltonians. First, we have considered a one-dimensional model of superlattice. The results show the efficiency of the method in the determination of quantum-well states and compare

favorably with the values calculated by the direct diagonalization of the Hamiltonian. Then, we have applied the OMM to a realistic ZnTe/CdTe superlattice within a semiempirical tight-binding description. The Hamiltonian parametrization of such strained semiconductors includes spin-orbit interactions and reproduces correct values for effective masses and deformation potentials. The electronic band structure of ZnTe/CdTe superlattices is obtained with very good accuracy and is in agreement with those derived by other methods. These results show that the moment method, which has been limited for a long time to the whole description of systems through the determination of the density of states, constitutes, in reality, a powerful method to calculate the energy states provided that the orthogonalized moments are used to obtain the recursion coefficients. Application of this method to the calculation of the electronic structure of quantum wires and quantum dots should be promising.

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- ¹For a survey, see *Proceedings of the 4th International Conference on Modulated Semiconductor Structures (MSS-4)*, edited by L. L. Chang, R. Merlin, and D. C. Tsui (North-Holland, Amsterdam, 1990); *Surf. Sci.* **228**, (1992).
- ²K. Ploog, in *Low-Dimensional Structures in Semiconductors*, Vol. 281 of *NATO Advanced Study Institute, Series B: Physics*, edited by A. R. Peaker and H. G. Grimmeis (Plenum, New York, 1991).
- ³J. N. Schulman and T. C. McGill, *Phys. Rev. B* **19**, 6341 (1979); J. N. Schulman and Yia Chung Chang, *ibid.* **31**, 2056 (1985).
- ⁴P. Vogl, H. Hjalmarsen, and J. D. Dow, *J. Phys. Chem. Solids* **44**, 365 (1983).
- ⁵R. Haydock, V. Heine, and J. J. Kelly, *J. Phys. C* **5**, 2845 (1972). See, for a review, *Solid State Physics: Advances in Research and Applications*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35; and *The Recursion Method and Its Applications*, edited by D. G. Pettifor and D. L. Weaire (Springer-Verlag, Berlin, 1985).
- ⁶Zi-fang Zhou, Shi-Yu Wu, and K. S. Dy, *Phys. Rev. B* **34**, 2632 (1986).
- ⁷K. S. Dy and Shi-Yu, *Phys. Rev. B* **38**, 5709 (1988).
- ⁸S. M. Anlage and D. L. Smith, *Phys. Rev. B* **34**, 2336 (1986).
- ⁹H. Aoki, *J. Phys. C* **13**, 3369 (1980).
- ¹⁰R. D. Graft, D. Lohrmann, G. Pastori Parravicini, and L. Resca, *Phys. Rev. B* **36**, 4782 (1987).
- ¹¹G. Giannozzi, G. Grosso, S. Moroni, and G. Pastori Parravicini, *Appl. Num. Math.* **4**, 273 (1988).
- ¹²R. D. Graft, G. Grosso, D. J. Lohrmann, L. Martinelli, S. Moroni, G. Pastori Parravicini, and L. Resca, in *Progress on Electron Properties of Solids*, edited by R. Girlanda *et al.* (Kluwer, Dordrecht, 1989), and references therein.
- ¹³G. Grosso, S. Moroni, and G. Pastori Parravicini, *Phys. Rev. B* **40**, 12 328 (1989).
- ¹⁴J. P. Gaspard and F. Cyrot-Lackmann, *J. Phys. C* **6**, 3077 (1973).
- ¹⁵J. P. Gaspard and P. Lambin, in *The Recursion Method and Its Applications*, edited by D. G. Pettifor and D. L. Weaire (Springer-Verlag, Berlin, 1985).
- ¹⁶P. Lambin and J. P. Gaspard, *Phys. Rev. B* **26**, 4356 (1982).
- ¹⁷E. Jurczek, *Phys. Rev. B* **32**, 4208 (1985).
- ¹⁸C. Benoit, *J. Phys. C* **20**, 765 (1987).
- ¹⁹C. Benoit, *J. Phys. Condens. Matter* **1**, 335 (1989).
- ²⁰C. Benoit and Gérard Poussigüe, in *High Performance Computing I*, edited by J.-L. Delaye and E. Gelenbe (North-Holland, Amsterdam, 1989).
- ²¹C. Benoit, E. Royer, and G. Poussigüe, *J. Phys. Condens. Matter* **4**, 3125 (1992).
- ²²P. Turchi, F. Ducastelle, and G. Treglia, *J. Phys. C* **15**, 2891 (1982).
- ²³A. Magnus, in *The Recursion Method and Its Applications*, edited by D. G. Pettifor and D. L. Weaire (Springer-Verlag, Berlin, 1985).
- ²⁴D. J. Chadi and M. L. Cohen, *Phys. Rev. B* **8**, 5747 (1973).
- ²⁵H. Mathieu, A. Chatt, J. Allègre, and J. P. Faurie, *Phys. Rev. B* **41**, 6082 (1990).
- ²⁶H. Tuffigo, N. Magnea, H. Mariette, A. Wasiela, and Y. Merle d'Aubigné, *Phys. Rev. B* **43**, 14 629 (1991).
- ²⁷Y. Merle d'Aubigné, H. Mariette, N. Magnea, H. Tuffigo, R. T. Cox, G. Lentz, Le Si Dang, J.-L. Pautrat, and A. Wasiela, *J. Cryst. Growth* **101**, 650 (1990).
- ²⁸E. Deleporte, J. M. Berroir, C. Delalande, N. Magnéa, H. Mariette, J. Allègre, and J. Calatayud, *Phys. Rev. B* **45**, 6305

- (1992).
- ²⁹L. Quiroga, C. Camacho, L. Brey, and C. Tejedor, *Phys. Rev. B* **40**, 3955 (1989).
- ³⁰D. Boiron, D. Bertho, A. Simon, and C. Jouanin, *Semicond. Sci. Technol.* **6**, A141 (1991).
- ³¹B. Gil and D. J. Dunstan, *Semicond. Sci. Technol.* **6**, 428 (1991).
- ³²C. Neumann, A. Nothe, and N. O. Lipari, *Phys. Rev. B* **37**, 922 (1988).
- ³³K. Strössner, S. Ves, Chul Koo Kim, and M. Cardona, *Solid State Commun.* **61**, 275 (1987).
- ³⁴W. Wardzynski, W. Gariat, A. Szynczak, and R. Kowalczyk, *Phys. Status Solidi B* **49**, 71 (1972).