

Minimal tight-binding Hamiltonian for semiconductors

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We present a minimal tight-binding Hamiltonian which describes properly both valence and conduction bands of tetrahedrally coordinated semiconductors. We find that, for a correct description of the electronic structure, it is necessary to include a realistic wave-function basis and at least the interaction matrix element between sp^3 orbitals in second-neighbor atoms pointing towards the common neighbor. Using Slater orbitals as basis functions and a six-parameter Hamiltonian, the band structure of silicon is reproduced with a root-mean-square deviation with respect to the experimental one of 0.3 eV.

Since the pioneer work of Slater and Koster¹ in 1954 the tight-binding method has been extensively applied to semiconductors. Not only the band structure of crystal-line structures has been studied but also defects like vacancies, impurities, surfaces, etc., have been analyzed within the tight-binding framework. Several different tight-binding Hamiltonians have been proposed in the past²⁻¹⁰ because many complicated problems can only be managed by using this simplified and yet realistic approach.

In order to keep the simplicity of the method it has been customary to assume an orthogonal basis localized at the different atoms of the system (Wannier functions,^{11,12} say). The matrix elements of the Hamiltonian in this basis are fitted to reproduce the experimental energy levels. In spite of the success of this approach it has several shortcomings. First, the matrix elements of the Hamiltonian in the assumed orthonormal basis have a difficult and in some cases meaningless interpretation (the chemical pseudopotential¹³ provides this interpretation in a complicated way). Second, since the basis is unknown, magnitudes like charge transfer between the atoms, dipole-matrix elements, etc. are of dubious validity. Third, the conduction bands and therefore the energy gap are poorly reproduced unless far-neighbor interactions are taken into account or *ad hoc* extensions of the atomic basis are introduced. Fourth, since the assumed basis is orthonormal it depends on the local environment of the atoms as the Hamiltonian matrix elements do. Therefore, these matrix elements are not transferrable from one local environment to another as is currently done in defect calculations.

To overcome these shortcomings while keeping a manageable number of parameters, we present a tight-binding Hamiltonian using a basis formed by atomic orbitals that reproduces accurately both valence and conduction bands of a prototype semiconductorlike silicon.

We assume an atomic orbitals basis formed by Slater

orbitals of the form

$$\Psi_{lm}(r, \theta, \phi) = Nr^2 e^{-\mu r} Y_{lm}(\theta, \phi) \quad (1)$$

where N is a normalizing constant, Y_{lm} is a spherical harmonic, and $p = r/a_0$. The coefficient μ is taken to be 1.75 which is the value obtained in total-energy calculations of clusters of silicon atoms. The overlap between these atomic valence orbitals can be calculated analytically.¹⁴ Results for the overlap S_{ij} between sp^3 orbitals labeled i and j (see Fig. 1) at first- and second-neighbor silicon atoms are given in Table I.

In order to obtain the minimal tight-binding Hamiltonian and therefore the minimum number of matrix elements to be included in the calculation we make the assumption that they are governed by the corresponding overlap matrix element (in the Hückel approximation they are proportional). In this way we observe that the overlap between two sp^3 orbitals in second-neighbor atoms and pointing towards their common nearest-neighbor atom is

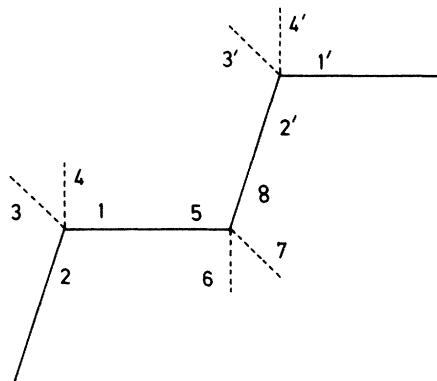


FIG. 1. Labeling of the sp^3 orbitals at first- and second-neighbor atoms in the diamond structure.

TABLE I. Overlap between sp^3 orbitals at first- and second-neighbor silicon atoms (see Fig. 1). The orbitals are Slater-type orbitals of the form of Eq. (1).

$\langle 1 5\rangle = 0.477$
$\langle 1 6\rangle = 0.046$
$\langle 2 6\rangle = 0.033$
$\langle 2 8\rangle = -0.058$
$\langle 1 2'\rangle = 0.038$
$\langle 1 3'\rangle = 0.011$
$\langle 1 1'\rangle = -0.012$
$\langle 3 1'\rangle = -0.005$
$\langle 3 3'\rangle = 0.003$
$\langle 3 4'\rangle = 0.006$

much larger than any other second-neighbor overlap and moreover it is larger than some of the nearest-neighbor overlap. We therefore consider a Hamiltonian which includes all the interactions between nearest-neighbor atoms and *only* the matrix element $\langle 1|H|2'\rangle$ and the corresponding overlap $\langle 1|2'\rangle$ (see Fig. 1). To obtain the Hamiltonian matrix elements we diagonalize the corresponding 8×8 matrix and fit the parameters (the Hamiltonian matrix elements) to the "experimental" band structure.¹⁵ We consider the four valence bands at the Γ , X , and L points of the Brillouin zone. For the conduction band we fit to the four energy levels of the Γ point and to the lower ones of the X and L points. The resulting band structure is shown in Fig. 2. The corresponding matrix elements are given in Table II. For the diagonal matrix element $\langle 1|H|1\rangle$ the atomic value -9.732 eV is taken. We observe a good overall agreement between this band structure and the "experimental" one. The root-mean-square deviation for the eigenvalues fitted being 0.31 eV. We ob-

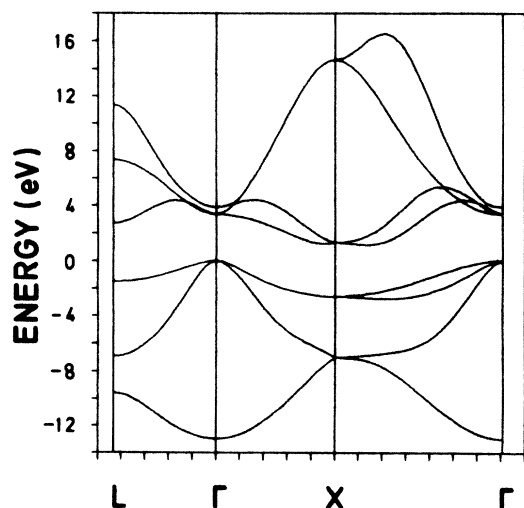


FIG. 2. Band structure of silicon calculated with the set of parameters of Table II and the corresponding overlaps of Table I. The band structures (the Hamiltonian matrix elements) have been obtained fitting to experimental values the lower eight, six, and five eigenvalues at the points Γ , X , and L , respectively.

TABLE II. Hamiltonian matrix elements in eV between the sp^3 orbitals given in Fig. 1. These parameters correspond to the silicon band structure drawn in Fig. 2.

$\langle 1 H 2\rangle = -1.069$
$\langle 1 H 5\rangle = -8.775$
$\langle 1 H 6\rangle = -1.097$
$\langle 2 H 6\rangle = -0.974$
$\langle 2 H 8\rangle = +0.713$
$\langle 1 H 2'\rangle = -2.487$

tain an indirect gap of 1.24 eV. In addition, the direct optical gap is of the order of 4 eV throughout the whole Brillouin zone. This clearly indicates a correct description of the band structure particularly in the vicinity of the energy gap. The energy levels calculated here and the experimental ones for the Γ , X , and L points of the Brillouin zone are given in Table III. It is important to indicate that the rms of these bands is similar to the best fitted band structure including up to third-nearest-neighbor interactions between orthogonal orbitals.⁷

We have tried to reduce the number of parameters and to study the effect of the overlap in the band structure.¹⁶ To this end we have performed the same calculation as above for two model Hamiltonians. We consider (i) a nearest-neighbor Hamiltonian with the same nonorthogonal basis as before and (ii) a six-parameter Hamiltonian *assuming* an orthogonal basis. The resulting band structures are shown in Figs. 3 and 4, respectively. We obtain a much worse band structure than in previous case with a very poor conduction band. The root-mean-square deviation in Figs. 3 and 4 with respect to the experimental bands is 1.09 and 0.74 eV, respectively. It is remarkable that the difference between Figs. 2 and 4 is that in the former a *realistic basis is included in the calculation but in both cases there are the same number of adjustable parameters.*

TABLE III. Calculated and experimental (Ref. 15) energy levels of silicon. The calculated values correspond to the Hamiltonian matrix elements of Table II and the band structure of Fig. 2.

	This work	Expt.
Γ_{1v}	-12.96	-12.36
$\Gamma_{25'v}$	0.00	0.00
Γ_{15c}	3.36	3.42
$\Gamma_{2'c}$	3.89	4.10
X_{1v}	-7.02	-7.69
X_{4v}	-2.62	-2.86
X_{1c}	1.31	1.17
$L_{2'v}$	-9.56	-9.55
L_{1v}	-6.92	-6.96
$L_{3'v}$	-1.50	-1.23
L_{1c}	2.73	2.23

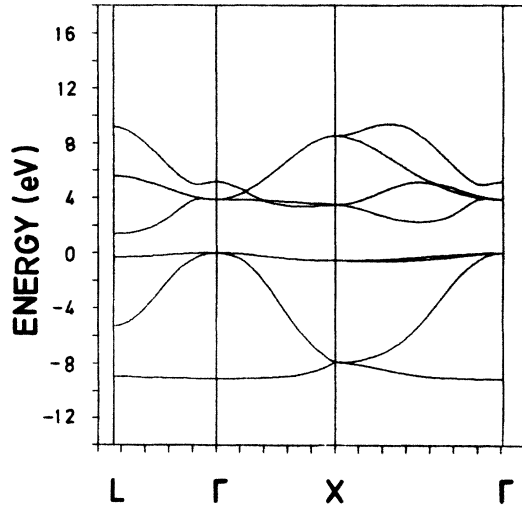


FIG. 3. Band structure of silicon calculated for the Slater-type orbitals basis described in the text and limiting the interactions (and the overlaps) to nearest-neighbor atoms. The Hamiltonian matrix elements have been obtained fitting to experimental values the lower eight, six, and five eigenvalues at the points Γ , X , and L , respectively.

In order to understand the origin of the different features in the band structure and how they depend on the different input parameters, we have calculated analytically, considering the symmetry of the diamond lattice, the energy levels at some high symmetry points of the Brillouin zone. The Hamiltonian includes all nearest-

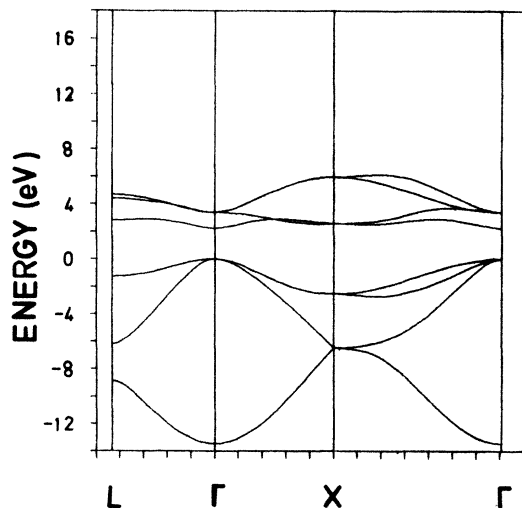


FIG. 4. Band structure of silicon calculated for an orthonormal basis. In addition to the interactions between nearest-neighbor atoms, the interaction $\langle 1 | H | 2' \rangle$ (see Fig. 1) between the sp^3 orbitals at next-nearest-neighbor atoms pointing towards the common neighbor is included in the calculation. The Hamiltonian matrix elements have been obtained by fitting to experimental values the lower eight, six, and five eigenvalues at the points Γ , X , and L , respectively.

neighbor interactions plus the matrix element

$$W = \langle 1 | H | 2' \rangle$$

and the overlap

$$\sigma = \langle 1 | 2' \rangle.$$

The splitting between the nondegenerate energy levels Γ_1 and Γ_2 is given by the solution of the matrix

$$\det \begin{vmatrix} E_s + 3(W - E\sigma) - E & 4(V_{ss\sigma} - ES_{ss\sigma}) \\ 4(V_{ss\sigma} - ES_{ss\sigma}) & E_s + 3(W - E\sigma) - E \end{vmatrix} = 0, \quad (2)$$

where $V_{ss\sigma}$ and $S_{ss\sigma}$ stand for the interaction and overlap between s orbitals at nearest-neighbor atoms. On the other hand the separation between the X_1 energy levels is given by the solution of

$$\det \begin{vmatrix} E_s - (W - E\sigma) - E & 4(V_{sp} - ES_{sp}) \\ 4(V_{sp} - ES_{sp}) & E_p + 3(W - E\sigma) - E \end{vmatrix} = 0. \quad (3)$$

Fitting these energy levels allows us to fix the parameters $V_{ss\sigma}, V_{sp\sigma} = -V_{sp}3^{1/2}$ between nearest-neighbor atoms and $E_s - E_p$.

In addition, the separation between the Γ_{15} and $\Gamma_{25'}$ energy levels is given by the solution of

$$\det \begin{vmatrix} E_p - (W - E\sigma) - E & 4(V_{xx} - ES_{xx}) \\ 4(V_{xx} - ES_{xx}) & E_p - (W - E\sigma) - E \end{vmatrix} = 0, \quad (4)$$

where $V_{xx} = (V_{pp\sigma} + 2V_{pp\pi})/3$ and $S_{xx} = (S_{pp\sigma} + 2S_{pp\pi})/3$ between nearest-neighbor atoms. A similar equation can be written for the X_4 splitting such that the Hamiltonian parameters enter only through the parameter $V_{xy} = (V_{pp\sigma} - V_{pp\pi})/3$. In this way we observe the effect of the different parameters. We notice two main effects of the overlap and the interaction $W = \langle 1 | H | 2' \rangle$. The overlap appears in the denominator of the solutions increasing the energy of the antibonding states making the conduction band more free-electron-like than in nonorthogonal basis calculations. One of the main effects of the interaction W is to make a k -dependent effective p -orbital atomic energy shifted by the matrix element

$$\langle p_x | H | p_x \rangle = W \{ -\cos(ak_x) [\cos(ak_y) + \cos(ak_z)] + \cos(ak_y)\cos(ak_z) \}. \quad (5)$$

This matrix element is positive at the Γ point and negative at the X point. This is clearly responsible for the indirect gap between these two points of the Brillouin zone since it raises the p -like bands near the Γ point and lowers them near the X point.

In conclusion, we have presented the minimal tight-binding Hamiltonian that provides us with a correct description of both the valence and conduction bands of a prototype semiconductorlike silicon. The results obtained with the model allows us to conclude the following.

(i) Inclusion of a realistic basis appears essential not only to reproduce adequately the conduction band but also to substantiate the physical meaning of the Hamiltonian matrix elements.

(ii) The inclusion of only one interaction between sp^3 orbitals in second-neighbor atoms improves in a funda-

mental way the band structure of silicon. Inclusion of other interactions improves even more the band structure but the already obtained parameters remain essentially unchanged (inclusion of the remaining interactions between second-neighbor atoms reduces the rms with respect to experiments to 0.17 eV). This stresses the paramount importance of the parameter W .

(iii) The obtained band structure reproduces well both the four valence and the lower conduction bands.⁷ The rms with respect to experimental ones is similar to the *best* band structure calculated in the literature using localized basis. The bands calculated by Louie⁶ using 10 orbitals per atom and interactions up to fifth-neighbor atoms have, for the symmetry points of the Brillouin zone, a rms of 0.26 eV. Also, our rms is similar to that corresponding to the tight-binding bands calculated by Papaconstantopoulos and Economou⁷ with interactions up to third-neighbor atoms and including 19 adjustable parameters. This clearly stresses the point that to reproduce the band structure using orthogonal basis, interactions between well separated atoms have to be considered.

(iv) We believe that we have obtained the minimal physical Hamiltonian that reproduces both valence and

conduction bands. The number of parameters is the same as in the sp^3s^* model⁸ with a much better description of the conduction band. In the case of the sp^3s^* a spurious empty band associated to the s^* orbitals appears in the conduction band.

(v) The band structure obtained can only be considered as a correct first approximation to the experimental band structure. In order to describe accurately all the conduction bands, atomic d -orbitals have to be included in the basis set as explicitly demonstrated by Louie.⁶

(vi) Due to the realistic basis, the Hamiltonian matrix elements depend only on the local environment and therefore can be transferred to other situations like surfaces, interfaces, vacancies, etc. At the same time, the Hamiltonian is simple enough to allow one to handle difficult atomic configurations like amorphous networks, alloys, etc., which cannot be considered using more sophisticated Hamiltonians. Work in this direction is in progress and will be published elsewhere.

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