PHYSICAL REVIEW B VOLUME 53, NUMBER 19 15 MAY 1996-I

Band-structure parameters by genetic algorithm

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(Received 10 November 1995)

A genetic algorithm has been used to solve a complex multidimensional parameter-fitting problem. We will focus on the parameters of an empirical tight-binding Hamiltonian. The method is used to approximate the electronic energy band structure if energy values are known for a few wave vectors of high symmetry. Compared to the usual manual procedure this method is more accurate and automatic. This approach, based on the extended Hückel theory (EHT), has provided a list of EHT parameters for IV-IV and III-V semiconductors with zinc-blende structure and helped us to find a symmetry in the EHT.

For very large systems, such as those found in the extended unit cells of quite common minerals or inhomogeneous crystals, *ab initio* methods for calculating the electronic structure of solids are still far from application because of the lack of computer power. In that field the semiempirical band structure methods still keep their own value and importance.[1,2] Considering the valence-band regime of nonmetallic compounds, one mainly deals with tight-binding procedures adjusting the parameters with respect to simple systems and transferring them to complicated structures.[3,4] Thus, there is a demand for computationally expedient techniques yielding the parameters of crystal electronic potentials according to experimental results or other targets which may implicitly contain these parameters.

In this paper we demonstrate the use of methods of evolutionary optimization in parameter inference of semiempirical physical models. We apply this method to the extended Hückel theory (EHT), an empirical tight-binding theory.[5] It provides a numerically fast method for the calculation of the electronic band structure and yields satisfactory results, particularly for the valence bands of many semiconductors and insulators. Other than the possible application to large systems, in simpler crystals there also arises the necessity for such methods.[6] Big computational tasks, like the theoretical determination of photoemission spectra, become feasible due to the EHT's enhanced speed.[7] The main idea is to use a small number of parameters, the EHT parameters, to deduce the one-electron Hamiltonian $\hat{H}(\vec{k})$ in a basis of atomic orbitals from the matrix of orbital overlaps $S(\vec{k})$. The latter have to be determined such that the resulting band structure $E(\vec{k})$ corresponds as closely as possible to a given band structure which may have been obtained experimentally or by a more elaborate theoretical method. The EHT, then, is a fast and convenient means to calculate the wave functions of a corresponding band structure. The inverse problem, i.e., finding the correct parameters for a given band structure, is usually solved by trial and error—a laborious and time-consuming task. An attempt to solve this problem by using feedforward neural networks to learn the inverse proved to be very difficult.[8] Here we recast the problem into an optimization task. An objective function is defined which quantitatively characterizes for each parameter vector the agreement of the resulting band structure with the target band structure. This function is maximized by a genetic algorithm.

In the extended Hückel theory the crystal wave functions $|n,\vec{k}\rangle$ are expanded in Bloch functions $|\vec{k},\alpha,l\rangle$ which are the basis for the Hamilton matrix. The band index n enumerates the energy eigenvalues for a Bloch vector $\vec{k}$, α is the orbital symmetry (e.g., s,p_x,p_y,p_z), and l is the index of the basis atom in the unit cell. The Bloch functions are made up of atomic orbitals whose radial parts are represented by normalized Slater functions.[9] To account for an orbital's reduced size in the solid, the orbital exponents have to be enlarged, yielding additional parameters to be fitted. The angle-dependent part is given by spherical harmonics.

The energy bands $E_n(\vec{k})$ are determined by solving the Schrödinger equation with Hamiltonian $\hat{H}$. Introducing $S_{\alpha l\beta m}(\vec{k}):=\langle\vec{k}\alpha l|\vec{k}\beta m\rangle$ and $H_{\alpha l\beta m}(\vec{k}):=\langle\vec{k}\alpha l|\hat{H}|\vec{k}\beta m\rangle$ with overlap matrix S and Hamilton matrix H we get a generalized eigenvalue problem.

The extended Hückel theory is based on the idea that larger orbital overlap means stronger coupling of atoms. For determining the matrix elements of H we use the following ansatz, which has been modified from Hoffmann[5] by Henk:[7]

$$H_{\alpha l\alpha l}(\vec{k})=-\widetilde{I}_{\alpha l}-K_{\alpha\alpha}I_{\alpha l}[S_{\alpha l\alpha l}(\vec{k})-1], \tag{1}$$

$$H_{\alpha l\beta m}(\vec{k})=-\tfrac{1}{2}K_{\alpha\beta}(I_{\alpha l}+I_{\beta m})S_{\alpha l\beta m}(\vec{k}) \text{ if } (\alpha l)\neq(\beta m). \tag{2}$$

The parameters $I_{\alpha l}$ and $\widetilde{I}_{\alpha l}$ can be viewed as the energies of the orbital α at atom l. The proportionality constant $K_{\alpha\beta}$ takes into account the Hamiltonian's dependence on the distance between neighboring sites. We thus deal with eleven parameters for a two-component solid of eight valence electrons per unit cell. One of the parameters $K_{\alpha\beta}$ or $I_{\alpha l}$ can be arbitrarily set to a nonzero value since the Hamilton matrix is invariant under a transformation in which $K_{\alpha\beta}$ are divided by K_{ss} and $I_{\alpha l}$ are multiplied by K_{ss}. Here, the volume band structure without spin-orbit interaction was calculated for simplicity. The generalization is straightforward. In constructing the overlap matrix between Bloch functions, the coupling up to fourth neighbor sites was included.

Genetic algorithms are able to maximize a scalar function in multidimensional binary space.[10,11] A population of bit strings is evaluated according to the scalar objective function. Those bit strings with the highest ‘‘fitness’’ will survive and will be replicated while the least fit are removed from the population. Some of the remaining strings are then randomly changed. A mutation operator reverses one or more bits randomly in the individual bit strings, and a crossover operator swaps fractions of bits between pairs of strings. Both operators are used to drive the stochastic search, while the selection procedure, in the meantime, focuses on promising regions in parameter space. The run is started with an initial population of strings whose bits are randomly set. These steps are iterated until the population converges to a satisfactory solution.

For the method presented here the electronic energies in the solid have to be available only for a rather small set of wave vectors $\vec{k}$. For the zinc-blende structures we use energies $E_{\vec{k}n}^{\mathrm{exp}}$ at high symmetry points $\vec{k} \in \{\Gamma, K, X, L\}$. The band index n counts from 1 to 8, yielding 32 values for the energies. These energies, which the parametrized Hamiltonian is to reproduce, are either gained experimentally or from more laborious theoretical means, such as self-consistent methods.

The objective function $d(\vec{p})$ to be maximized is defined as

$$d(\vec{p}) = -\left(\frac{1}{\sum_{\vec{k}'n'} w_{\vec{k}'n'}} \sum_{\vec{k}n} w_{\vec{k}n} [E_{\vec{k}n}(\vec{p}) - E_{\vec{k}n}^{\mathrm{exp}}]^2 \right)^{1/2}. \quad (3)$$

Here $\vec{p}$ denotes the vector of the band-structure parameters, $E_{\vec{k}n}(\vec{p})$ the electronic energy value calculated with the Hamiltonian of parameters $\vec{p}$, and $w_{\vec{k}n}$ a weight chosen from the interval $[0,100]$ in accordance with the importance of energy $E_{\vec{k}n}$. There is a strong emphasis on the occupied bands. In the end it was possible to use one set of weights for all solids except in a few hard cases. Better compliance at crucial energies will usually result in worse performance at less essential energies. The difference $E_{\vec{k}n}(\vec{p}) - E_{\vec{k}n}^{\mathrm{exp}}$ is squared to penalize large deviations more heavily.

The vector $\vec{p}$ of band-structure parameters is optimized by the genetic algorithm. The parameters are converted to binary numbers for this purpose. The binary numbers are concatenated to form a string of bits, the so-called ‘‘genome,’’ on which the genetic algorithm operates. The binary coding used here is a GRAY code,[12] which improves the performance of the genetic algorithm compared to a regular binary coding. With respect to numerical optimization, the GRAY coding behaves smoothly under bit mutation, so that the algorithm can perform a local stochastic search in ‘‘fitness’’ space by one-bit mutation in parameter space.

The algorithm is stopped after a certain number of iterations or when the fitness values of the individuals of the population have converged. The individual with the highest fitness is then decoded into the vector of parameters $\vec{p}$. The dispersion in $\vec{k}$ space outside of the points of high symmetry is not included in the objective function. Since the EHT may lead to band structures which fit closely at the target points but may be wrong elsewhere, these results have to be discarded.

To test our method, we looked for a parameter vector for an arbitrarily fixed band structure given by the silicon crystal structure and with silicon orbitals but created by using arbitrary EHT parameters. In this case it is assured that the band structure is exactly reproducible by the extended Hückel theory. As a result, the band structure could be reproduced by applying the genetic algorithm to five randomly chosen populations of ten individuals each, to a maximum energy difference of 0.016 eV between the target and the newly parametrized band structure. The accuracy of this result is solely limited by the accuracy chosen for the discrete GRAY coding of the EHT parameters.

We have applied the method to zinc-blende semiconductors and have taken the target energies from Ref. 13 and references therein, which provide theoretical and experimental results. The EHT will not necessarily be able to exactly reproduce these target band structures. Our method, however, will find closest fits.

We have used the genetic algorithm simulator PGA (Ref. 14) with a configuration of 60-bit strings.

The intervals from which parameters are to be determined by the algorithm are $K_{ss}=1$, K_{sp} and K_{pp} from $[0,6]$, $\widetilde{I}_{\alpha l}$ from $[-9,30]$, and $I_{\alpha l}$ from $[-30,90]$. A selection procedure was chosen in which the probability to select an individual for reproduction is proportional to its fitness rank inside its population (rather than to its fitness value). At each iteration, two individuals are chosen according to the selection procedure, and through crossover two complementary children are obtained. They are mutated as well, and the resulting offspring are fed back into the population, replacing the least fit members. The mutation operator used randomly changes each bit with a probability governed by the fraction of equal bits between the parents: the probability would be 0.0 for two totally dissimilar parents, and increase up to a chosen value of 0.1 if the parents were identical.

The optimization procedure works as follows: the coefficients of the atomic wave functions, the lattice constant, the target energies, and the weights for the solid are provided to the program. First, to test the choice of weights, we run the genetic algorithm with ten randomly chosen initial populations of ten individuals each for 20 000 iterations. The resulting band structures are checked for possible adjustment of the weights if crucial energies have large errors. After a common set of weights had been established, further changes in general were not necessary in our calculations. With the final weights a higher accuracy run with ten initial populations of 100 individuals each is done for 100 000 iterations. In many cases this number may be unnecessarily high but it proved to reliably provide accurate parameters. Ten populations running on Sun 10-52 workstations need ten hours of computation time.

For three zinc-blende solids (Si, CdTe, and GaAs) we have parameters previously obtained without any automatic optimization procedure. For these crystals we use our method to determine parameter vectors and compare the resulting band structure with the manual results. For silicon, seven EHT parameters are needed, whereas for the two heteropolar solids cadmium telluride and gallium arsenide

TABLE I. EHT parameters for group-IV elements, IV-IV, and III-V compounds and CdTe determined by evolutionary optimization. The superscript ''so'' indicates that the effect of spin-orbit interaction was taken into account for these parameters of CdTe (the two additional parameters are $\lambda_0=-0.156$ and $\lambda_1=0.781$). The subscript ''hand'' points out the manually achieved parameters. Max. error gives the maximum energy difference between computed and target values for the valence band and the gap; source gives the reference for the target energies. For this table the orbital exponents have been reduced by a fraction of 0.25 (0.20) for s (p) waves. It is $K_{ss}=1.0$ and the index 0 (1) refers to the anion (cation).

Solid	K_{sp}	K_{pp}	$\tilde{I}_{s0}$	$\tilde{I}_{p0}$	$\tilde{I}_{s1}$	$\tilde{I}_{p1}$	I_{s0}	I_{p0}	I_{s1}	I_{p1}	Max. error	Source
C	0.809	1.000	9.32	0.00			29.06	21.45			0.46 eV	15
Si	0.773	1.000	6.88	0.00			23.44	12.07			0.48 eV	16
Ge	0.803	1.000	7.83	0.00			25.78	13.24			0.41 eV	17
α-Sn	0.961	1.000	6.67	0.00			36.90	12.08			0.32 eV	17
SiC	0.563	0.375	12.33	-2.30	10.50	0.14	13.13	20.63	45.00	60.00	0.47 eV	18,13
BN	0.375	0.563	-4.13	-5.34	16.59	4.41	13.13	7.50	56.25	86.25	0.36 eV	19
BP	0.844	1.875	-1.08	-7.17	6.84	-2.91	56.25	1.88	9.38	11.25	0.32 eV	18
BAs	1.500	1.688	2.58	-2.91	2.58	1.97	-22.50	-20.63	-13.12	7.50	0.88 eV	20
AlP	0.281	0.188	11.11	4.41	2.58	-0.47	15.00	60.00	31.88	39.38	0.27 eV	21
AlAs	0.750	0.563	20.25	11.11	10.50	9.89	30.00	39.38	20.63	28.13	0.26 eV	21
AlSb	0.563	0.375	3.19	-4.13	-4.73	-7.17	15.00	16.88	1.88	-9.38	0.22 eV	21
GaP	0.563	0.375	23.30	15.38	14.77	12.33	33.75	63.75	35.63	50.63	0.17 eV	17
GaAs	0.844	0.844	15.38	7.45	14.16	7.45	39.38	22.50	24.38	22.50	0.16 eV	17
$\mathrm{GaAs}_{\mathrm{hand}}$	0.961	1.122	16.95	9.14	15.34	6.93	40.08	20.32	26.24	17.73	0.17 eV	17
GaSb	0.656	0.656	2.58	-6.56	-2.91	-7.78	11.25	5.63	16.88	-1.88	0.35 eV	17
InP	0.938	0.844	5.02	-3.52	-1.08	-4.73	11.25	1.88	18.75	7.50	0.25 eV	17
InAs	0.563	0.281	9.28	-0.47	1.97	-1.69	18.75	30.00	16.88	24.38	0.23 eV	17
InSb	0.938	0.656	3.80	-5.34	-4.73	-5.34	11.25	0.00	-26.25	13.12	0.29 eV	17,22
CdTe	0.469	0.281	14.77	6.23	9.89	3.19	28.13	52.50	15.00	39.38	0.19 eV	17
$\mathrm{CdTe}_{\mathrm{hand}}$	1.000	1.266	9.30	0.90	5.30	-1.70	23.38	7.90	10.11	5.69	0.47 eV	17
$\mathrm{CdTe}^{\mathrm{so}}$	0.938	0.563	15.98	8.06	1.36	7.45	30.00	30.00	26.25	20.63	0.30 eV	17,23

eleven parameters have to be determined. For GaAs and CdTe—where the manual fits are very good—fits of equal or even better quality could be achieved. The parameter vectors are given in Table I. The result for CdTe is displayed in Fig. 1, which typically shows the agreement with the target band structure. It is achieved by the genetic algorithm even for the conduction band where the EHT is known to be less suitable.

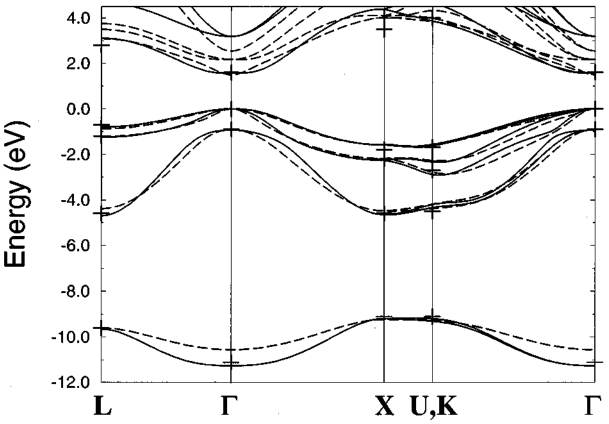

FIG. 1. The target energies of the CdTe band structure are denoted by plus symbols. The best manual fit is drawn with long dashes, the genetic algorithm result with a solid line. Spin-orbit interaction has been introduced via a localized coupling of the atomic sites, yielding an additional parameter for each species.

We have determined EHT parameters for CdTe and for those group-IV elements, IV-IV, and III-V compounds which are semiconductors and crystallize in zinc-blende structure: see Table I.

Table I is a compilation of EHT parameters for this rather large class of semiconducting materials. The parameters were calculated with moderate effort. Since the EHT parameters are known to be independent of bond length, this formalism covers a wide range of applications.

For certain zinc-blende crystals, for example, those made up of one component, we have found a symmetry in the EHT. A large number of parameter vectors gained from the genetic algorithm led to band structures which are identical except for a shift in the absolute energy scale. To see this, we drop the irrelevant atom index l and define a new vector of parameters $\vec{p}\,'=[\tilde{I}_s,\tilde{I}_p,I_s,K_{pp}I_p,K_{sp}(I_s+I_p)/2]$, which includes all the factors necessary for the construction of the matrix H. Guided by the variation of the parameter vectors, we observed that the Hamiltonian obeys $H(\vec{p}\,'+\lambda\vec{u})=H(\vec{p}\,')-\lambda S$ with vector $\vec{u}=(1,1,1,1,1)$. For the energies, this means that $E_{n\vec{k}}(\vec{p}\,'+\lambda\vec{u})=E_{n\vec{k}}(\vec{p}\,')-\lambda$. In this case the number of parameters can be reduced by two, e.g., by setting $K_{pp}:=1.0$ and $\tilde{I}_p:=0.0$. This symmetry occurs only where at least one of the three following relations is valid: $K_{pp} = -K_{sp}/(K_{sp}-2)$, $I_{s0} = I_{s1}$, or $I_{p0} = I_{p1}$. For solids of one component both of the last conditions are satisfied.

In this paper we have shown that a genetic algorithm can be used to determine the parameters of an empirical tight-binding Hamiltonian for zinc-blende semiconductors. A list of EHT parameters for the IV-IV and III-V semiconductor series was computed. The method works with automatic control, has moderate computational costs, and provides results superior to those achieved by traditional methods of determining the parameters. The method has helped us to find an interdependence of the parameters, which enables us to eliminate two parameters for one-component solids. We are confident that the method will work for other than zinc-blende solids and that it can be applied to various other fields of physics where problems of model inversion or multidimensional parameter optimization occur.

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