

## Cyclic Cluster Approach to Three-Dimensional Solids: Quasi-Relativistic INDO Treatment

A. Zajac,<sup>†,||</sup> P. Pelikán,<sup>\*,‡,||,⊥</sup> J. Noga,<sup>§,||</sup> P. Baňacky,<sup>†,||</sup> S. Biskupič,<sup>‡,||</sup> and M. Svrček<sup>||</sup>

*Institute of Chemistry, Faculty of Natural Sciences, Comenius University, SK-84215 Bratislava, Slovakia,  
Department of Physical Chemistry, Slovak University of Technology, SK-81237 Bratislava, Slovakia,  
Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-84236 Bratislava, Slovakia, S-Tech, Inc.,  
Uršulínska 3, SK-81101 Bratislava, Slovakia, and Faculty of Chemistry, Technical University Brno,  
CZ-63700 Brno, Czech Republic*

*Received: July 23, 1999; In Final Form: November 17, 1999*

A recent implementation of the cluster crystal orbital (CCO) method for electron structure calculations of solids within the quasi-relativistic INDO treatment has been tested for a wide scale of model systems including insulators, semiconductors, metals, semimetals, and superconductors. Within the method, a sufficiently large portion of the crystal is essentially treated as a supermolecule (cluster) in which, due to imposed cyclic Born–Karman boundary conditions, all the unit cells experience the same surroundings, while all the interactions within the cluster are preserved. Hence, unwanted effects due to the cluster boundaries are removed, and transition into the complex quasi-momentum space is made possible and uniquely defined. Within the approach, the advantages of the crystal orbital method and the simple cluster model are linked simultaneously. The current implementation, based on the quasi-relativistic INDO Hamiltonian and parametrized for all elements of the periodic table, allows for very fast SCF calculation of clusters containing tens of thousands of atoms. A reasonable balance is reached between the physical model considered (sufficient scope of long-range interactions, large enough number of **k**-points) and the rigorousness of the method used (type of the Hamiltonian and wave functions used).

## Introduction

With the development of new computer technologies, extensive systems have become a subject of growing interest to computational physicists and chemists. Among the systems, those with translation periodicity are of special interest. Two distinct approaches, based on the Hartree–Fock Hamiltonian, are used in the calculations of the electronic structure of solids: (1) the Crystal Orbital (CO) method, and (2) methods based on a cluster model.

The crystal orbital<sup>1,2</sup> method is formulated in the reciprocal crystal lattice that allows the use of Bloch functions as a basis, which ensures the periodicity of an infinite crystal. To be exact, one has to include all the interactions within a chosen reference unit and its interactions with an essentially infinite number of neighboring atoms. At the same time, an exact integration in the reciprocal space is equivalent to a summation over an infinite number of **k**-points. In practice, one is forced to apply various cutoff criteria, approximations of infinite sums, and replacement of the integration in the Brillouin zone by a sum over a finite—sometimes rather small—number of **k**-points.<sup>1,2</sup> The aforementioned approximations applied within ab initio calculations of complex solid-state materials may yield results beyond acceptable reliability. In such cases, or if only qualitative information for a substantially lower price is needed, semiempirical treatments are still useful.<sup>3</sup>

On the other hand, within the model cluster (i.e., a supermolecular) based approach, the solid state system is replaced by a cluster containing a finite number of atoms. In general, the bigger the cluster, the closer the calculated results are to the real bulk values. This approach, in particular is convenient to chemists because it provides a quasi-molecular picture of the solids. Nevertheless, for computational reasons, the calculations must again be restricted to small clusters that, in turn, cause significant errors linked to the boundary effects (unsaturated bonds on the cluster boundaries, terminating atoms, etc.). Our recent calculations show that the impact of the boundary effects is at unacceptable level even for clusters containing several hundred atoms.<sup>4</sup>

Interesting approaches for band-structure calculations, based on the so-called cyclic-cluster model, were already suggested within the semiempirical theories in early 1970s.<sup>5–10</sup> This rather simple approach has been applied in chemisorption of boron nitride and graphite on the level of EHT<sup>5</sup> and CNDO/2,<sup>6</sup> and the approach is mainly represented by small periodic clusters<sup>7,8</sup> and the so-called large unit cell method.<sup>9</sup> Both are compared in detail in ref 10. A more extensive review of cyclic-cluster approaches of that time is given in the paper by Deak.<sup>11</sup> Recently, we tested the convergence properties toward the bulk limit for a modified, more general, and unambiguously defined procedure based on the cyclic-cluster approach.<sup>12</sup> Illustrative results of band-structure calculation for different electronic types of solids, ranging from insulators to semiconductors, metals, semimetals, and superconductors, are presented in this paper. Formally, the computational procedure leads to the use of the complete Hartree–Fock Hamiltonian (with electron–electron interactions included) and is applicable on different levels such

\* Author to whom correspondence should be addressed.

<sup>†</sup> Comenius University.

<sup>‡</sup> Slovak University of Technology.

<sup>§</sup> Slovak Academy of Sciences.

<sup>||</sup> S-Tech, Inc.

<sup>⊥</sup> Technical University Brno.

as ab initio,<sup>13</sup> semiempirical,<sup>14</sup> or DFT<sup>15</sup> theories. We have used a quasi-relativistic INDO Hamiltonian,<sup>16,17</sup> applied for cyclic clusters containing several thousand atoms. To keep the paper self-containing, the main features of our method are briefly reviewed in the next section. More details concerning a specific implementation within the quasi-relativistic INDO Hamiltonian are given in our previous paper.<sup>12</sup>

### Cluster Crystal Orbital Method

The use of extremely large clusters in solid simulation leads to automatic inclusion of the long-range interactions that may have an important impact on the electron properties. The cluster crystal orbital (CCO) method considers finite clusters containing many thousands of atoms. The cluster size in each dimension should be about 5–6 nm to reach the bulk limit.<sup>12</sup> Elimination of the boundary effects and a (pseudo-) translational periodicity of the wave function are ensured by applying the modulo-periodic boundary conditions. This allows a transformation from the atom-centered orbital basis into the Bloch orbital basis. Reciprocal space is defined by a finite number of  $\mathbf{k}$ -points unambiguously determined from the constructed cluster. For the cluster size mentioned above, the use of the resulting density matrix in full-band-structure calculations is justified.

Given a set of lattice vectors  $\mathbf{a}_i$  ( $i = 1, 2, 3$ ) the finite cluster is built up by translationally replicating the elementary unit cell in the respective lattice vector directions  $N_i$  ( $i = 1, 2, 3$ ) times. Then,  $N = N_1 N_2 N_3$  is the total number of unit cells considered in the cluster.  $M$  atomic orbital basis functions  $|p^{\mathbf{R}}\rangle$  are associated with each elementary unit cell. Atomic orbital basis functions are described by a pair of indices  $p$  and  $\mathbf{R}$  in which  $p$  refers to the index of atomic orbital within a given cell ( $p$  ranges from 1 to  $M$ ) and  $\mathbf{R}$  covers the range of all possible lattice translations

$$\mathbf{R} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 \quad (1)$$

$n_i$  ( $i = 1, 2, 3$ ) indicates one of the possible  $N_i$  translations in the direction  $\mathbf{a}_i$ . The reciprocal space vector  $\mathbf{k}$  is defined in a standard way

$$\mathbf{k} = \frac{m_1}{N_1} \mathbf{b}_1 + \frac{m_2}{N_2} \mathbf{b}_2 + \frac{m_3}{N_3} \mathbf{b}_3 \quad (2)$$

where the reciprocal lattice vectors  $\mathbf{b}_i$  fulfill the condition  $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{ij}$ . The idea behind the cyclic-cluster approach is to impose the same surroundings on all unit cells of the cluster. The interactions of the central unit cell are imposed on the rest of the cells. For a finite cluster, a “ring periodicity” is imposed by adopting the identity

$$\mathbf{R} + \mathbf{R}' = \sum_{i=1}^3 \left\{ n_i + n'_i - N_i \text{int} \left( \frac{2(n_i + n'_i)}{N_i} \right) \right\} \mathbf{a}_i \quad (3)$$

where  $\text{int}()$  is the integer part function. For a cluster constructed in a way described above, the modulo-translation symmetry is guaranteed.<sup>12</sup> Hence, for all integrals over totally symmetric one-particle (such as  $\hat{h}$ ) and two-particle (such as  $\hat{g}$ ) operators (and, of course, for many-particle operators), the translation periodicity (Born–Karman periodic conditions) within the considered cluster, mathematically described by

$$\langle p^{\mathbf{R}+\mathbf{R}'} | \hat{h} | q^{\mathbf{R}'} \rangle = \langle p^{\mathbf{R}} | \hat{h} | q^{\mathbf{O}} \rangle = h_{pq}^{\mathbf{RO}} \quad (4)$$

$$\langle p^{\mathbf{R}_1+\mathbf{R}'} | q^{\mathbf{R}_2+\mathbf{R}'} | \hat{g} | r^{\mathbf{R}'} s^{\mathbf{R}_3+\mathbf{R}'} \rangle = \langle p^{\mathbf{R}_1} q^{\mathbf{R}_2} | \hat{g} | r^{\mathbf{O}} s^{\mathbf{R}_3} \rangle \quad (5)$$

has to be fulfilled for all lattice translations  $\mathbf{R}$ . The physical interpretation of eqs 4 and 5 is such that each unit cell of the cluster ‘feels’ such an environment as if it were in the center of the cluster. This assumption would be valid for an infinite cluster, while otherwise the requirements of eqs 4 and 5 are not applicable in general and ambiguities may also arise with multicenter two-electron integrals. Hence, in ab initio treatments one needs some sort of averaging manipulation with integrals.<sup>18</sup> However, due to the partial ZDO (zero differential overlap) approximation in the used INDO method,<sup>14</sup> the requirements of eqs 4 and 5 are automatically fulfilled for all integrals considered. Therefore, transformation to Bloch orbital basis is unambiguously given by the following finite summations:

$$|p^{\mathbf{k}}\rangle = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \exp(i\mathbf{k} \cdot \mathbf{R}) |p^{\mathbf{R}}\rangle \quad (6)$$

After performing this Fourier transformation, the Fock matrix factorizes into  $N$  blocks of the size  $M \times M$ , where  $M$  is the number of atomic orbitals in the elementary unit cell, i.e.

$$F_{pq}^{\mathbf{k}\mathbf{k}'} = F_{pq}^{\mathbf{k}\mathbf{k}} \delta_{\mathbf{k}\mathbf{k}'} = \sum_{\mathbf{R}} F_{pq}^{\mathbf{R}\mathbf{O}} \exp(i\mathbf{k} \cdot \mathbf{R}) \quad (7)$$

The cluster choice determines exactly all the  $N_{\mathbf{k}} = (N_1 N_2 N_3 + 1)/2$  independent values of the wave vector  $\mathbf{k}$ .

The necessary Fock matrix elements of the closed-shell systems in INDO Hamiltonian approximation are

$$F_{pq}^{\mathbf{RO}} = h_{pq}^{\mathbf{RO}} + \sum_{\mathbf{R}_1, \mathbf{R}_2}^N \sum_{r,s}^{\text{cell}} P_{rs}^{\mathbf{R}_3 \mathbf{O}} (2 \langle p^{\mathbf{R}} r^{\mathbf{R}_1} | \hat{g} | q^{\mathbf{O}} s^{\mathbf{R}_2} \rangle - \langle p^{\mathbf{R}} r^{\mathbf{R}_1} | \hat{g} | q^{\mathbf{R}_2} s^{\mathbf{O}} \rangle) \quad (8)$$

$(\mathbf{R}_3 = \mathbf{R}_1 - \mathbf{R}_2)$

$$P_{pq}^{\mathbf{RO}} = \frac{1}{N} \sum_{\mathbf{k}} P_{pq}^{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{R}) \quad (9)$$

$$P_{pq}^{\mathbf{k}} = \sum_m^{\text{occ}} (c_{pm}^{\mathbf{k}})^* c_{qm}^{\mathbf{k}} \quad (10)$$

Having the  $\mathbf{F}$  matrix, one performs its diagonalization, calculates the new density matrix, and returns to the Fock matrix until self-consistency is achieved. With an increasing value of  $N$ , the bulk limit is approached:

$$E_{\text{HF/cell}}^{\text{bulk}} = \lim_{N \rightarrow \infty} \left( \frac{E_{\text{HF}}(N)}{N} \right) \quad (11)$$

It has been shown<sup>12</sup> that this limit can, in fact, be accomplished rather soon. Because for the converged results the density matrix can safely be treated as one corresponding to the bulk, a posteriori calculations for characteristic paths in the  $\mathbf{k}$ -space, or for any point within the first Brillouin zone, are fully justified.

### Illustrative Results and Discussion

Of course, one cannot expect quantitatively very accurate results from semiempirical theories such as the one described above. Nevertheless, semiempirical methods are often very useful even if they provide only qualitatively reliable results. To test the range of applicability of the presented method, the band structures of insulators, semiconductors, semimetals,

**TABLE 1: Comparison of INDO–CCO Results with Other Data**

method system	energy band gaps [eV]				lattice parameters [ $10^{-10}$ m]	
	CCO <sup>a</sup>	CO <sup>b</sup>	INDO CO <sup>c</sup>	exp <sup>19</sup>	INDO–CCO	exp <sup>19</sup>
diamond	9.95	13.9 <sup>22</sup>	9.2 <sup>24</sup>	6.5	3.685	3.566
silicon	3.59	9.4 <sup>23</sup>	5.8 <sup>24</sup>	1.2	5.402	5.431
germanium	1.95		1.9 <sup>24</sup>	0.7	5.463	5.658
gallium phosphide	4.72			2.9	5.368	5.451
gallium arsenide	2.81			1.5	5.461	5.653
gallium antimonide	2.54			0.8	5.780	6.095
aluminum phosphide	4.34			3.63	5.475	5.467
aluminum arsenide	3.34			3.13	5.715	5.660
aluminum antimonide	2.55			2.32	6.121	6.136
indium phosphide	1.85			1.424	5.799	5.876
indium arsenide	0.60			0.418	6.112	6.058
indium antimonide	0.33			0.235	6.523	6.479
boron nitride	11.93		13.4 <sup>24</sup>	6.0–14.5	3.809	3.615

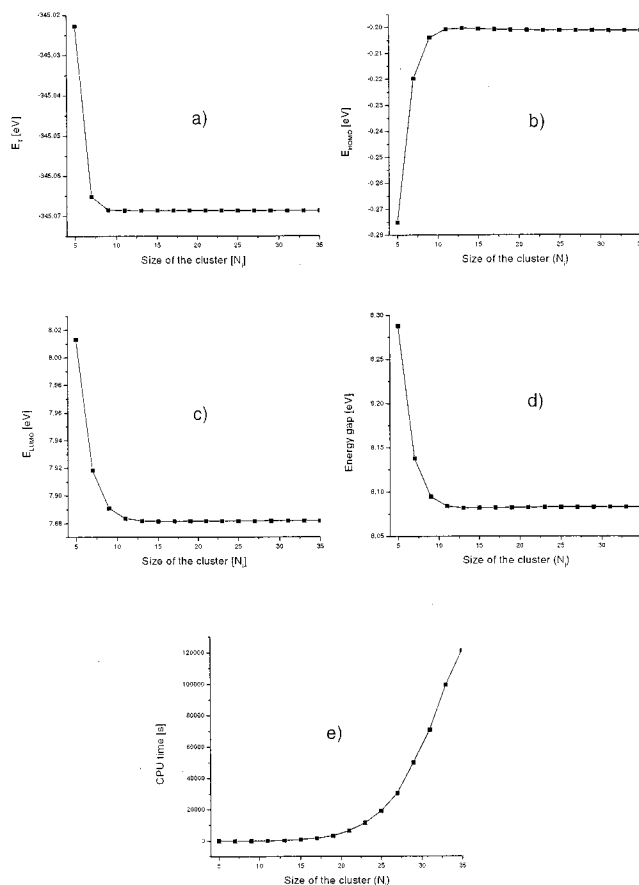
<sup>a</sup> INDO–CCO Cluster Crystal Orbital method (present paper). <sup>b</sup> CO Crystal Orbital method.<sup>1</sup> <sup>c</sup> INDO CO INDO Crystal Orbital method.<sup>3</sup>

metals, and superconductors have been calculated. At this point, it must be stressed that, in spite of the notion of “semiempirical” theories, the parametrization of the quasi-relativistic INDO method is based on the results of ab initio Fock–Dirac calculations of the isolated atoms. The only “empirical” parameter  $K$  (the scaling constant) appears at calculation of the off-diagonal, one-electron, two-center integrals of the electron–nuclear attraction

$$h_{pAqB} = T_{pAqB} - \frac{1}{2} S_{pAqB} \left( \frac{\xi_p^A}{n_p^A} + \frac{\xi_q^B}{n_q^B} \right) K \quad (12)$$

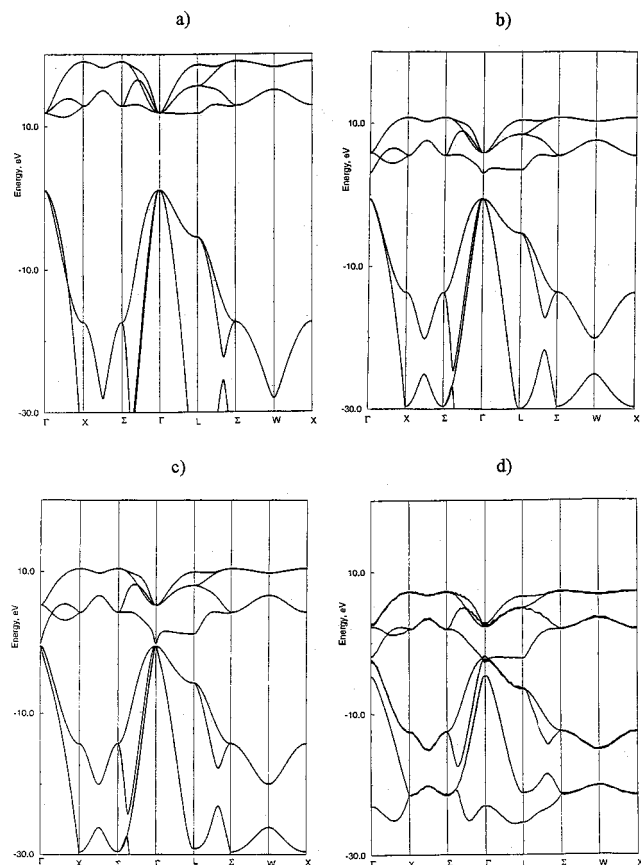
where  $T_{pAqB}$  is the electron–kinetic part,  $\xi_p^A$  stands for the orbital exponent of the Slater-type atomic orbital  $p$  of the atom  $A$ , and  $n_p^A$  is the corresponding principal quantum number. It should be pointed out that the value of the scaling constant  $K$  influences mainly the calculated bandwidths, and the band-gaps, but also the geometric parameters. Empirically determined compromise between the two leads to the value of  $K = 1.2$ . This value of  $K$  is a result of our experience and experimentation with a wide range of systems. This “standard” parametrization for solids has been used throughout this work. It was our intention to show results with the *standard* scaling factor, rather than to optimize the scaling parameter with respect to some properties of individual systems. We will return to this point later.

In Figure 1 we have briefly summarized the convergence properties of the cyclic cluster method with respect to the size of the cluster, using the results obtained for diamond. Besides the dependence for the energies of frontier orbitals, band gap, and total energy per unit cell, we also show the CPU time progression (for an IBM 6000 591 workstation). Note that the number of atoms in the cyclic cluster varies from 250 to 85 750; the number of  $\mathbf{k}$ -points varies from 63 to 21 438; and, finally, the number of (valence) basis functions included in the calculation varies from 1000 to 343 000 Slater-type atomic orbitals for the cluster sizes from  $5 \times 5 \times 5$  to  $35 \times 35 \times 35$ . In calculation of clusters containing just  $7 \times 7 \times 7$  unit cells, accuracy of few hundredths of an eV is reached, while increasing the number of unit cells to  $15 \times 15 \times 15$ , one essentially obtains the bulk limits within an error range less than 0.001 eV. Although the diamond system turned out to have the best convergent properties, other systems studied in ref 12 exhibited a similar behavior. In the relevant interval of appropriate cluster sizes, the dependence of CPU time on the size of a cluster is just slightly different from linear.



**Figure 1.** The illustration of convergence properties on the size of considered clusters of diamond: (a) total energy per unit cell; (b) highest occupied orbital; (c) lowest unoccupied orbital; (d) energy gap; (e) CPU time on IBM workstation. Total number of atoms in the cluster is  $N_t^3$ , number of basis functions  $4 \times N_t^3$ .

It turns out that except for narrowing of the band gap, no change in topology of the bands of the series of materials in ref 12 was observed when the cluster size grew from  $5 \times 5 \times 5$  to  $17 \times 17 \times 17$  (the latter being the bulk limit). In Table 1, results of geometry optimization, i.e., optimization of the lattice parameters, for selected systems, together with energy band gaps, are presented. The results are compared with experimental and other literature data. This table shows that even though with the *standard* scaling parameter one obtains rather large errors for some of the band gaps, those are of comparable accuracy to other available values<sup>21–24</sup> from other one-electron theories nowadays used for three-dimensional solids. Strictly speaking,

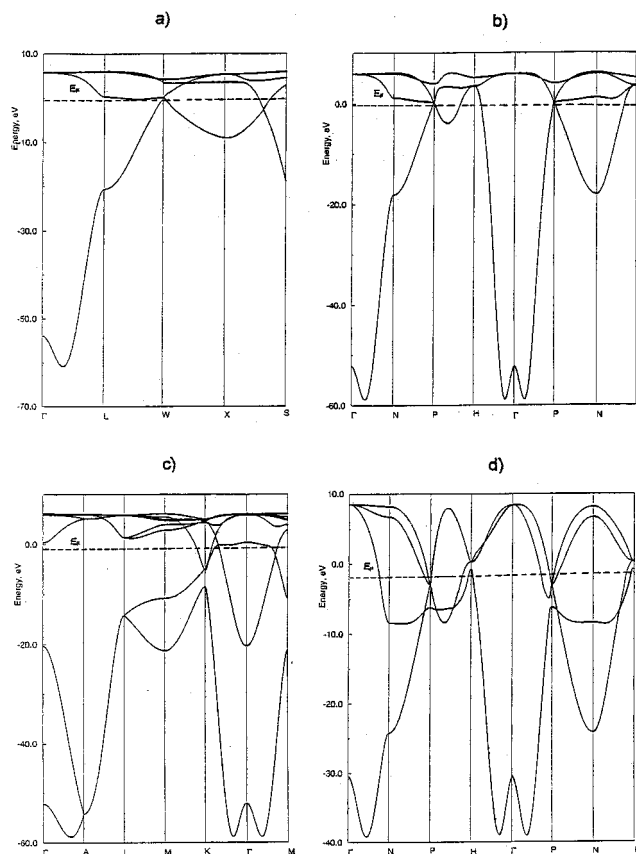


**Figure 2.** Energy band structure along the main symmetry directions of the first Brillouin zone: (a) diamond; (b) silicon; (c) germanium; (d)  $\alpha$ -tin.

band gap, defined as a minimum difference between the highest occupied and the lowest unoccupied bands, is not the most appropriate quantity to compare with the experiment. The excitation energy would be preferable, but its correct calculation for solids is not an easy task, because the electron correlation may be important. This is, however, a drawback of all Hartree–Fock-based methods. Therefore, one cannot clearly judge which effect is due to the approximations inherent in the QR–INDO method, and which is due to the Hartree–Fock approach itself. Moreover, as some *ab initio* calculations indicate (see, e.g., ref 2), the energy band gaps may be strongly dependent on the basis set used. With increasing of the latter, the energy gap is decreased. Note also that in our case, the HOMO and LUMO were taken as the top of the valence and the bottom of the conduction bands along the special symmetry directions within the Brillouin zone which are established for the pertinent space groups.<sup>20</sup>

A relative error within 5% for the optimized geometries is quite acceptable, and we can expect a similar accuracy for covalent weakly polar-bounded compounds, such as those studied here. For highly ionic systems, however, this has to be investigated, because in that case the total dipole moment of the cluster may cause a stronger dependency on the shape of the adopted cluster, and hence, also a slower convergence toward the bulk limit with the size of the cluster. Also, because of the limitations of the INDO method, one can hardly expect reliable results for very weakly bounded systems.

In Figures 2–6, we show the ability of the present method to reproduce some characteristic features of the band-structure topologies. The notation for the symmetry points of the first Brillouin zone is taken from ref 20.



**Figure 3.** Energy band structure along the main symmetry directions of the first Brillouin zone: (a) calcium (face-centered cubic); (b) calcium (body-centered cubic); (c) calcium (hexagonal); (d) aluminium (body-centered cubic).

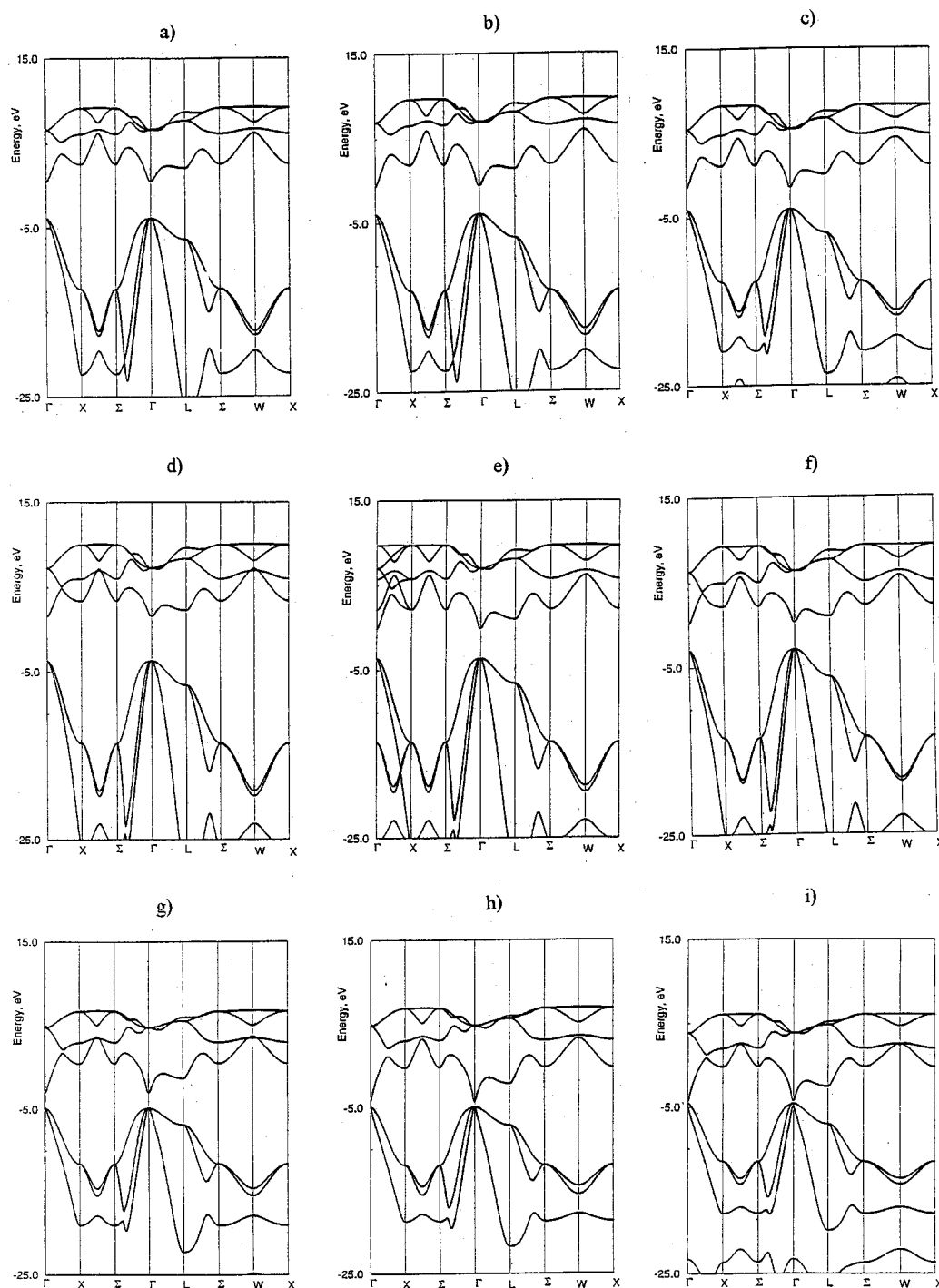
In Figure 2, energy bands around the Fermi level for valence isoelectronic series from diamond to tin are displayed. All the structures correspond to face centered cubic Bravais lattice; hence, the topology of their energy bands is similar. On the other hand, one can recognize a wide indirect gap for diamond, which is an insulator. Essentially narrower, but now direct, gap is seen for the wide-gap semiconductor silicon. Even narrower gap can be seen for the typical narrow-band semiconductor germanium, and, finally, tin shows the qualitatively correct band structure as a metal.

In Figure 3 we show the band structures for other metallic systems—calcium and aluminium. All three modifications of calcium<sup>25–27</sup> correctly describe the metallic behavior. The band structure for body-centered cubic modification of aluminium<sup>28</sup> is also qualitatively correct.

Results of band-structure calculations for technically important semiconductors of III–V type, phosphides, arsenides, and antimonides of the third group of elements, aluminium, gallium, and indium are illustrated in Figure 4. In this series, the energy gap between the valence and conductive bands is gradually narrowed. Correct trends with respect to experimentally measured gaps are indicated by our results.

The results of band-structure calculations for isoelectronic hexagonal boron nitride and graphite are illustrated in Figure 5. From the pictures presented, it is clear why the boron nitride has insulating properties with wide energy gap, whereas graphite is a semimetal with conductive properties. Remaining symmetry lines in the first Brillouin zone of graphite are illustrated in Figure 5c. This figure reveals three times degenerated  $\pi$  orbitals in the *H* point. This degeneracy is removed along the symmetry





**Figure 4.** Energy band structure along the main symmetry directions of the first Brillouin zone: (a) aluminium phosphide; (b) aluminium arsenide; (c) aluminium antimonide; (d) gallium phosphide; (e) gallium arsenide; (f) gallium antimonide; (g) indium phosphide; (h) indium arsenide; (i) indium antimonide.

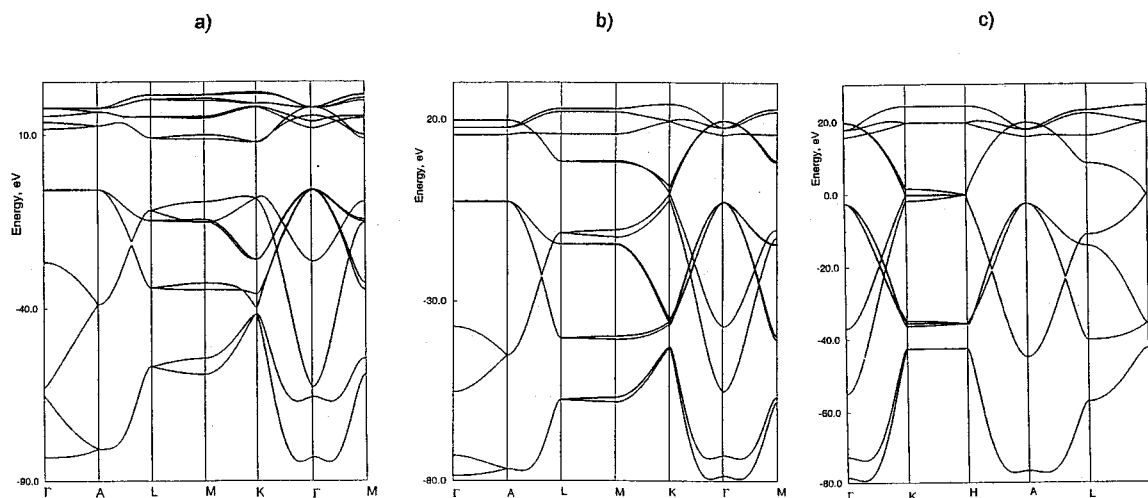
line between points *H* and *K*. This effect was experimentally confirmed using a scanning tunneling microscopy technique.<sup>29</sup>

The results of calculation for high-temperature superconducting material  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ , with critical temperature at 109 K, are illustrated in Figure 6. The band structure obtained by the method presented is comparable with the calculations of other authors.<sup>30–32</sup>

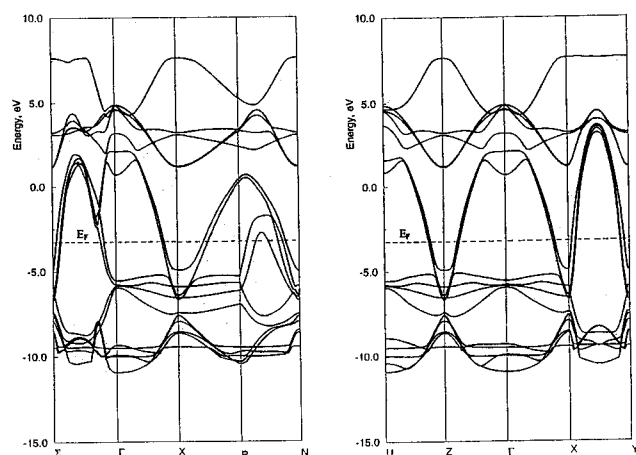
It may be concluded that the model presented herein can be effectively used to calculate the electron structure of solids with periodic structures. At least in combination with semiempirical methods (e.g., quasi-relativistic INDO), the ‘saturated’ cyclic cluster, i.e., one that mathematically corresponds to the bulk, can easily be achieved.

## Conclusions

From the illustrative examples, some important features and application perspectives of the presented method for the calculation of the electron structure of solid state materials with translation symmetry can be summed up, as follows: (1) The method presented offers an effective tool for a fast calculation and acceptable description of the electronic and structural properties of systems with periodic structure. (2) The CPU time requirements are relatively low, and the results are obtained within a short time. Therefore, the application of the method for the standard calculations in the areas of solid-state physics and chemistry, chemical synthesis, and crystallography seems



**Figure 5.** Energy band structure along the main symmetry directions of the first Brillouin zone: (a) boron nitride (hexagonal); (b), (c) graphite.



**Figure 6.** Energy band structure along the main symmetry directions of the first Brillouin zone of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ .

to be very useful. (3) The method might play an important role in the area of education—it can bridge the fields of physics and chemistry and help in the education of chemists solving the problems of solid-state chemistry. On the other hand, it can help solid-state physicists to acquire a ‘feeling’ for the chemical aspects of the problem considered. (4) The method can serve as a valuable tool for calculations of very complex crystalline materials, which cannot be dealt with using current ab initio methods. (5) Because of the possibility of working with a considerably large unit cell, calculations of defects in materials appear to be feasible. (6) The applied quasi-relativistic INDO method is parametrized for all atoms of the periodic table and includes dominant relativistic effects. This allows calculations of a number of interesting systems containing heavy atoms.

We are, of course, aware of the weak points of the method. Above all is the fact that the method is, by its nature, approximative. However, in performing the quantum chemical calculations, a correct balance must be achieved between the physical relevancy of the considered model and the rigorousness of the applied method. In view of this, even the most extensive ab initio calculations with insufficient scope of the interactions with neighbors and a not large enough number of  $\mathbf{k}$ -points, and/or a limited wave function basis set, do not yield sufficiently correct results. It is namely the above-mentioned model–method balance reached within our approach that we consider crucial and which makes the approach useful.

**Acknowledgment.** The authors to express cordial thanks to S-Tech, Inc., for arrangement of computational facilities and Slovak Grant Agency VEGA (grants A-13/99 and 1/4012/98) for partial financial support.

## References and Notes

- (1) *Quantum-Mechanical Ab Initio Calculations of the Properties of Crystalline Materials*; Pisani, C., Ed.; Springer: Berlin, 1996. Dovesi, R.; Pisani, C.; Roetti, C.; Causa, M.; Saunders, V. R. *CRYSTAL92, An Ab Initio Electron LCAO-Hartree-Fock Program for Periodic Systems*; QCPE Program No. 577, 1992.
- (2) Ladik, J. *Phys. Rep.* **1999**, *313*, 171.
- (3) Böhm, M. C.; Schulte, J. *Mol. Phys.* **1996**, *87*, 735. Schedel-Niedrig, T.; Böhm, M. C.; Werner, H.; Schulte, J.; Schlögl, R. *Phys. Rev. B* **1997**, *55*, 13542.
- (4) Pelikán, P.; Baňacký, P.; Biskupič, S.; Noga, J.; Zajac, A.; Svrček, M. *Progress in Coordination and Organometallic Chemistry*; Slovak Technical University Press: Bratislava, Slovakia, 1997.
- (5) Bennet, A. J.; McCarroll, B.; Messmer, R. P. *Surf. Sci.* **1971**, *24*, 191.
- (6) Bennet, A. J.; McCarroll, B.; Messmer, R. P. *Phys. Rev. B* **1971**, *3*, 1397.
- (7) Zunger, A. *J. Phys. C* **1974**, *7*, 96.
- (8) Zunger, A. *J. Chem. Phys.* **1975**, *62*, 1861. Zunger, A. *J. Chem. Phys.* **1975**, *63*, 1713.
- (9) Dobrovetskii, A. M.; Evarestov, R. A. *Phys. Status Solidi B* **1974**, *66*, 83. Evarestov, R. A.; Lovchikov, V. A. *Phys. Status Solidi B* **1977**, *79*, 743.
- (10) Evarestov, R. A.; Petrashen, M. I.; Ledovskaya, E. M. *Phys. Status Solidi B* **1976**, *76*, 377.
- (11) Deák, P. *Acta Phys. Acad. Sci. Hung.* **1981**, *50*, 247.
- (12) Noga, J.; Baňacký, P.; Biskupič, S.; Boča, R.; Pelikán, P.; Svrček, M.; Zajac, A. *J. Comput. Chem.* **1999**, *20*, 253.
- (13) McWeeny, R. *Methods of Molecular Quantum Mechanics*; Academic Press: London, 1992.
- (14) Pople, J. A.; Beveridge, D. L. *Approximate Molecular Orbital Theory*; McGraw-Hill Book Company: New York, 1970.
- (15) *Recent Advances in Density Functional Methods, Part I and II*; Chong, D. P., Ed.; World Scientific: Singapore, 1995, 1997.
- (16) Boča, R. *Int. J. Quantum Chem.* **1987**, *31*, 941.
- (17) Boča, R. *Int. J. Quantum Chem.* **1988**, *34*, 385.
- (18) Varga, S.; Noga, J. Unpublished work.
- (19) *Landolt-Börnstein*, New Series; Madelung, O., Ed.; Vol. 17; Springer-Verlag: Berlin-Heidelberg-New York, 1982.
- (20) Bradley, C. J.; Cracknell, A. P. *The Mathematical Theory of Symmetry in Solids*; Clarendon Press: Oxford, 1972.
- (21) Dovesi, R.; Pisani, C.; Ricca, F.; Roetti, C. *Phys. Rev. B* **1980**, *22*, 5936.
- (22) Dovesi, R.; Causá, M.; Angonoa, G. *Phys. Rev. B* **1981**, *24*, 4177.
- (23) Dovesi, R.; Pisani, C.; Roetti, C.; Dellarole, P. *Phys. Rev. B* **1981**, *24*, 4170.
- (24) Ramírez, R.; Böhm, M. C. *Int. J. Quantum Chem.* **1988**, *34*, 47.
- (25) Bernstein, B. T.; Smith, J. F. *Acta Crystallogr.* **1959**, *12*, 419.
- (26) Smith, J. F.; Bernstein, B. T. *J. Electrochem. Soc.* **1959**, *106*, 448.

- (27) Schottmiller, J. C.; King, A. J.; Kanda, F. A. *J. Phys. Chem.* **1958**, 62, 1446.
- (28) Cooper, A. S. *Acta Crystallogr.* **1962**, 15, 578.
- (29) Tománek, D.; Louie, S. G.; Mamin, H. J.; Abraham, D. W.; Thomson, R. E.; Ganz, E.; Clarke, J. *Phys. Rev. B* **1987**, 35, 7790.
- (30) Hybertsen, M. S.; Matthes, L. F. *Phys. Rev. Lett.* **1988**, 60, 1661.
- (31) Hennan, F.; Kasowski, R. V.; Hsu, W. Y. *Phys. Rev. B* **1988**, 38, 204.
- (32) Szpunar, B.; Smith, Jr., V. H. *Phys. Rev. B* **1992**, 45, 10616.
- (33) Noga, J.; Baňacký, P.; Biskupič, S.; Pelikán, P.; Zajac, A. *SOLID98, A Program System for Calculating Electronic Structure of Periodic Solid State Systems*; S-Tech. Inc., Bratislava, Slovakia, 1998, <http://www.stech.sk>.