

# ENERGY BANDS AND THEIR PRESSURE DEPENDENCE OF DIAMOND- AND ZINCBLLENDE-TYPE CRYSTALS BY MOLECULAR ORBITAL METHOD

*by*

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## Abstract

The extended Hückel theory is found to reproduce fairly well the band structures of Si, Ge, GaAs and GaP by adjusting some of the parameters. The calculated pressure dependence of the energies of the various band extrema agrees qualitatively with the observed one. On the contrary, a preliminary calculation shows that the complete neglect of differential overlap method with no adjustable parameters can not reproduce the band structure of Si.

## 1. Introduction

Recently many authors have carried out semiempirical LCAO calculations for energy bands of semiconductors<sup>1)-4)</sup>. The LCAO calculations for perfect crystals are very useful in calculating the electronic structures of defects in crystals, crystal surfaces and amorphous states. The extended Hückel theory (EHT)<sup>5)</sup> has widely been used for the LCAO calculation because it is a very simple LCAO approach and gives rather good results. However, some of the parameters in the EHT are necessary to be adjusted in order to make the LCAO band structure match the band structure determined by experiments or more exact calculations. So far such calculations have been performed for diamond<sup>1)</sup>, graphite<sup>2)</sup>, tellurium<sup>3)</sup> and silicon<sup>4)</sup>. In the present note, energy bands and their pressure dependence are calculated for Si, Ge, GaAs and GaP by the EHT method in order to investigate the usefulness and applicability of the EHT method.

## 2. Method of Calculation

In the EHT approximation, the matrix element of the effective one electron Hamiltonian is given by

$$H_{ii} = -I_i \tag{1}$$

$$H_{ij} = -\frac{1}{2}K_{ij}(I_i + I_j)S_{ij} \quad \text{for } i \neq j. \tag{2}$$

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Here  $I_i$  is the empirical ionization energy of the electron in the atomic orbital (AO)  $\chi_i$ ,  $K_{ij}$  is an empirical parameter between 1 and 2. The AO's are approximated by Slater-type orbitals,  $r^{n-1}e^{-\mu r}$  ( $n$ : principal quantum number), with Clementi's orbital exponents  $\mu^{61}$ .  $s$  and  $p$  orbitals for valence electrons are taken into account.

In the present work,  $K_{ss}$ ,  $K_{sp}$  and  $K_{pp}$  which are  $K_{ij}$  for  $i$  and  $j$  being  $s$  and  $s$ ,  $s$  and  $p$ , and  $p$  and  $p$  orbitals, respectively, are taken to be adjustable parameters to reproduce the band structures of Si and Ge calculated by the empirical pseudopotential method (EPM)<sup>7)</sup> or observed by experiments. The ionization energy of  $s$ -orbital,  $I_s$ , is also adjusted because it is expected to increase by the change of the electron configuration to  $sp^3$  from  $s^2p^2$  in forming the crystal.

The adjusted values of  $K_{ss}$ ,  $K_{sp}$ ,  $K_{pp}$  and  $I_s$  for Si and Ge are shown in Table 1. Each of  $K_{ij}$ 's has nearly the same value for Si and Ge.  $K_{ss}$  and  $K_{sp}$  are found to be smaller than  $K_{pp}$ . This tendency is also reported by Kamimura et al. and appears to be reasonable<sup>8)</sup>. The adjusted  $I_s$  shown in Table 1 is larger than that of the free atom as is expected.

For GaAs and GaP,  $K_{ij}$ 's are estimated from those adjusted for Si and Ge in the following way. Considering that both Ga and As are adjacent to Ge in the periodic table, for GaAs we use those adjusted for Ge. Similarly, for GaP we use the arithmetic mean of those adjusted for Si and Ge. Since GaAs and GaP are heteropolar crystals, we take into account the changes of the ionization energies by the charge transfer  $Q$  between two kinds of atoms.  $Q$  is estimated by Pauling's formula<sup>9)</sup>

$$Q_A = \sum_B [1 - \exp \{ -\frac{1}{4}(X_A - X_B)^2 \} ], \quad (3)$$

where  $X_A$  and  $X_B$  are the electronegativities of the atom  $A$  and  $B$ , respectively. Here the sum is over the atoms  $B$  which make the bond with the atom  $A$ .

### 3. Results and Discussion

Figure 1 shows the band structures for Si, Ge, GaAs and GaP obtained in this way. The calculated energies of various extremum points in the energy bands are shown in Table 2 with those by the EPM<sup>7)</sup> or experiments. The results for Si and Ge without adjusting  $I_s$  are also shown in the table for comparison. In this case, adjusted values of  $K_{ss}$ ,  $K_{sp}$  and  $K_{pp}$  are, respectively, 1.41, 1.30 and 1.70 for Si and 1.26, 1.28 and 1.62 for Ge. These values are slightly different from those in Table 1. If  $I_s$  is not adjusted, the energy of  $\Gamma_{2'c}$  for Si differs largely from the EPM result<sup>7)</sup> or the observed result. By adjusting  $K_{ss}$ ,  $K_{sp}$ ,  $K_{pp}$  and  $I_s$ , the energy bands calculated for Si and Ge are found to reproduce those by the EPM<sup>7)</sup> or experiments fairly well except the high energy region of the conduction band. The results for GaAs and GaP are also satisfactory by considering that no adjustable parameter is used for them.

Table 1  
 $K_{ss}$ ,  $K_{sp}$ ,  $K_{pp}$  and  $I_s$  for Si and Ge.  
The values in parentheses show  $I_s$ 's  
for the configuration of  $s^2p^2$ .

	Si	Ge
$K_{ss}$	1.34	1.27
$K_{sp}$	1.28	1.26
$K_{pp}$	1.70	1.62
$I_s$ (eV)	15.68 (15.16)	17.00 (15.62)

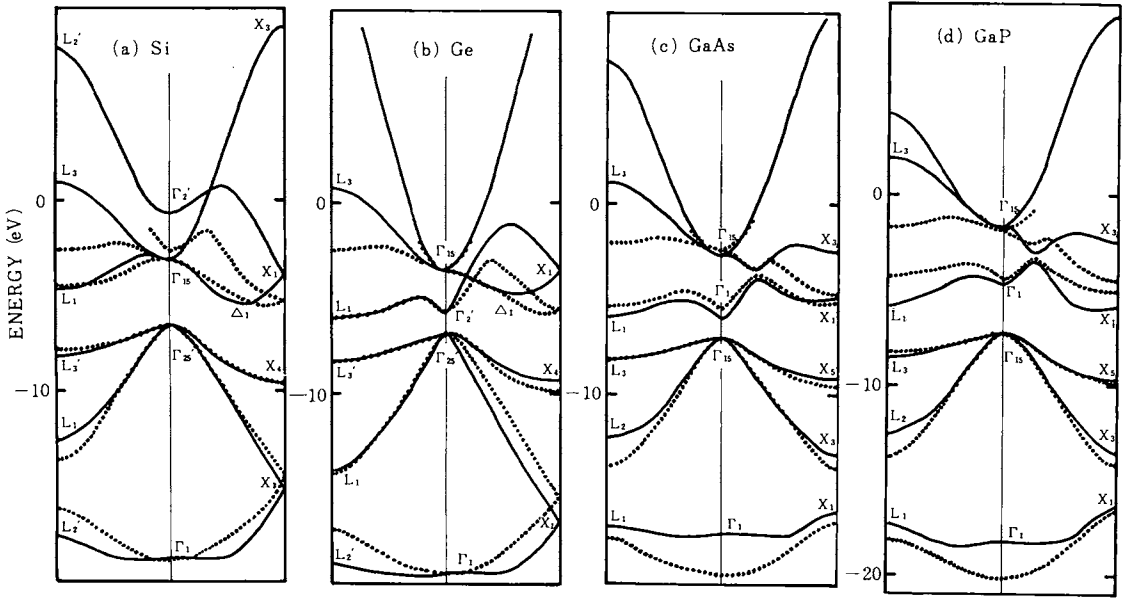


Fig. 1. The calculated band structures for (a) Si, (b) Ge, (c) GaAs and (d) GaP (solid lines). The dotted lines are those by the EPM<sup>7)</sup>.

The hydrostatic pressure dependence of the energies of the various band extrema is calculated by changing the lattice parameter. The results are shown in Table 3 with the observed ones<sup>10)</sup> or those by the EPM<sup>11)</sup>. The present results agree qualitatively with them.

If we take the  $sp^3$  hybridized orbitals instead of the atomic orbitals as the basis functions for calculating the off-diagonal elements shown in Eq. (2), the calculated energy band is found to differ drastically from those by the EPM. Recent calculations for amorphous Se and As-Se by Chen also show that the use of the hybridized orbitals as the basis functions leads to wrong

Table 2

The energies (in eV) of various extremum points in energy bands with respect to the top of the valence band.

(a) Those by the EPM or experiments. (b) The present results. (c) The results without adjusting  $I_s$ .

	Si			Ge		
	(a)	(b)	(c)	(a)	(b)	(c)
$\Gamma_{1v}$	-12.36	-12.16	-12.16	-12.57	-12.60	-10.92
$\Gamma_{15c}$	3.42	3.41	3.41	3.24	3.24	3.24
$\Gamma_{2'c}$	4.10	5.85	8.85	0.99	0.98	0.99
$L_{2'v}$	-9.55	-11.00	-10.90	-10.30	-12.03	-10.20
$L_{1v}$	-6.96	-5.98	-5.51	-7.42	-7.20	-6.35
$L_{3'v}$	-1.23	-1.60	-1.60	-1.44	-1.44	-1.44
$X_{1v}$	-7.69	-8.50	-7.89	-8.56	-10.00	-8.57
$X_{4v}$	-2.86	-2.95	-2.95	-3.20	-2.58	-2.58
$L_{1c}$	2.23	1.87	3.31	0.8	0.78	0.75
$\Delta_{1c}$	1.1	1.11	1.08	-	2.04	2.00

Table 2 (continued)

	GaAs		GaP	
	(a)	(b)	(a)	(b)
$\Gamma_{1v}$	-12.4	-10.2	-12.99	-10.9
$\Gamma_{1c}$	1.6	1.1	2.88	2.6
$\Gamma_{15c}$	4.8	4.4	5.24	5.7
$L_{1v}$	-10.5	-9.7	-10.60	-9.9
$L_{2v}$	-6.7	-5.1	-6.84	-5.3
$L_{3v}$	-1.2	-1.1	-1.10	-1.2
$L_{1c}$	1.6	1.2	2.79	1.4
$L_{3c}$	4.8	8.2	5.74	9.3
$X_{1v}$	-9.7	-9.1	-9.46	-9.1
$X_{3v}$	-6.8	-6.1	-7.07	-6.3
$X_{5v}$	-2.8	-2.2	-2.73	-2.5
$X_{1c}$	2.2	2.1	—	1.4

Table 3

The pressure dependence  $dE_g/d(\ln V)$  (in eV) of the energies  $E_g$  of various band extrema with respect to  $\Gamma_{25'v}$  or  $\Gamma_{15v}$ . (a) The present results. (b) Those by the EPM. (c) The observed results.

	Si			Ge		GaAs		GaP
	(a)	(b)	(c)	(a)	(c)	(a)	(c)	(a)
$\Gamma_{15c}$	-1.69	0.7		-1.6		-4.79		-8.6
$\Delta_{1c}$	2.38	1.6	1.5	0.93	0~1.5	0.00		-0.3
$\Gamma_{25'c}(\Gamma_{1c})$	-31.00	-13.4		-25.38	-9	-17.23	-7~-9	-19.7
$\dot{L}_{1c}$	-12.39	-4.4		-7.24	-3.8	-8.22		-11.6

results<sup>12)</sup>. Chen put  $H_{ij}$  between different hybridized orbitals of the same atom to zero by using Eq. (2) because  $S_{ij}=0$ , but we took it into account by using the separation between atomic s and p levels. Nevertheless, the results are unreasonable.

In the present calculation, the interaction between atoms within 6th neighbors is taken into account. If we take into account the interaction between atoms within only second neighbors, it leads to the very unreasonable results and the energy band by the EPM can not be reproduced.

The complete neglect of differential overlap (CNDO) method<sup>13)</sup> with no adjustable parameters is also applied for the calculation of the band structure of Si for comparison. The result is shown in Fig. 2. The width of the valence band is very large ( $\sim 34$  eV) and the overall agreement with the EPM or the observed band structure is not good.

#### 4. Conclusion

It is found that the EHT calculation with adjusted  $K_{ij}$  can reproduce fairly well the band structure for Si, Ge, GaAs and GaP. The pressure dependence of the energies of the various band extrema for these crystals calculated by the method is also not unreasonable.

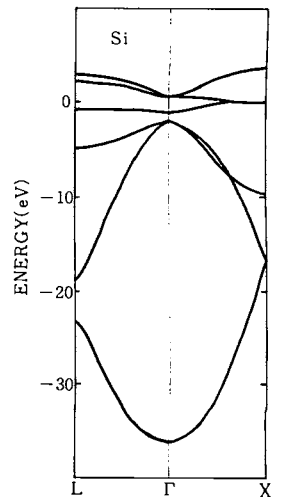


Fig. 2. The band structure for Si calculated by the CNDO method.

Consequently the present results are expected to be able to be used for the calculation of the electronic structures of defects in crystals, crystal surfaces and amorphous states. The CNDO method with no adjustable parameters is found not to be able to reproduce well the band structure of Si.

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