

The Band Structure of Diamond

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Received: March 19, 1996[⊗]

Within the extended-Hückel theory we present the influence of carbon 3s orbitals on the band structure of diamond. 3s orbitals are shown to account for the indirect band gap. The results of EHMO-ASED (atom superposition and electron delocalization) calculations agree well with orthogonalized plane-wave (OPW), pseudopotential, and ab initio studies; bond length and bulk modulus are nicely reproduced. For comparison, calculated bond lengths for a few selected hydrocarbons and for C₆₀ are included.

1. Introduction

The electronic structure, lattice constant, bulk modulus, and other physical properties of diamond have been extensively studied and are well-known.^{1–7} Messmer and Hoffmann have contributed insight by means of extended-Hückel molecular orbital (EHMO) calculations. While Hoffmann focused on the graphite to diamond conversion,⁸ Messmer aimed already 25 years ago at the description of the band structure and obtained good qualitative agreement with ab initio and experimental studies.⁹ He accounted for the indirect band gap by a large contraction of the carbon 2s orbital and by applying a different Wolfsberg–Helmholz parameter K for s–p-type interactions. The EHMO method is noted for its conceptual simplicity with respect to the parameters used, thus allowing a transparent discussion of the results obtained.^{10–12} We have therefore reinvestigated these calculations and have found that inclusion of contracted 3s orbitals is sufficient to obtain a good description of the band structure of diamond. In addition, bond length and bulk modulus as calculated by the EHMO-ASED (atom superposition and electron delocalization) method compare well with experimental findings.

For comparison we include bond lengths calculated for a few selected hydrocarbons and the “buckminsterfullerene” C₆₀ as a link between the “organic” carbon and the “inorganic” carbon we meet in diamond.

2. Method

The total energy $E_{\text{tot}}(R)$ along the coordinate R is given as a superposition of the extended-Hückel^{13,14} binding energy $\Delta E_{\text{EHMO}}(R)$ and a two-body electrostatic repulsion term¹⁵ $E_{\text{rep}}(R)$ between the centers α and β , respectively:

$$E_{\text{tot}}(R) = \Delta E_{\text{EHMO}}(R) + E_{\text{rep}}(R) \quad (1)$$

where

$$E_{\text{rep}} = \sum_{\alpha < \beta} E_{\text{Rep}_{\alpha\beta}} \quad (2)$$

TABLE 1: Coulomb Integrals H_{ss} and Slater Exponents ζ_s ($\kappa = 1$ Was Used)

element	n	ζ_{ns}	H_{ss}/eV	ζ_{np}	H_{pp}/eV
H	1	1.3	–13.6		
C	2	1.71	–21.4	1.625	–11.4
C	3	5.5	3.25		

The extended-Hückel binding energy $\Delta E_{\text{EHMO}}(R)$ is expressed as

$$\Delta E_{\text{EHMO}}(R) = E_{\text{EHMO}}(R) - \sum_s b_s^0 E_s^0 \quad (3)$$

with $\sum_s b_s^0 E_s^0$ being the sum of atomic valence orbital ionization energies, each of them times the orbital occupation number b_s^0 . E_{EHMO} is given as a sum over the one-electron states E_i times its occupation b_i :

$$E_{\text{EHMO}} = \sum_i b_i E_i \quad (4)$$

$$E_i = \sum_{\alpha_s} c_{i,\alpha_s}^2 H_{\alpha_s,\alpha_s} + 2 \sum_{\alpha_s < \beta_t} c_{i,\alpha_s} c_{i,\beta_t} H_{\alpha_s,\beta_t} \quad (5)$$

s and t indexing the atomic orbitals. The coefficients c_{i,α_s} of the atomic orbitals are determined by the variation principle, while the Coulomb integrals H_{α_s,α_s} are based on experimental valence orbital ionization energies (VOIEs).^{16,17} The off-diagonal elements H_{α_s,β_t} are calculated as

$$H_{\alpha_s,\beta_t} = \frac{1}{2} K S_{\alpha_s,\beta_t} (H_{\alpha_s,\alpha_s} + H_{\beta_t,\beta_t}) \quad (6)$$

For the Wolfsberg–Helmholz parameter K , we use the weighted formula in a slightly modified distance-dependent form:

$$K = 1 + k e^{-(\delta/2)(R-d_0+|R-d_0|)} \quad (7)$$

with

$$k = \kappa + \Delta^2 - \Delta^4 \kappa \quad \text{and} \quad \Delta = \frac{H_{\alpha_s,\alpha_s} - H_{\beta_t,\beta_t}}{H_{\alpha_s,\alpha_s} + H_{\beta_t,\beta_t}} \quad (8)$$

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[⊗] Abstract published in *Advance ACS Abstracts*, June 1, 1996.

The distance-dependent form used in earlier studies^{15,16,18,19} differs from eq 7 merely in the sense that the K dependence on

TABLE 2: Comparison of Experimental and Calculated C–C and C–H Distances of Some Representative Hydrocarbons

compound	C–C		C=C		C≡C		–C–H		=C–H		≡C–H	
	expt	calc	expt	calc	expt	calc	expt	calc	expt	calc	expt	calc
CH ₄							1.094	1.08				
CH ₃ –CH ₃	1.55	1.64					1.111	1.07				
CH ₂ =CH ₂			1.339	1.33					1.085	1.07		
H–C≡C–H					1.203	1.24					1.061	1.06
C ₆ H ₆			1.396	1.40					1.083	1.06		
C ₆₀ ^a			1.439	1.45								

^a Weighted average of the two different bond lengths.

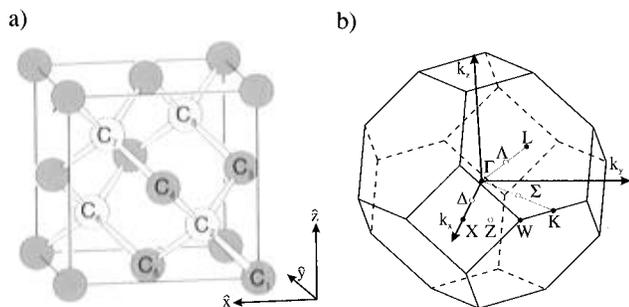


Figure 1. (a) Conventional cubic cell of the diamond lattice. For clarity, sites corresponding to one of the two interpenetrating face-centered cubic lattices are unshaded. Nearest neighbor bonds have been drawn in. The four nearest neighbors of each carbon atom form vertices of a regular tetrahedron. (b) The first Brillouin zone for the face-centered cubic lattice. The point Γ is the center of the zone and possesses the highest symmetry. K , L , W , and X are points; Λ , Δ , Σ , and Z lines of high symmetry.

the internuclear distance R only holds if R overcomes the sum of the orbital radii d_0 , calculated by the respective Slater exponents and quantum numbers (cf. eqs 13 and 14 in ref 15). This avoids the problem of K growing too large for diffuse orbitals. κ is not a new parameter but just another way to express the weighted Wolfsberg–Helmholz parameter K . This is best seen by inspection of eqs 7 and 8 at $R = d_0$. The computational treatment of the solid state remains the same, but the conception of Bloch sums was introduced to account for the translational symmetry.¹⁹ Calculations were carried out with the modified programs QCPE116²⁰ and QCPE571,²¹ applying the parameters given in Table 1. δ was chosen to be 0.35 \AA^{-1} for the molecules and 0.13 \AA^{-1} for diamond, respectively.

3. Hydrocarbons

The bond lengths of a representative selection of hydrocarbons and the “buckminsterfullerene” C₆₀ were determined. In Table 2 the calculated bond lengths are compared to the gas-phase geometries. In view of the fact that a single parameter set has been used, the agreement between computation and experiment has to be considered good. However, the C–C bond length in ethane is overestimated. As already discussed in an earlier study,¹⁸ this could be adjusted by optimizing the parameters, which is not the aim of the present work.

4. Diamond

The diamond lattice (formed by the carbon atoms in a diamond crystal) consists of two interpenetrating face-centered cubic Bravais lattices, displaced along the body diagonal of the cubic cell by one quarter of the diagonal’s length (cf. Figure 1a).²² It can be regarded as a face-centered cubic lattice with the two-point basis 0 and $(a/4)(\hat{x} + \hat{y} + \hat{z})$, where a is the length of the cube side. To avoid complicated back-folding,^{10,11} a primitive unit cell is used, which is spanned by three vectors

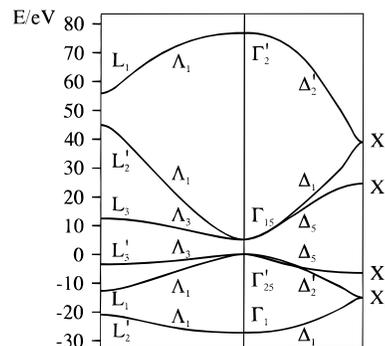


Figure 2. EHM0 band structure of diamond without carbon 3s atomic orbitals.

starting in a cube corner (i.e. C_1) pointing to the centers of the adjoining vertices. The corresponding Brillouin zone is depicted in Figure 1b.²³

An intensively discussed physical property of diamond is its band structure. The band structure calculated along the most relevant symmetry lines in the first Brillouin zone is shown in Figure 2. The computed valence bands are in good agreement with *ab initio* calculations.²⁴ The conduction band defined by the points L_3 , Γ_{15} , and X_3 also agrees well. The level ordering (Γ_{15} below Γ'_2) is now widely accepted^{1,2,24} and contradicts other tight-binding²⁵ and some pseudopotential calculations.³ The valence band width ($\Gamma_1 - \Gamma'_{25}$) is 25.8 eV, and the direct band gap amounts to 4.8 eV compared to the experimental values²⁶ of 24.2 ± 1 and 6.0 eV, respectively.²⁷ However, certain features of the conduction bands are quite poorly reproduced. Γ'_2 lies much too high in energy, and no minimum in the $\langle 100 \rangle$ direction can be found. Messmer tried to account for these features by contracting the 2s orbitals to $\xi_{2s} = 2.0$ and by changing the K value of s–p-type interactions.⁹ A more general approach is to keep parameters constant but to augment the basis by carbon 3s-type functions, which is physically meaningful. The resulting band structure of this augmented ASED-EHMO calculation is presented in Figure 3. The numerical values are compiled in the second column of Table 3. Γ'_{25} lies at an energy of -8.9 eV. For better comparison with calculations reported in the literature it is set to zero.

Little change is observed in the valence band region, which is not surprising as the 3s orbitals are too high in energy to significantly mix into the low-lying bands, even though the bandwidth is shifted up to 27.1 eV. The energy difference between the two symmetry points Γ'_{25} and Γ_{15} at the center of the Brillouin zone and the development of the doubly degenerate band (Λ_3 , Δ_5) remain unaffected. Dramatic alteration is, however, found in the conduction band region. Most striking is the indirect band gap arising along the Δ -line at $(0, 0, 0) \rightarrow (0.35, 0, 0)$ with an energy separation of ~ 4.0 eV. Messmer reports a minimum in the conduction band at 0.5 in the $\langle 100 \rangle$ direction of the reciprocal space. An *ab initio* LCAO band

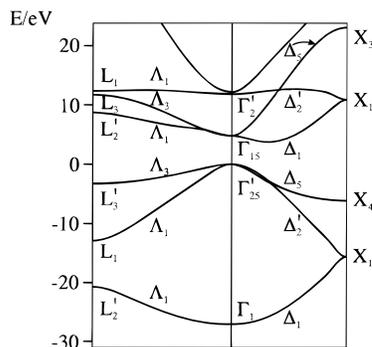


Figure 3. EHM0 band structure of diamond with carbon 3s atomic orbitals.

TABLE 3: Comparison of Band Structures of Diamond Calculated by Different Methods (All Energies Are Given in eV. For Better Comparison We Set Γ_{25} to Zero)

state	present work		OPW-SCF ^a PERT	pseudo ^b potential	EHMO ^c	ab initio ^d
	I	II				
Γ_1	-25.8	-27.1	-21.0	-27.5	-18.8	-29.9
Γ_{25}	0.0	0.0	0.0	0.0	0.0	0.0
Γ_{15}	4.8	4.8	7.1	8.4	4.7	13.8
Γ_2	72.5	11.9	14.3	13.1	13.3	
X_1	-14.3	-15.7	-13.5	-18.4	-10.6	
X_4	-6.2	-6.2	-5.5	-6.6	-4.4	
X_1	36.7	10.9	6.0	6.0	7.9	
X_3	23.2	23.2	21.1	>26.0	16.8	
L_2'	-19.8	-20.8	-15.2	-22.8	-15.5	
L_1	-12.0	-12.9	-12.2	-15.6	-8.6	
L_3'	-3.3	-3.3	-2.0	-3.1	-2.3	
L_1	52.9	12.4	9.8	7.7	8.7	27.8
L_3	11.8	11.8	11.1	9.2	9.1	

^a Reference 1. ^b Reference 30. ^c Reference 9. ^d Reference 5.

structure study by Chaney et al. leads to similar conclusions.²⁴ The experimental value of the indirect band gap determined by neutron diffraction measurements is 5.46 eV at $(0, 0, 0) \rightarrow (0.78 \pm 0.02, 0, 0)$.²⁸ Moreover, we obtain a correct level ordering at X with X_1 below X_3 . The two lowest bands along Λ are relatively flat and of Λ_1 and Λ_3 symmetry, respectively. They cross along this line, in agreement with most pseudopotential² and ab initio calculations.⁵

We conclude our study on diamond by calculating two bulk properties, namely, bond length and bulk modulus. The carbon-carbon distance R was altered in a range from 1.3 to 2.0 Å, and the energy per unit cell E was sampled at 120 points in the irreducible Brillouin zone, thus constructing the potential energy curve $E(R)$. A minimum energy was found at $R_0 = 1.6$ Å, in good agreement with the experimental value of 1.55 Å.²²

The bulk modulus B is given by²⁹

$$B = -V \left(\frac{\partial^2 E}{\partial V^2} \right)_T \quad (9)$$

The volume of the primitive unit cell is one quarter of the conventional fcc cell; hence

$$V(R) = \frac{1}{4} \left(\frac{4}{\sqrt{3}} R \right)^3 \quad (10)$$

where R is the next neighbor distance. Assuming a harmonic potential in the region of equilibrium bond length ($R \approx R_0$) we get

$$E(R) \approx kR^2 \quad (11)$$

for the potential energy and finally arrive at the following

equation for the bulk modulus:

$$B = \frac{k}{8\sqrt{3}R_0} \quad (12)$$

which holds for diamond and all zincblende-type structures. With $k = 760$ J/m² at a bond length of 1.6 Å, we calculate $B = 3.43 \times 10^{11}$ Pa, compared to the experimental value of $B_{\text{exp}} = 4.43 \times 10^{11}$ Pa.

5. Conclusions

The results of EHM0-ASED calculations agree well with OPW-SCF, pseudopotential, and ab initio studies; bond length and bulk modulus are nicely reproduced. Augmentation of the basis set by carbon 3s atomic orbitals can account for the indirect band gap in diamond by maintaining all advantages of the EHM0 theory. Hence, it seems possible that the extension of the basis set will be successful in other tight-binding calculations where the description of the conduction band region causes difficulties.

Acknowledgment. We acknowledge financial support by the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung project NF. 20-040598.94/1.

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