

Application of SCF Perturbation Theory to the Study of Tetrahedrally Bonded Valence Crystals

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The bond interaction method has been applied to the study of hexagonal and cubic BeO, BN and diamond. It is found that the CNDO method yields the cubic structure as the more stable forms of BN and diamond; the BeO calculation did not converge well. It is concluded that the method is limited to the study of relatively covalent systems.

Key words: Tetrahedrally bonded valence crystals

1. Introduction

The SCF perturbation based treatment of inter-bond interactions described in Ref. [1] is applied here to the study of tetrahedrally bonded valence crystals. The resultant theory in many ways resembles that of Coulson, Redei and Stocker [2], and may be regarded as an extension of their method to the SCF level of approximation.

The band structures of simple valence crystals have received considerable attention in recent years. Much of this work has been recently reviewed by Messmer [3]. However, little attention has been given to the relative stabilities of different but structurally related valence crystals of the same substance. For example, the Zincblende and Wurtzite structures both consist of tetrahedrally coordinated lattices, but differ in the conformation of their bonds, with the most noticeable difference being in the conformation of their vicinal bonds. In the Zincblende lattice, all vicinal bonds are staggered with respect to one another, whereas in the Wurtzite structure eclipsed bonds are to be found. One consequence of this difference in the atomic arrangements is that the Madelung constant for the Wurtzite structure is slightly larger than that of the Zincblende [4]. Thus, it has been argued that ionic substances would tend to crystallize in the Wurtzite in

preference to the Zincblende structure [4]. For a partially ionic substance this would be offset by the existence of energetically unfavourable eclipsed bond interactions. The question then arises at what point in the electronegativity scale would one structure be favoured over the other? This is investigated here by calculating the binding energies of hexagonal and cubic BeO, BN and diamond lattices.

It has been known for some time that BN can be prepared in either the cubic (F43m) or the hexagonal (P6₃/mmc) modification [5, 6]; the cubic form being the one more easily prepared. The well known form of diamond is of course cubic, but recently a hexagonal modification has been recovered from meteorites [7]. BeO crystallizes in several modifications. The most stable appears to be a distorted Wurtzite lattice [8].

Molecular orbital calculations, based on the CNDO/2 approximation [9], are reported here for the cubic and hexagonal forms of BeO, BN and CC. Although recent calculations [10] on cubic diamond suggest that some modification to the CNDO parameters are necessary to obtain satisfactory band structures, the well documented success of the original theory in calculating the conformations of simple molecules argues that it can be meaningfully applied to the study of the *relative* stabilities of the above two lattices.

2. Theory

The objective here is the solution of the Roothaan SCF equations [11] for a valence crystal by an adaptation of the SCF perturbation method presented in Ref. [1] for saturated molecules. Following this method, the crystal basis set is chosen to consist of sp^3 hybrid functions centered on each atom of the lattice. These functions are ordered so that any two hybrid functions pointing along a common bond direction are adjacent in the basis set list. The purpose of this assumption is to partition the crystal Fock and density matrices into sub-matrices. Those sub-matrices that occupy the diagonal positions of the full matrix, and which therefore have elements between hybrids in the same bonds, are referred to as intra-bond sub-matrices. Those occupying off-diagonal positions are referred to as inter-bond sub-matrices. The basis of the method is to build up the full crystal density matrix, or as much of it as is needed, through the calculation of these density sub-matrices.

Although the method is applicable at all levels of approximation to the complete SCF equations, it will be introduced here by means of the relatively simple CNDO/2 approximation [9]. Under this approximation, the Fock matrix, F , for the valence electrons of the entire crystal are given by

$$F_{mm} = -0.5 (A + I)_{mm} + 0.5 \gamma_{AA} - 0.5 P_{mm} \gamma_{AA} + \sum_B^{\text{crystal}} (Q_B - Z_B) \gamma_{AB} \quad (1)$$

$$F_{mn} = \beta_{mn} - 0.5 P_{mn} \gamma_{AB} \quad m \neq n \quad (2)$$

Here A , I and β are the usual CNDO/2 parameters and γ_{AB} is the CNDO/2 average

Coulomb integral between atoms A and B. Q_B and Z_B are the total electron population and the effective nuclear charge, respectively, of atom B; P is the crystal density matrix.

Because of the chosen basis set order, the full crystal Fock and density matrices can be conveniently partitioned into sub-matrices. Thus, the intra-bond Fock sub-matrix for the R 'th bond is given by

$${}^{RR}F_{mm} = -0.5(A+I)_{mm} + 0.5\gamma_{AA} - 0.5{}^{RR}P_{mm}\gamma_{AA} + \sum_C^{\text{crystal}}(Q_C - Z_C)\gamma_{AC},$$

$m=1 \text{ or } 2$ (3)

$${}^{RR}F_{12} = {}^{RR}\beta_{1,2} - 0.5{}^{RR}P_{12}\gamma_{AB}$$

(4)

where the R 'th bond connects lattice atoms A and B. Similarly, for the inter-bond Fock sub-matrix between bonds R and S :

$${}^{RS}F_{mn} = {}^{RS}\beta_{mn} - 0.5{}^{RS}P_{mn}\gamma_{AC}, \quad m, n=1 \text{ or } 2$$

(5)

where the hybrid orbitals labelled m and n are associated with lattice atoms A and C, respectively. Note, when R and S label different bonds attached to a common atom, A and C will be the same.

3. The Inclusion of Crystal Symmetry

The complete solution of the crystal SCF problem in principle requires, taking the symmetric character of P into account, the calculation of $\frac{1}{2}N_b(N_b+1)$ density sub-matrices; N_b is the total number of bonds in the crystal. The presence of the extensive crystal symmetry of a perfect lattice greatly reduces this number. If, by virtue of this symmetry, all bonds are equivalent, a single reference bond may be arbitrarily selected and only its intra-bond density sub-matrix need be calculated together with all inter-bond sub-matrices between this bond and the remaining

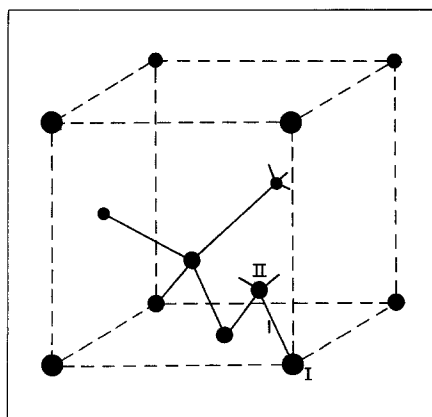


Fig. 1. Portion of the cubic unit cell showing staggered bonds and sites I and II

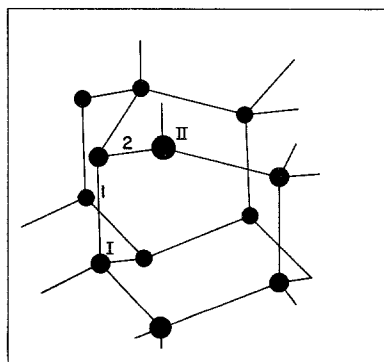


Fig. 2. Portion of hexagonal unit cell showing both the staggered and eclipsed bond pairs, sites I and II and bonds 1 and 2

bonds in the lattice. In practice, relatively few of these need be calculated since they decrease exponentially with separation from the reference bond.

In addition to reducing the number of equations to be solved, crystal symmetry also leads to an appreciable simplification to the diagonal elements of the intra-bond Fock sub-matrices. The atomic electron populations, Q , of Eq. (3) are equal between translationally equivalent atoms and may therefore be factored from out of the Coulomb lattice sums. Thus, assuming there are only two site species, I and II, of Figs. 1 and 2 present, the diagonal elements of ${}^{RR}F$ are given by:

$${}^{RR}F_{mm} = -0.5(A+I)_{\text{II}} + 0.5\gamma_{AA} - 0.5{}^{RR}P_{mm}{}^{RR}\gamma_{AA} + (Q_{\text{I}} - Z_{\text{I}})\Gamma_{\text{I,I}} + (Q_{\text{II}} - Z_{\text{II}})\Gamma_{\text{I,II}} \quad (6)$$

where it is assumed that atom A, on which m is centered, occupies a site of type I, and

$$\Gamma_{\text{I,II}} = \sum_{\text{B}}^{\text{II}} \gamma_{\text{AB}} \quad (7)$$

$$\Gamma_{\text{I,I}} = \sum_{\text{B}}^{\text{I}} \gamma_{\text{AB}} \quad (8)$$

The summations in (7) and (8) are restricted to atoms occupying sites of type I and II, respectively.

The inter-bond Fock sub-matrices remain unaffected by lattice symmetry under the CNDO approximation; essentially, they are already so simple that further simplification is unlikely.

4. The Perturbation Fock Sub-Matrices

Following the method given in Ref. [1], the crystal is treated at the zeroth order of perturbation as a collection of mutually polarizing but otherwise independent bonds; all Hamiltonian matrix elements neglected at this level of approximation are included as first-order terms.

The zero order intra-bond Fock sub-matrix is given with this choice of perturbation by

$${}^{RR}F_{12}^{(0)} = -0.5(A+I) + 0.5\gamma_{AA} - 0.5{}^{RR}P_{mm}^{(0)}\gamma_{AA} + (Q_{\text{I}}^{(0)} - Z_{\text{I}})(\Gamma_{\text{II}} - \Gamma_{\text{I,II}}) \quad (9)$$

$${}^{RR}F_{12}^{(2)} = {}^{RR}\beta_{12} - 0.5{}^{RR}P_{12}^{(0)}\gamma_{AB} \quad (10)$$

Use has been made in the derivation of this equation of the fact that the overall neutrality of the crystal requires

$$Q_{\text{I}}^{(0)} - Z_{\text{I}} + Q_{\text{II}}^{(0)} - Z_{\text{II}} = 0 \quad (11)$$

By definition, all zero order inter-bond sub-matrices are zero.

$${}^{RS}F^{(0)} = 0 \quad R = S \quad (12)$$

All remaining Hamiltonian matrix elements not included at the zeroth order,

together with the contributions from their induced changes in P , are included in the first order Fock sub-matrices.

All contributions from the one and two electron matrices have been included for the intra-bond Fock sub-matrices at the zero order. Since, under the CNDO approximation, there are no electron repulsion terms involving inter-bond density sub-matrices, ${}^{RR}F^{(1)}=0$ at this level of approximation. Higher order intra-bond Fock sub-matrices will not in general be zero, since first order inter-bond interactions lead to second and higher order bond polarizations. These changes in the intra (and inter) bond density sub-matrices have to be made self consistent through the solution of the SCF perturbation equation at the corresponding order.

$${}^{RS}F_{mn}^{(1)} = {}^{RS}\beta_{mn} - 0.5 {}^{RS}P_{mn}^{(1)} {}^{RS}\gamma_{AB} \quad (13)$$

where ${}^{RS}\gamma_{AB}$ is the CNDO Coulomb integral between atoms A and B of bonds R and S, respectively.

All of the crystal Hamiltonian matrix elements have now been included in the calculation, but higher order Fock sub-matrices arise through higher order induced changes in the density matrix, P . Thus for $x > 1$

$${}^{RR}F_{mn}^{(x)} = -0.5 {}^{RR}P_{mn}^{(x)}\gamma_{AA} + Q_I^{(x)}(\Gamma_{I,I} - \Gamma_{I,II}) \quad (14)$$

where use has been made of the charge conserving relation

$$Q_I^{(x)} + Q_{II}^{(x)} = 0 \quad \text{all } X > 0 \quad (15)$$

$${}^{RS}F_{mn}^{(x)} = -0.5 {}^{RS}P_{mn}^{(x)} {}^{RS}\gamma_{AB} \quad x > 1 \quad (16)$$

here R may equal S if m does not equal n .

The density sub-matrices may be calculated iteratively from these equations by the SCF perturbation method presented in Ref. [12].

5. The Convergence of the Electrostatic Contributions to ${}^{RR}F$

The SCF perturbation calculations based on Eqs. (8) and (14) for ${}^{RR}F$ converge well when both lattice sites are occupied by atoms of the same species. However, for polar crystals the zero order equations appear to have multiple solutions, none of which refine well at the higher orders and, moreover, depend on the summation radius chosen for Γ . This behaviour persists, but to a lesser extent, even when a rather large summation radius of about 40 Å is used. To overcome this difficulty, stabilize the perturbation calculations and reduce the computation time, the Coulomb lattice sums are replaced by Madelung constants. This can be effected by rewriting the Coulomb integral γ as

$$\gamma_{AB} = \frac{1}{R_{AB}} + \delta_{AB} \quad (17)$$

where R_{AB} is the distance between atoms A and B and δ is an exponential function [13]. Since δ_{AB} decreases exponentially with distance, it yields an absolutely

convergent series when summed over an infinite lattice. The Coulomb lattice sums, Γ , may be written as

$$\Gamma_{II} = \sum'_S \frac{1}{R_{RS}} + {}^{RR}\gamma_{AA} + \sum'_S \delta_{RS} \quad (18)$$

on substitution for Γ in Eqs. (8) and (14) yields

$$\begin{aligned} {}^{RR}F_{11}^{(0)} = & -0.5 (I+A)_{11} + 0.5 {}^{RR}\gamma_{AA} - 0.5 {}^{RR}P_{11}^{(0)} {}^{RR}\gamma_{AA} + (Q_A^{(0)} - Z_A) \\ & \times \{M/\tau_0 + {}^{RR}\gamma_{AA} + \Delta_{I,I} - \Delta_{I,II}\} \end{aligned} \quad (19)$$

$$\begin{aligned} {}^{RR}F_{22}^{(0)} = & -0.5 (A+I)_{22} + 0.5 {}^{RR}\gamma_{BB} - 0.5 {}^{RR}P_{22}^{(0)} {}^{RR}\gamma_{BB} + (Q_B^{(0)} - Z_B) \\ & \times \{M/\tau_0 + {}^{RR}\gamma_{BB} + \Delta_{II,II} - \Delta_{II,I}\} \end{aligned} \quad (20)$$

where the bond R is between atoms A and B of sites I and II, respectively. M is the dimensionless Madelung constant of the crystal, τ_0 is the shortest bond length and Δ is a lattice sum of δ 's:

$$\Delta_{II} = \sum'_C \delta_{AC} \quad (21)$$

And for the higher orders

$${}^{RR}F_{11}^{(x)} = -0.5 {}^{RR}P_{11}^{(x)} {}^{RR}\gamma_{AA} + Q_A^{(x)} \{M/\tau_0 + {}^{RR}\gamma_{AA} + \Delta_{I,I} - \Delta_{I,II}\} \quad (22)$$

$${}^{RR}F_{22}^{(x)} = -0.5 {}^{RR}P_{22}^{(x)} {}^{RR}\gamma_{BB} + Q_B^{(x)} \{M/\tau_0 + {}^{RR}\gamma_{BB} + \Delta_{II,II} - \Delta_{II,I}\} \quad (23)$$

All of the calculations reported in this paper based on the above formulation of F . The two Madelung constants necessary for the calculations on the cubic and hexagonal lattices, respectively, were taken from Ref. [4].

6. Energy Calculation

The total energy of the crystal, \mathcal{W} , is given by

$$\mathcal{W} = \frac{1}{2} \sum_m \sum_n P_{mn} \{H_{mn} + F_{mn}\} + \frac{1}{2} \sum_A \sum_B \frac{Z_A Z_B}{R_{AB}} \quad (24)$$

On partitioning all of these matrices into sub-matrices and taking the crystal symmetry into account, equation reduces to

$$\begin{aligned} \mathcal{W} = & \frac{N_b}{2} \sum_{m=1}^2 \sum_{n=1}^2 {}^{RR}P_{mn} ({}^{RR}H_{mn} + {}^{RR}F_{mn}) + \frac{N_b}{2} \sum_S^{\text{crystal}} \sum_{m=1}^2 \sum_{n=1}^2 {}^{RS}P_{mn} \\ & \times ({}^{RS}H_{mn} + {}^{RS}F_{mn}) + \frac{N}{2} \sum_B^{\text{crystal}} \frac{Z_A Z_B}{R_{AB}} \end{aligned} \quad (25)$$

where N and N_b are, respectively, the number of atoms and bond in the crystal. Since there are twice as many bonds as there are atoms,

$$N_b = 2N$$

and the average energy per bond, W , is given by

$$W = \frac{1}{2} \sum_{R \geq S} \sum_m \sum_n {}^{RS}P_{mn} ({}^{RS}H_{mn} + {}^{RS}F_{mn}) + \frac{1}{4} \sum_B \frac{Z_A Z_B}{R_{AB}} \quad (26)$$

This expression may be expanded order by order and the nuclear repulsion incorporated into the zero order contribution to yield electrostatic energy contribution in terms of the Madelung constant for the crystal under investigation.

The calculations reported here included contributions from all orders up to and including the third.

7. Structural Data for the Calculations

All of the calculations reported here are based on the cubic or hexagonal lattices shown in Figs. 1 and 2 and using the unit cell data given in Table 1. The data for the hexagonal BN has been rounded slightly to ensure an exact tetrahedral nearest neighbour environment within the lattice. Thus the experimentally reported a_0 and c_0 were changed from 2.55 and 4.20 Å to 2.5562 and 4.1742, respectively.

Table 1. Assumed unit cell dimensions

Substance	Cubic	Hexagonal		Bond length
	a_0	a_0	c_0	r_0
Diamond	3.5668	2.5221	4.1185	1.5444
BN	3.615	2.556	4.1742	1.5653
BeO	3.8235	2.7036	4.4150	1.6556

The basis set for all of the calculations consists of four sp^3 hybrid functions, built from the corresponding Slater $2s$ and $2p$ orbitals, on each atom pointing directly towards the four nearest neighbours. A list of these functions is set up within the reference unit cell in terms of a list of the unit cell atoms and the bond vectors which connect them. The next step in the calculation after the basis set has been organized is the construction of a list of all pairs and triplets of bonds between the reference bonds of the origin unit cell and the remainder of the lattice. This task is quite time consuming, but fortunately it need be undertaken only once for each lattice structure. Moreover, because of lattice symmetry only one reference bond is required for the cubic lattice and only two for the hexagonal lattice. The bond pair list for the present calculation was taken to include next nearest neighbour bonds. The list of triplets of bonds is constructed by a double scan of the list of bond pairs.

The Δ lattice sums of Eqs. (19–23) were taken to include all atoms within a sphere of 10 Å of a reference atom. This was found to be sufficient since these sums are strongly convergent.

8. Results

The environment of the chemical bonds in the hexagonal and cubic crystals are different. Each chemical bond has twenty-four nearest neighbour interactions in the crystal. These sets of interactions are the same for all bonds in the infinite cubic lattice and consist of the following interactions:

$$6H_1 + 6H_{180} + 12H_{60} \quad (27)$$

where H_1 is the interaction between two bonds originating from the same atom, and H_ϕ is the interaction between two vicinal bonds with an azimuthal angle ϕ . There are two sets of bonds, 1 and 2 of Fig. 1, in the hexagonal lattice and these are distinguished by their interactions with the remainder lattice. The 24 nearest neighbour interactions for bond I are the same as those listed in Eq. (27) for the cubic case. Bond II has the following contributions: (28)

$$6H_1 + 4H_{180} + 2H_0 + 8H_{60} + 4H_{120}$$

The interbond energies, calculated from $^{RS}P^{(1)}$, listed in Table 2 suggest that these interactions would favour the cubic over the hexagonal structure. The calculation of the total crystal energy per bond for both structures of diamond does yield the cubic modification as the more stable.

Table First order inter-bond energies for diamond and BN

Crystal	W_1	W_0	W_{60}	W_{120}	W_{180}
C-C	-0.2144×10^{-2}	-0.2801×10^{-2}	-0.4033×10^{-3}	-0.3531×10^{-2}	-0.1065×10^{-1}
B-N	-0.1602×10^{-1}	-0.1234×10^{-1}	-0.4358×10^{-2}	-0.3707×10^{-2}	-0.1213×10^{-1}

In the case of the BN structures, the effect of the unfavourable inter-bond interactions of the hexagonal lattice could be offset by an increased electrostatic contribution resulting from the slightly higher Madelung constant for this lattice. However, it turns out, under the CNDO approximation at least, that the net atomic charges are too small to achieve this effect, so that the cubic remains the predicted stable structure for this substance, Table 3. Thus, returning to the question raised in the introduction concerning the electrostatic stabilization of the hexagonal relative to the cubic lattice, it is apparent that a large measure of

Table 3. Calculated net atomic populations and lattice energies (a. u.) for hexagonal and cubic diamond, BN and BeO

	CC		BN		BeO	
	Cubic	Hex.	Cubic	Hex.	Cubic	Hex.
Q_1	0.0	0.0	0.3828	0.3872	0.6559	0.6675
W_{inter}	-0.0656	-0.0633	-0.1268	-0.1228	-0.2833	-0.2799
W_{MAD}	0.0	0.0	-0.0203	-0.0208	-0.0563	-0.0584
W_{total}	-3.6194	-3.6179	-3.9666	-3.9646	-5.0632	-5.0618

charge transfer is required to offset the disadvantage of the eclipsed bonds in the former structure. The calculated atomic charges for BN, Table 4, are in close agreement with those reported by Philips [14] and by Coulson *et al.* [2].

Calculations were also undertaken for hexagonal and cubic BeO lattices, although there is no experimental evidence that this substance exists in the cubic form; one of the stable forms of BeO, on the other hand, may be viewed as a strongly distorted cubic lattice. Unfortunately, the method did not work well and the results are only of interest from a numerical point of view. Although the individual SCF interactions for each order of the perturbation are strongly convergent, the calculated charge densities, Table 4, suggest that the perturbation series is not. This could perhaps be remedied by the selection of a more ionic solution for the zero order starting bond orbitals. In any event, the method as described here seems to be limited to relatively covalent crystals.

Table 4. Zero, second and third order atomic electron populations for BN and BeO. The first order densities are zero as a consequence of the choice of perturbation and diamond densities are zero as a result of crystal symmetry

	BN	BeO
$Q^{(0)}$	0.0171	0.1294
$Q^{(2)}$	0.4541	0.2018
$Q^{(3)}$	-0.0840	0.3363

9. Summary and Conclusions

The bond interaction method has been extended to the study of three-dimensional valence crystals. The method appears to work well for covalent and slightly ionic systems, but shows evidence of divergence in the perturbation series when applied to relatively ionic systems such as BeO. This problem could, perhaps, be remedied by the substitution of a more ionic zero order starting solution. As it stands, however, the method is limited to the study of covalent and partially ionic crystals.

The CNDO/2 method found the cubic uniformly more stable than the hexagonal structure for all three crystals studied. These results are in agreement with experiment in the cases of diamond and BN in as far as the cubic crystals are more easily prepared than the hexagonal. In the case of BeO, the slightly distorted hexagonal lattice seems to be the most stable modification. Comparison between experiment and theory is meaningless in this case since the perturbation expansion did not reach a satisfactory level of convergence.

Although limited to the study of relatively covalent solids, the method nonetheless has a wide range of applicability since many important substances, SiC for example, fall in this category. Moreover, this SCF perturbation approach lends itself well to the study of lattice impurities and defects. In this regard, it has the advantage over cluster calculations of providing results at a well defined level of approximation.

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