

ITERATIVE EXTENDED HUCKEL CALCULATION ON HEXAGONAL BORON NITRIDE

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Some properties of two-dimensional boron nitride are treated in a truncated crystal approach, employing the iterative extended Huckel method in a charge self-consistent calculation. The values of the band width, band gap, charges, equilibrium distance, and sublimation energy are in satisfactory agreement with experiment.

THE USE of a tight binding scheme for calculating the electronic properties of slightly ionic solids such as boron nitride^{1,2} is known to present some difficulties as to the change in the free atom quantities due to charge transfer, hybridization and overlapping effects manifested in the crystalline environment. It was pointed out² that the use of the tight binding approximation as an interpolation scheme³ to determine the values of the disposable parameters appearing in the matrix elements would require a large amount of experimental data. The alternative tight binding approaches previously proposed either consider only π bands with semiempirical parameters taken from the molecular ($B_3N_3H_6$ borazine) spectra,¹ or introduce a set of arbitrary scaling factors, selected to yield the known width of the forbidden gap.² These methods do not take into account in a consistent way the effect of charge redistribution on the π and σ bands, and thus are inadequate for calculating stability, equilibrium distances, charges and the distance dependence of the band gap.

We report here the results of a calculation on hexagonal boron nitride using an iterative, charge self-consistent LCAO semiempirical method (Iterative Extended Huckel method - IEXH),⁵ which takes account of these effects. This method treats a finite cluster of atoms simulating two-dimensional hexagonal boron nitride (point group D_{3h}) by an atomic basis set composed of Slater orbitals for the valence states $2S, 2P_x, 2P_y, 2P_z,$

retaining all overlaps and interactions, and approximating the off-diagonal matrix elements of the effective one-electron Hamiltonian by the Cusachs approximation^{5a}

$$H_{ij}^{A,B} = \delta_{ij}^{A,B} (1 - 0.5 \delta_{ij}^{A,B}) (H_{ii}^{A,A} + H_{jj}^{B,B}) \quad (1)$$

where the diagonal elements $H_{ii}^{A,A}$ are charge dependent ionization potentials of orbital i in atom A

$$H_i^A(Q) = H_i^A(0) - Q^A \Delta H_i^A \quad (2)$$

and the free atom orbital energy $H_i(0)$ and its charge dependence ΔH_i^A are obtained from smoothing of atomic spectroscopic ionization potentials over various degrees of ionization^{6b} Solving the secular equations for an initial guess of net charges Q^A yields wave functions that are submitted to Mulliken population analysis.⁷ Net atomic charges are then computed in a way that leaves the projection of the centroid of the charge onto the line connecting two atoms unchanged (not by the usual procedure of dividing the nonsymmetric heteronuclear bond charge into equal parts), and a new set of secular equations is solved, until charge self-consistency is obtained. An under-relaxation technique is used to achieve good convergence. The success of methods similar to that outlined above in calculations of small molecules was suggested^{6,8} to arise from the close resemblance of the matrix elements obtained to those yielded by the Hartree-Fock method. The main

Table 1. Comparison of IEXH results for the $B_{12}N_{12}H_{12}$ cluster with theoretical and experimental results

Property	Tight binding (2)	Tight binding (1)	IEXH	Exper	Method
gap (eV)	5.4	4.6	3.0	3.6 3.9	X-ray emission ¹¹ absorption ¹²
valence π width (eV)	1.2	2.2	3.2	—	
valence $2S$ width (eV)	1.3	—	4.4	2.2	X-ray emission ¹¹
$2S_V$ band maximum (eV)	$E_3 - 16.2$	—	$E_2 - 18.8$	$E_2 + 19.4$	ESCA ¹³
$\pi\pi^*$ transition (eV)	6.6	—	6.0	6.2	dielectric constant ²
work function (eV)	11.8	—	11.6	—	
$Q_B^{\pi}(e)$			0.51	0.45	NQR ¹⁴
$R_{2z}(A)$			1.5	1.45	crystallography ¹⁵
mean sublimation energy (eV)			8.0	6.6	thermochemistry ¹⁶

disadvantage of the method lies in its inability to include a large number of atoms in the calculation, and hence, in the computation reported here hydrogens surrounding the cluster were employed as boundary conditions. However, the striking similarity found between the valence band of the coronene molecule ($C_{24}H_{12}$, D_{5h}) and graphite⁹ (which is isoelectronic to hexagonal boron nitride and possesses a very similar crystal structure) and the gradual approach of the electronic gap of simple aromatic polyacene molecules towards that of graphite, as the size of the molecule increases,¹⁰ support the validity of finite cluster representation of boron nitride

Table 1 shows the results of calculation for coronene-like boron nitride ($B_{12}N_{12}H_{12}$, D_{5h}), as compared with results from other sources.

The results of similar calculations on clusters of different sizes and symmetries such as $B_3N_3H_{10}$, $B_{12}N_{10}H_{12}$, $B_{14}N_{14}H_{14}$ indicate that the band gap, band width and charges converge as the cluster size increases, the gap for the largest cluster calculated is within 10% of that for the other clusters, and the band width and charges are within 5%.

Contrary to the scaled tight binding calculation, a significant overlap between σ and π valence states is observed and no superficial π shell or rigid σ core is obtained, while in the conduction states there is a more distinct separation between these bands. A deep core state composed mainly of nitrogen $2S$ atomic states is well separated and practically unaffected by cluster size

and small distance variations. Its energy near the maximum density of states is given in the table with respect to the center of the forbidden band E_3 . The observations seem to be confirmed by experimental band studies^{11, 12}

The work function is probably greatly overestimated both in the previous tight binding calculations and in ours, because of the absence of explicit correlation effects. On going from the borazine molecule to our representation of boron nitride, a decrease in the calculated ionization potential from 12.1 to 11.6 eV is observed, whereas a much larger decrease would be expected on the basis of the experimental results for the similar benzene-graphite system. The effect of charge iteration on the work function is nevertheless in the right direction, lowering it from the uniterated value of 12.9 to 11.6 eV.

Calculating atomic charges for different nearest neighbor distances R indicates that the effect of crystallization on charge redistribution is to transfer $0.5e$ from the π nitrogen state to boron, while the σ effect is the reverse, $0.8e$ being transferred from the σ boron state to nitrogen making the boron finally $0.3e$ more positive than in its neutral atomic state. This result is contrary to the conventional B^+N^- structure inferred from boron-nitrogen chemistry. An increase in the boron π charge and a decrease in the nitrogen π charge is observed on going from the borazine molecule to bigger clusters, and this trend seems to saturate for the biggest cluster considered, resulting in a boron π charge Q_B^{π} comparable to

that inferred from NQR studies. The uniterated values of Q_B^- and $Q_B^{n.e.}$ are 0.1 and 1.5e respectively, indicating an incomplete charge redistribution in this calculation.

The $\pi \rightarrow \pi^*$ band gap was found to decrease as a function of R , approximately as $R^{-1.3}$. Since the band gap at the P point in the Brillouin zone results mainly from the difference in atomic P_z energies of boron and nitrogen, $H_{P_z, P_z}^{B, B} - H_{P_z, P_z}^{N, N}$, this distance dependence is due to variation of these quantities through charge redistribution in the crystal. Applying the same concept to the uniterated calculation results in a weaker R dependence, of $R^{-0.7}$. This is to be compared with the distance dependence of $R^{-2.5}$ found for the band gap in tetragonal III-IV crystals,¹⁷ resulting mainly from the antisymmetric gap due to the interaction term $H_{P_z, P_z}^{III, IV}$. The effect of charge iteration on the band gap of hexagonal boron nitride is thus important. In the uniterated calculation the band gap increases to 5.9 eV. The effect of iteration on the valence band width is smaller, resulting in a decrease of 3% from its uniterated value.

It should be noted that in the scaled tight binding approach² the reductive factors are not determined self-consistently with charge distribution. Moreover, since in that treatment the experimental data selected to be reproduced can be related only to π bands, there is no physical way of scaling σ type interactions. The π tight binding of Taylor and Coulson,¹ on the other hand, employs molecular parameters which include to some extent the effect of charge distribution, but neither its distance dependence in the crystal, nor the effect of the core, could be treated in such a theory.

Keeping in mind that IEXH calculations are based on atomic quantities only, the overall agreement between the results and experimental data is satisfactory. The main source of error in this calculation probably lies in the boundary conditions employed. Application of cyclic boundary conditions together with more accurate atomic charge dependent quantities seem to be the main improvements required.

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Quelques propriétés d'un cristal bidimensionnel de nitrure de bore sont traitées par la méthode d'approche du cristal tronqué. On utilise un calcul 'self-consistent' de charge dans la méthode itérative étendue de Huckel.

Les valeurs des largeurs de la bande permise et de la bande interdite, des charges, de la longueur de la liaison à l'équilibre, et de l'énergie de sublimation sont en accord avec l'expérience