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A molecular calculation of electronic properties of layered crystals: I. Truncated crystal approach for hexagonal boron nitride

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Abstract. A truncated crystal approach is applied to the hexagonal boron nitride structure and electronic properties such as work function, different band widths, energy of band-toband transition and cohesion energy are studied and compared with tight binding, OPW methods and experimental optical and thermochemical data. It is demonstrated that whenever the relation between one-electron energy levels of a finite molecular cluster and energy states at the Brillouin zone of the crystal are established, good results can be obtained.

Properties that are not amenable to calculation by simple band theories, like energy of Frenkel pair formation, point defect states and dependence on interatomic distance of various energy states, are computed by the same method and discussed with reference to experiment.

1. Introduction

The fact that large molecules became amenable to quantum mechanical calculations with the aid of fast and large computers has recently stimulated interest in molecular type calculations of solid state properties. This approach, characterized by solving the LCAO problem for a finite zone of the crystal (usually 20-40 atoms) treated as a supermolecule, has proved to be useful in accounting for a variety of electronic properties (Baetzold 1971, Bennett et al 1967, Gornostansky 1971, Larkins 1971, Messmer et al 1971, Moore and Carlson 1965 and Zunger 1972). While conventional tight binding methods that have been applied to hexagonal layered solids employing fixed free-atom potentials (Doni et al 1969, Bassani and Parravicini 1967, Taylor and Coulson 1952) do not properly account for the effects of charge redistribution between the interacting atoms in the unit cell, the molecular approach makes it possible to account for the variation of atomic potentials due to the crystalline environment via selfconsistent calculations (Zunger 1972). Due to this feature, interatomic distance dependence of electronic properties, such as gaps, bandwidths and work functions, are amenable to calculation. Thus one can discuss stability of structures, equilibrium distances, ionicity and density dependence of different bands within the scope of the molecular approach. Another advantage of this method lies in its ability to treat localized defect states on the same basis as crystal eigenstates, thereby providing a correlative scheme between band theory and defect molecule description (Larkins 1971, Hayns 1972).

The difficulties encountered with the truncated crystal method involve the general

nonmonotonic character of various electronic properties such as instability of work function (Baetzold 1971) band gap (Baetzold 1971, Larkins 1972) valence band width (Larkins 1972) and bond energy (Gornostansky 1971), as a function of cluster size, and the nonphysical effect of the boundary conditions employed for finite clusters on properties such as band gap and valence band width (Larkins 1972), energy of vacancy formation (Moore and Carlson 1965) and charges (Messmer and Watkins 1971, Bennett *et al* 1971, Moore and Carlson 1971).

In paper I we treat the heteropolar case of hexagonal boron nitride investigating effects of charge redistribution, cluster size and boundary conditions on various electronic properties. In paper II we propose a different molecular calculation of electronic properties of layered crystals based on the representation of energy states in the crystalline Brillouin zone by one-electron energies of small periodic molecular clusters capable of treating the above mentioned problems.

2. Simple π electron truncated crystal calculations

Since the optical data on hexagonal crystals are mainly related to the π bands, some simple considerations concerning these states are presented before proceeding with all valence electron truncated crystal calculations.

It seems that the effect of cluster size on various electronic properties of layered hexagonal compounds can be best intuitively viewed by applying the semiempirical LCAO method to the π electrons of two dimensional structures. We chose the geometry of the cluster as shown in figure 1, after Bradburn *et al* (1948), where there are *m*, *n*



Figure 1. Two dimensional array of boron nitride-like molecules employed for open cluster calculations.

hexagons in the direction of the two hexagonal axes, respectively. The cluster wave function is constructed as a linear combination of atomic $2p_z$ orbitals of atoms A and B, $\phi_{rs}^{A}, \phi_{rs}^{B}$ respectively, of the unit cell

$$\Psi = \sum_{r=1}^{2m} \sum_{s=1}^{2n+1} C_{rs} \phi_{rs}^{(\mathbf{A}, \mathbf{B})}$$
(1)

where r, s label the atoms in the two dimensional array as shown in figure 1. Defining matrix elements of the one-electron hamiltonian as done by Roothaan and Mulliken (1948) in molecular calculations gives

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$$\begin{aligned} \alpha_{\rm A} &= \langle \phi_{rs}^{\rm A} | h | \phi_{rs}^{\rm A} \rangle & \alpha_{\rm B} &= \langle \phi_{rs}^{\rm B} | h | \phi_{rs}^{\rm B} \rangle & \beta &= \langle \phi_{rs}^{\rm A} | h | \phi_{r,s+1}^{\rm B} \rangle \\ \delta &= \frac{1}{2} (\alpha_{\rm A} - \alpha_{\rm B}) & E_0 &= \frac{1}{2} (\alpha_{\rm A} + \alpha_{\rm B}) & S &= \langle \phi_{cs}^{\rm A} | \phi_{\gamma,s+1}^{\rm A} \rangle \\ \gamma &= E_0 - \beta S & d &= \frac{\delta}{\gamma}. \end{aligned}$$

$$(2)$$

The secular equations of an m by n cluster in the nearest-neighbour approximation yields a determinantal equation that can be solved (Rutherford 1972) to yield the energy eigenvalues

$$E_{i}(m,n) = E_{0} + \frac{-\gamma S g_{i}^{2}(m,n) \pm \gamma \{ d^{2} [1 - g_{i}^{2}(m,n)S^{2}] + g_{i}^{2}(m,n) \}^{1/2}}{1 - g_{i}^{2}(m,n)S^{2}}$$
(3)

where $g_i^2(m, n)$ is a discrete function, bounded between 0 and 9 and given by:

$$g_i^2(m,n) = 1 \qquad m \text{ times}$$

= 1 + Z_k^2 + 2Z_k cos $\phi_k \qquad 2mn \text{ times} \qquad (4)$

where

$$i = 1, 2 \dots m(2n + 1) = N/2$$

and

$$Z_k = 2\cos \frac{k\pi}{2(n+1)}$$
 $k = 1, 2...n$

where ϕ_k is the solution of the trigonometric equation

$$Z_k \sin\left(2m+1\right)\phi_k + \sin 2m\phi_k = 0 \tag{5}$$

and N is the number of atoms in the cluster. We define the one electron band gap as the difference between the highest occupied and lowest vacant molecular orbitals, the π bandwidth as the difference between highest and lowest occupied molecular orbitals of π symmetry, the binding energy per atom (BE) as $2\sum_{i=1}^{N/2} E_i(m, n)/N - E_0$, and the cluster ionization potential as the energy of the highest occupied molecular orbital. For infinite layers $(m, n \to \infty)$, the band gap becomes

$$\Delta = 2\delta \tag{6}$$

(in the homopolar case $\delta = 0$, so $\Delta = 0$).

It is possible to obtain the function $g_i^2(m, n)$ for every desired m, n by solving equations (3), (4) and (5) numerically. The results of Roothaan and Mulliken (1948) on the borazine molecule ($B_3N_3H_6$) were obtained for m = n = 1, where $g^2(1, 1) = 1, 1, 4$, and the results of the π electron calculation on aromatic homonuclear (d = 0) hydrocarbons (Coulson *et al* 1965), such as perylene (m = n = 2), anthracene (m = 1, n = 3) etc were also obtained as particular cases. Figure 2 shows the variation of the band gap, band width, binding energy per atom and ionization potential as a function of the m = n cluster of graphite and boron nitride-like molecules.

Some remarks on these simple considerations follow.

(i) Band gap, work function and π bandwidth are nonmonotonic functions of cluster size. The convergence towards infinite layer values is governed by the heteropolarity parameter d, in the way that a larger d favours faster convergence. Thus, the convergence for the homopolar case of graphite is slow, while small clusters (m = n = 2, 3) of boron nitride already simulate these properties of the infinite layer within 10% or less. It is

also noted that the convergence of symmetrical clusters (m = n) is usually better than for nonsymmetrical ones. There is no finite and small cluster that exactly simulates some of the above mentioned properties of an infinite layer. It seems therefore that the cluster of 32 carbon atoms arranged hexagonally, chosen by Bennett *et al* (1967) to investigate work function changes during chemisorption on graphite, is perhaps too small for this purpose.

(ii) The binding energy of π electrons per atom is a monotonic function of cluster size (Bradburn *et al* 1948); the variation of this property with cluster size is smooth. Thus, clusters of at least m = n = 2 or 3, including the σ electron effects, could serve to calculate bulk cohesive energy reasonably. The results of Bennett *et al* (1967) for all valence electron calculations for a 32 carbon atom cohesive energy are indeed in reasonable agreement with experimental data on graphite.

(iii) The work functions of an infinite layer (α_c for graphite and α_N for boron nitride) are greatly overestimated if the α take their free atom values: the valence state ionization potential of 2P electrons in carbon, as given by Skinner and Pritchard (1953), is 11·2 eV while the experimental work function of graphite (Fomenko 1966) is 4·3 eV. This suggests that computation methods that do not take into account the σ core effect on π states (Taylor and Coulson 1952) together with the effect of selfconsistent charge redistribution in the cluster, are not adequate for predicting this property (Bassani and Parravicini 1967, Doni and Parravicini 1969, Taylor and Coulson 1952, Coulson and Taylor 1952).

(iv) A correlative scheme between one-electron energies of finite molecular clusters and energies in the Brillouin zone of the infinite crystal can easily be obtained within the π approximation by applying the tight binding method for a layered D_{3h} and D_{6h} structures (Coulson and Taylor 1952). The lattice containing two atoms per unit cell is treated by assuming one 2p_z atomic function per site. A normalized crystal state is formed by linear combinations of these auxiliary functions, and the 2 × 2 secular determinant is solved in the nearest-neighbour approximation to yield the dispersion relation, in terms of the matrix elements, of the one-electron effective hamiltonian γ , E_0 , d already defined in equation (2):

$$E_{k_1k_2} = E_0 + \frac{-\gamma S Z_{k_1k_2} \pm \gamma \left| d^2 (1 - Z_{k_1k_2}^2 S^2) + Z_{k_1k_2}^2 \right|^{1/2}}{1 - Z_{k_1k_2}^2 S^2}$$
(7)

where

$$Z_{k_1k_2}^2 = 3 + 2\cos k_1 a + 2\cos k_2 b + 2\cos (k_1 a - k_2 b)$$
(8)

and a and b are the primitive lattice vectors. For the infinite lattice, $Z_{k_1k_2}^2$ ranges continuously between 0 and 9, the points $Z_{k_1k_2}^2 = 0$ and $Z_{k_1k_2}^2 = 9$ being the edge and bottom of the occupied band, respectively, while $Z_{k_1k_2}^2 = 1$ is the Q saddle point which exhibits a Van Hove singularity of the density of states (Doni and Parravicini 1969). Expression (7) is formally analogous to expression (3) for finite two-dimensional clusters, except for the different definition of $g_i^2(m, n)$ and $Z_{k_1k_2}^2$ in equations (4) and (8). Thus within the π approximation, the use of the new quantum numbers Z and g correlates each molecular energy level of the configurations in figure 1 with a crystal state.

This correlative scheme could be simply demonstrated in the case of the $\pi\pi^*$ bandto-band transition in graphite and hexagonal boron nitride, occurring at the peak of the joint density of states (the Q saddle point in the Brillouin zone), which is represented in the above description as a Z = 1 to Z = -1 transition. Since *every* finite molecular cluster of the kind shown in figure 1 possesses energy levels corresponding to $g^2 = 1$ (equation 4), it is possible to calculate the crystal transition energy from small molecular cluster calculations, provided the cluster is large enough so that the values of γ and dhave converged. Indeed the lowest transition in the benzene and borazine clusters (m = n = 1) corresponding to a g = 1 to g = -1 excitation were measured to occur at 4.9 eV in benzene and 6.5 eV in borazine (Roothaan and Mulliken 1948) while the experimental band-to-band transition energies for graphite and boron nitride are close to these values, being 4.8 eV (Greenaway *et al* 1969) and 6.5 \pm 0.3 eV (Vilanov 1971, Choyke 1969 unpublished data; see Doni and Parravicini 1969) for graphite and boron nitride respectively.

Since every molecular cluster contains the state $g^2 = 1$, calculations of the π transition energies of different clusters with increasing number of atoms by full $\sigma + \pi$ quantum chemical methods could be useful in estimating the convergence of γ and d.

3. Semi-empirical computation methods

We employed three different all valence electron, semi-empirical LCAO methods: the extended Huckel (EXH, Hoffman 1963), the iterative extended Huckel (IEXH, Rein et al 1969) and the intermediate neglect of differential overlap (INDO, Pople and Beveridge 1970). These methods have been extensively compared with each other (Andre et al 1971, Pullman 1970) and their derivation from the ab initio Hartree-Fock scheme discussed (Blyholder and Coulson 1968, Pople and Beveridge 1970). In order to get a feeling for the sensitivity of these methods towards different electronic properties, computations were carried out on the borazine molecule $(B_3N_3H_6)$, which closely resembles the unit of hexagonal boron nitride structure, and compared with some experimental results and *ab initio* calculations. The parameters for the EXH calculation were the original ones suggested by Hoffman (1964) taken from atomic spectra, those for IEXH were taken from the work of Cusachs and Reynolds (1965), and the INDO parameters were those suggested originally by Pople et al (1970). The geometry of the molecule was that of the crystallographically determined D_{3h} structure (Harshbarger et al 1969). The nonempirical LCAO-MO-SCF computations existing in the literature involve different choices of gaussian basis functions and include 114 functions in the work of Armstrong and Clark (1970), and 180 gaussian lobe functions in Peyerimhoff and Buenker's (1970) work. The results are summarized in table 1.

All three semi-empirical methods yield a σ type orbital as highest occupied one-electron energy, while the highest π orbital lies 0.46 eV, 0.87 eV or 0.64 eV lower as calculated by the EXH, IEXH and INDO methods, respectively. The order of these two levels as calculated by *ab initio* methods is reversed and the difference in the two energies is similar to that obtained in the semi-empirical calculations. This feature was also noted in the work of Kuznesof and Shriver (1960). Experimental photoelectron spectra seem to support on the other hand the assignment of π ionization potential (Bock and Fuss 1971).

The one-electron energies of the other high occupied states as calculated by EXH and IEXH reproduce the *ab initio* results fairly well, while INDO results are seen to be worse for more bound states. The SCF *ab initio* methods overestimate the experimental ionization potential by several eV and a similar discrepancy occurs with the semi-empirical methods. This feature is attributed to a lack of correlation energy and is often met in molecular calculation at that level.

The SCF orbital energies obtained from *ab initio* calculations indicate that the highest filled σ mo is less stable than the most bonding π mo by 1.54 eV. Such intermingling effects of σ and π states appear to a similar extent also in the semi-empiricial calculations and indicate that the conventional picture previously used employing a π shell and a σ core is inadequate for describing this system. This overlapping effect has importance in the calculation of the electronic bands in the crystals and suggests that selfconsistent coupling between π and σ bands should be introduced.

The lowest σ orbitals show an increasing proportion of nitrogen character with decreasing orbital energy. The most stable of these, the a'_1 level which is almost a pure 2S orbital, is calculated by *ab initio* methods to have a nitrogen to boron ratio of scf

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Property	EXH	IEXH	INDO	π -SCF ^(a)	LCAO-MO- SCF ^(b)	LCAO-MO- SCF ^(e)	Experiment
Ionization potential (eV)	13·10 (σ)	12·10 (σ)	1 3 ·82 (σ)	13·50 (π)	11.69 (π)	12·70 (π)	10·3 ^(d) 9·77 ^(e)
$E_{e'}(\sigma)$ (eV)	13.10	12.10	13.82		13.10	_	
$E_{e''}(\pi)$ (eV)	13.56	13.27	14.46	13.50	11.69		·
$E_{a''}(\pi)$ (eV)	14.37	15.12	22.19	15.48	14.64		
$Q_{\rm B}^{\pi}$	0.252	0.462	0.515	0.334	_	0.409	$\begin{array}{c} 0.33 \pm 0.13^{(f)} \\ 0.24^{(g)} \\ 0.46^{(h)} \end{array}$
$Q_{\rm N}^{\pi}$	1.747	1.131	1.485	1.666	<u> </u>	1.591	_
π bond moment	0.468	0.462	0.587	0.509			—
$[Q_{\rm HB}/Q_{\rm HN}]^2$	0.41	3.15	1.88			2.2	3·5 ⁽ⁱ⁾

Table 1. Calculated and experimental results for the borazine molecule. Notation of D_{3h} point group

(a) Perkins and Wall (1966)

(b) Peyerimhoff and Buenker (1970)

(c) Armstrong and Clark (1970)

(d) Watanabe and Kubo (1959)

(e) Kuznesof *et al* (1967)

(f) Whitesides et al (1971)

(g) Watanabe et al (1960)

(h) Rector et al (1949)

(i) Giambiagi et al (1966)

coefficients of 5:1. A 4·3:1 ratio is exhibited in the EXH and IEXH calculations. This MO is expected to yield the bottom of the valence band in boron nitride, which is known from experimental density of states measurements (Hamerin *et al* 1970) to be of largenitrogen 2S character.

Charge iterative methods (IEXH, INDO) reproduce atomic charges better than the noniterative EXH method, which is known to overestimate polarity (Hoffman 1964). The partial π charge on boron was estimated experimentally from the nuclear quadrupole coupling constant of Whitesides *et al* (1971) to be 0.33 ± 0.13 e. Rector *et al* (1949) estimated a charge of 0.49 from analyses of borazine and benzene spectra. Analysis of the experimental diamagnetic anisotropy of ring current due to π electrons by the MO model yields a somewhat lower value of 0.24 e (Watanabe *et al* 1960). These values are in rough agreement both with the *ab initio* and the semi-empirical calculations, the IEXH and INDO values being closer to the experimental value than EXH results.

When the C_2 nonplanar conformation of borazine suggested as a possibility by electron diffraction measurements (Harshbarger *et al* 1969) was analyzed, a dipole moment of 0.5 Debye was calculated by IEXH, and 0.9 Debye by INDO as compared with the experimental value of 0.67 D (Ramaswamy 1935) in the gaseous state, and 0.5 D (Watanabe *et al* 1960) in benzene solution. All three semi-empirical methods predict the D_{3h} planar configuration to be more stable by 2–16 kcal/mole than the twisted C_2

configuration. The result of the *ab initio* calculation of Armstrong and Clark (1970) suggests an energy difference of 40.5 kcal/mole in favour of the D_{3h} planar configuration.

IR measurements of the intensity of the BH stretch as compared with the NH stretch indicate a ratio of 3.5:1 (see Gambiagi *et al* 1966). The square of the ratio between charge transferred from boron to its adjacent hydrogen (Q_{BH}) to charge transferred from hydrogen to its adjoint nitrogen (Q_{NH}) is approximately proportional to the ratio of the two IR vibrational stretching intensities, as the intensity is proportional to the dipole change with distance $(\partial \mu / \partial R)^2$ which in turn is proportional to the charge transferred, for small displacements where the variation of the charge with bond distance is small. This was verified in a particular calculation where Q_{BH} and Q_{NH} were calculated for small changes in the corresponding R_{BH} and R_{NH} distances and only small dependence was revealed. It is therefore possible to check the sensitivity of the semi-empirical methods to transfer of charge by computing the IR intensity ratio. The values quoted in table 1 indicate that IEXH and INDO again reproduce such features better than the non-iterative EXH method.

Since none of the semi-empirical methods examined yields both charges and one electron energies satisfactorily, we use EXH and IEXH methods throughout this work for computing energies, while INDO and IEXH are used for charges. Since the INDO method involves explicit electron-electron and nuclear-nuclear interactions, this method is also used for investigating the interatomic distance-dependence of various quantities.

4. Truncated crystal all-valence electron calculation on boron nitride

4.1. One electron energy spectrum

Calculations with the Slater 2s, $2p_x$, $2p_y$, $2p_z$ atomic basis set, retaining all overlaps and interactions, were performed on molecular clusters I–V (figure 3) by extended Huckel and iterative extended Huckel methods. The atomic potentials employed are those mentioned in the previous section. Correction of the diagonal elements for Madelung energy was introduced as suggested by Jorgensen *et al* (1967). The one-electron energy levels were analyzed to yield energy bandwidths and the band gap, and the results are summarized in tables 2 and 3.

Property (eV)	$B_8 N_8 H_{10}$	$B_{10}N_{10}H_{12}$	$B_{12}N_{10}H_{12}$	$B_{12}N_{12}H_{12}$	$B_{14}N_{14}H_{14}$
Band gap	5.599	5.465	5.491	5.493	5.443
π band width	1.490	1.57	1.418	1.589	1.690
p band width	5.30	5.46	5.47	5.13	5.59
2s band width	3.849	4.15	3.985	4.325	4.497
Total band width	17.346	17.54	17.570	17.610	17.821
Work function	12.775	12.67	12.678	12.762	12.598
Transition energy	6.43	6.4	6.3	6.2	6.2
Binding energy	7.40	7.47	7.36	7.20	7.23

Table 2. Calculated energy bands of the molecular clusters I–V by the extended Huckel $_{\mbox{(EXH)}}$ method

The various quantities calculated for the largest cluster approach the values of the preceding clusters within 8%. A similar convergence rate was obtained in the π calculations (figure 2). Long range electrostatic interactions do not change the convergence

Table 3. Calculated energy bands of the molecular clusters I–V by the iterative extended Hückel (IEXH) method

Property (eV)	$B_8N_8H_{10}$	$B_{10}N_{10}H_{10}$	$B_{12}N_{10}H_{12}$	$B_{12}N_{12}H_{12}$	$B_{14}N_{14}H_{14}$
band gap	2.90	2.87	2.939	3.00	2.95
π band width	3.36	3.41	3.472	3.2	3.31
p band width	5.58	5.86	5.95	5.70	5.81
2s band width	4.94	4.29	4.40	4.40	4.42
total band width	16.91	17.26	17.33	17.40	17.53
work function	11.71	11.61	11.52	11.6	11.49
transition energy	5.6	5.7	5.8	6.0	5.96
binding energy	7.9	7·9	7.8	8.0	8.05



Figure 2. Dependence of ionization potential θ , π band bap Δ , binding energy BE and π band width W on the dimension N of the open two-dimensional cluster. The number of atoms in each cluster is 2N. Calculation performed by the EXH method on π bands. (a) Boron nitride-like clusters. (b) Graphite-like clusters.



Figure 3. Boron nitride-like molecular clusters calculated: I $B_8N_8H_{10}$; II $B_{10}N_{10}H_{12}$; III $B_{10}N_{12}H_{12}$; IV $B_{12}N_{12}H_{12}$; V $B_{14}N_{14}H_{14}$.

picture significantly due to the relatively small net atomic charges and symmetric arrangement of charges around each central atom (Kimel 1964).

The effects of one-electron energy states introduced by IEXH, as compared with EXH results, are narrowing of gaps, lowering of work function and broadening of valence sub-bands, the overall bandwidth changing only slightly. Experimental and theoretical calculations on the boron nitride crystal are summarized in table 4.

Property	Experiment	Method	Theoretical	Method
band gap (eV)	5.4	reflectivity ^(a)	4.6	π tight binding ^(e)
	5.83	absorption ^(b)	5.4	$\pi + \sigma$ tight binding ^(f)
	3.6	x-ray emission ^(c)	3.6	OPW ^(g)
			5.44	EXH
	3.9	absorption ^(d)	2.95	IEXH
valence band width (eV)			13.6	$\pi + \sigma$ tight binding ^(f)
			27.8	OPW ^(g)
	18.6	x-ray emission ^(c)	17.8	EXH
			17.5	IEXH
2s band minimum (eV)	$E_0 \pm 19.4$	ESCA ^(h)	$E_0 + 16.2$	$\pi + \sigma$ tight binding ^(f)
	·		$E_{0} + 18.4$	EXH
			$E_0 + 18.8$	IEXH
band-to-band	6.5	dielectric constant(i)	6.6	$\pi + \sigma$ tight binding ^{((f)}
transition energy (eV)	6.2	dielectric constant ^(j)	6.2	ЕХН
			5.96	IEXH
work function (eV)			11.8	$\pi + \sigma$ tight binding ^(f)
. ,			6.4	OPW ^(g)
			12.60	EXH
			11.50	IEXH
binding energy (eV)	6.6	thermochemistry	7.23	EXH
		•	8.0	IEXH
$R_{\rm eq}(\rm{\AA})$	1.446	crystallography ⁽⁽¹⁾	1.48	EXH
rd			1.50	IEXH

Table 4. Experimental and theoretical values for boron nitride

^(a) Larach and Shrader (1956)

^(b) Baronian (1972)

^(c) Formichev (1971)

^(d) Rand and Roberts (1968)

(e) Taylor and Coulson (1952)

(f) Doni and Parravicini (1969)

(g) Nakhmanson and Smirnov (1972)

^(h) Hamrin et al (1970)

⁽ⁱ⁾ Vilanov (1971)

(i) W J Choyke (1969 unpublished data; see (f))

^(k) Janaf International Thermochemical Tables (1965)

⁽¹⁾ Pease (1952)

The effects of iteration towards charge selfconsistency (Zunger 1972) in the IEXH method are demonstrated in table 5. The charge selfconsistent distribution is shown to decrease the gap between allowed and forbidden bands, to decrease the work function and to increase the occupied sub-bandwidth, a trend observed also in passing from free atom tight binding calculation (Doni *et al* 1969) to OPW (Nakhmanson and Smirnov 1972).

When advancing from the borazine molecule (table 1) to larger clusters, the band gap and ionization potential decrease. Such a trend is also observed in the experimental results on conductivity threshold and optical excitation data of carbon aromatic molecules, as the size of the molecule increases.

The lowest occupied sub-band is mainly of nitrogen 2s character and its variation with cluster size and small interatomic distance changes is small, thus behaving as a core

state. Its lowest energy point (Γ point in the Brillouin zone) is referred to in tables 2 and 3 as the 2s band minimum. The π sub-band is narrow compared with the value of 4.94 eV in similar calculations on graphite clusters by the EXH method, and 5.3 eV in IEXH calculations. The overall occupied bandwidth is smaller than the experimental value both in tight binding and in truncated crystal EXH and IEXH calculations[†].

Table 5. Comparison between iterated and uniterated results for a $B_{12}N_{12}H_{12}$ cluster, by the IEXH method. Iterations are terminated when the difference between successive iterations is less than 0.01

Property	Uniterated	Iterated
band gap (eV)	5.94	3.00
π band width (eV)	1.85	3.2
p band width (eV)	5.22	5.70
2s band width (eV)	4.47	4.40
total band width (eV)	16.97	17.40
work function (eV)	12.9	11.61
boron π charge (e)	0.11	0.513
nitrogen π charge (e)	1.59	0.906
boron σ charge (e)	0.585	1.19
nitrogen σ charge (e)	4.21	2.98

Contrary to the conventional nonselfconsistent tight binding results, the highest occupied state both in EXH and in IEXH calculations is of σ character, the highest occupied π state lying some 0.4–0.5 eV below, while on graphite clusters the highest occupied state turns out to be a π state by both methods.

Cluster models with a finite number of atoms do not yield a continuous density of state function and only a histogram description is possible. This sampling procedure shows that the energy difference between states of maximum density in the π^* and π bands corresponding to $g^2 = 1$ is 6.2 eV in EXH and 5.96 eV in IEXH respectively, for the largest clusters, as compared with the values of 6.5 eV obtained experimentally for the $\pi \to \pi^*$ transition at the Q₂ point in the Brillouin zone by Vilanov (1971) and 6.2 eV by Choyke (1969 unpublished data; see Doni and Parravicini 1969). The good convergence of this property with cluster size (borazine already yields a value of 5.9 eV in the IEXH method), as found in our calculations suggests that for the two largest clusters considered the atomic parameters are only slightly changed (see also § 4.3).

Variation of interatom distances, for the symmetric cluster $B_{12}N_{12}H_{12}(D_{3h})$, reveals a minimum of total energy at 1.48 Å for EXH method, 1.50 Å for IEXH, as compared with 1.446 Å obtained experimentally (Pease 1952). Since the tight binding methods mentioned here employ fixed free atom potentials and scaling parameters, whose dependence on interatomic distance in the crystal is unknown, it is not possible to calculate this property within these schemes for comparison.

The binding energy per atom converges smoothly with cluster size, reaching the value of 7.23 eV in the EXH calculation, and 8.0 eV in IEXH calculation, as compared with the thermochemical value of 6.6 eV (*Janaf International Thermochemical Tables* 1965).

 $[\]dagger$ Similar large discrepancies are exhibited in empirical tight binding (Bassani and Parravicini 1967) as well as in *ab initio* calculations (Corbato 1959) on the occupied bandwidth in graphite, the former method giving a value of 13.8 eV and the latter 18.5 eV, as compared with the recent experimental value (Thomas *et al* 1971) of 30 eV. This experimental value is however an upper bound.

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The work function was probably overestimated, both in previous tight binding calculations (Doni and Parravicini 1969) and in the present molecular calculation, because of the absence of explicit correlation effects. A decrease in the work function is observed due to charge iteration in the IEXH method, lowering it from the uniterated value of 12.9 eV to the iterated value of 11.6 eV. This incomplete suppression of molecular ionization energy in the crystal is observed also in homonuclear crystals, as graphite, (the experimentally determined ionization potential of benzene is 9.6 ± 0.2 eV (Loughran *et al* 1960), of graphite 4.3 eV (Fomenko 1966) while the tight binding calculated value (Bassani and Parravicini 1967) for graphite is 8.95 eV), indicating that the mechanism of charge redistribution is probably less important than explicit correlation effects.

The effect of the boundary conditions employed was checked by eliminating the hydrogen atoms surrounding the cluster. An increase of 0.8-1.2 eV in the band gap is observed. Optimizing the Slater orbital exponents, as suggested by Larkins (1971), reduces the gap: a 20% reduction of the 2p orbital exponent reduces the gap back to 4.9 eV in the EXH calculation and to 2.38 eV in the IEXH calculation, for the largest cluster. It is therefore in principle possible to obtain better agreement with experiment by such procedures. However, it is felt that such details must not be pressed too closely, for these improvements are beyond the underlying approximations in the quantum chemical methods employed. A different approach to molecular calculations presented in paper II avoids the problem of such boundary effects entirely by introducing periodic boundary conditions.

4.2. Charges

Charges for the internal atoms, as calculated from population analysis of the wave functions in several molecular clusters by IEXH and INDO methods, are summarized in table 6. The variation of the calculated charges between different clusters is in both methods with 5%, the INDO method yielding consistently higher charges than the IEXH method.

Charge	B ₈ N ₈ H ₁₀ I€XH	$B_{10}N_{10}H_{12}$ Iexh	$\begin{array}{c} B_{12}N_{10}H_{12}\\ IEXH \end{array}$	$\begin{array}{c} B_{12}N_{12}H_{12}\\ IEXH \end{array}$	$B_8N_8H_{10}$ indo	B ₁₂ N ₁₂ H ₁₂ INDO
$Q_{\rm B}^{\pi}$	0.527	0.522	0.518	0.513	0.572	0.550
$\tilde{Q}_{\rm N}^{\pi}$	0.928	0.918	0.907	0.906	1.430	1.400
$\tilde{Q}_{\rm B}^{\sigma}$	1.188	1.188	1.189	1.191	2.141	2.140
\tilde{Q}_{N}^{σ}	3.060	3.071	3.087	2.983	3.82	3.710
$Q_{\rm B}^{\rm net}$	0.309	0.313	0.318	0.319	0.293	0.299
$\tilde{Q}_{\rm N}^{\rm net}$	-0.181	-0.188	-0.179	-0.193	-0.254	-0.260

Table 6. Calculated π charges (Q^{π}) , σ charges (Q^{σ}) and net charges (Q^{net}) for the central atoms of various molecular clusters by IEXH and INDO methods

It is evident from inspection that the nitrogen π charge is transferred from nitrogen to boron atoms when the molecular cluster is compared with the free atom, while the σ boron charge is transferred to nitrogen, making the latter finally more negative, in accord with the notion that nitrogen is more electronegative. Similar calculations on homonuclear graphitic clusters performed by us indicate that only little charge exchanged between the π and σ frame of the atoms involved in these clusters which is consistent with σ 'rigid core' picture in carbon chemistry. This B⁺N⁻ picture contradicts the conventional B⁻N⁺ structure involved in boron-nitrogen chemistry (see for instance many articles in Boron Nitrogen Chemistry 1964) the latter notion being mainly based on considerations involving only the π frame. These results are in line with Hoffman's suggestion (Hoffman 1964). The large effect manifested by the σ frame on the charge suggests that π electron calculations involving a 'rigid σ core', for such heteronuclear systems with nonzero atomic net charges are unreliable. This conclusion is in line with the fact that there is a significant overlap between σ and π bands.

LCAO cluster model calculations make it possible to describe not only formal point charges, but also charge density functions, by standard techniques. Equivalently, the classical potential generated by this charge could also describe the bonding in the crystal, yielding a more sensitive picture (Bonaccorsi 1970). Figure 4 describes the



Figure 4. Potential generated by the electron plus nuclear charge density along the BN bond, as obtained by solution of the Poisson equation for INDO density.

potential function along the central B–N bond as obtained by numerical solution of the Poisson equation[†] for the charge density obtained from an INDO calculation of a cluster. It is interesting to note that the electronegativity scale defined here by the classical Poisson potential agrees with the Pauling scale, namely the ratio $V_{\rm N}/V_{\rm B} = 1.5$ between the peak potentials of nitrogen and boron is equal to the Pauling electronegativity ratio between the respective atoms $I_{\rm N}/I_{\rm B} = 3.0/2.0 = 1.5$.

The charges of the internal atoms in a $B_{12}N_{12}H_{12}$ cluster were computed as a function of R_{BN} distance by repeating the calculations for R_{BN} between 14Å and 1.8Å. The boron σ charge was observed to increase at the expense of the nitrogen σ charge as the distance between atoms increases, while the boron π charge increases from 0.537 e at $R_{BN} = 1.40$ Å to 0.542 e at $R_{BN} = 1.54$ Å, and then decreases at the expense of the nitrogen π charge, up to its zero free-atom value. Since the boron π charge could be taken as a measure of benzene-like double-bond character ($Q_B^{\pi} = 1$ corresponds to 100% benzene-like double-bond character at $R_{BN} = 1.40$ Å to 54.2% double-bond character at $R_{BN} = 1.40$ Å to 54.2% double-bond character at $R_{BN} = 1.40$ Å to 54.2% double-bond character at $R_{BN} = 1.54$ Å. This result is less than the order of magnitude speculated by Pauling (1966) (11% increases in double-bond character followed by a decrease of 0.03Å in the bond length) to explain the large compressibility of boron

[†] The computer program for this calculation was kindly provided by Mr S Serbernik, Technion, Israel

nitride in its basal plane. The boron π charge at the equilibrium nuclear configuration, for this molecular cluster, is 0.513e for the IEXH calculation and 0.550e for the INDO calculation, as compared with the experimental value of 0.45e obtained in nuclear quadrupole resonance of boron nitride (Silver and Bray 1960).

As indicated in the simple π electron treatment of § 2, the highest occupied and lowest vacant π states of the two-dimensional infinite boron nitride crystal, corresponding to $g^2 = 0$, are pure nitrogen and boron states, respectively. This result remains unchanged even if more than nearest neighbours are included, except for changing the corresponding energies. (The irreducible representation of the two dimensional group D_{3h} of the P point in the Brillouin zone does not mix nitrogen and boron $2p_z$ states belonging to different Bloch states.) In finite molecular clusters, where the smallest g^2 value is close but not equal to 0, the states are not pure any longer. The effect of this contamination of the highest filled π molecular orbital (HF π MO) and lowest empty π molecular orbital (LE π MO) on the corresponding energies was calculated by applying population analysis to the corresponding π states of clusters I–V (figure 3). Figure 5 demonstrates this



Figure 5. One-electron energy of highest filled π molecular orbital (HF π MO) and lowest empty π molecular orbital (LE π MO) as a function of nitrogen and boron character, respectively.

behaviour, as calculated by the IEXH method. Since there is a nonzero electronegativity difference between the atoms in the unit cell, the simple picture of dividing the bond charge into two equal parts in invalid. Instead a different procedure which involves one and two centre contributions to the moment and leaves the projection of the centroid of charge on the line connecting the atoms unchanged is employed (Rein *et al* 1969). The crystal limit of zero contamination of the P_2^- and P_1^- states is approached by most of the clusters (I, II, \dot{V}) within 2%, suggesting they present reasonable models for simulating the $\pi\pi^*$ band gap in the infinite crystal. For more refined calculations on the magnitude of the gap, CI treatment should be applied.

It is evident that the lowest $\pi\pi^*$ electronic transition is an internal charge transfer transition similar to that observed in molecules (Nagukura *et al* 1954), carrying the system from an initial state where the charge is on nitrogen atoms, to a final state where

most of the charge is concentrated on boron atoms. The energy of this transition decreases as the purity of the HF π MO and LE π MO increases, the boron state (LE π MO) being the more sensitive to charge contamination. Such internal charge-transfer transitions, polarized in the molecular 0001 plane, are dipole-allowed optical transitions, and should be observed in the UV spectrum of boron nitride.

It was suggested previously that two-dimensional truncated crystal methods should be applied to the study of work function changes during chemisorption of various atoms on hexagonal structures (Bennett *et al* 1967, 1971). The analysis given above indicates that one should choose a cluster with the lowest g^2 value possible, as a model for a finite substrate in order to ensure a low contamination of the work function. Such clusters are not necessarily the largest ones. A $B_{10}N_{10}H_{12}$ perylene-like cluster, for instance, simulates the character of the highest filled molecular orbital of an infinite layer better than the $B_{12}N_{10}H_{12}$ structure does, the former having 98.9% nitrogen π character, and the latter only 93.7% nitrogen character. This is due to the fact that the former clusters contain one-electron energy levels with their g^2 value closer to the value of 0 near the Brillouin zone corner than the latter.

4.3. Molecular band structure calculation

Since the crystalline environment introduces inductive effects of charge rearrangement on the atomic quantities, a simple tight binding treatment based on free atom quantities is inadequate in the heteropolar case of boron nitride. An alternative approach to the simple molecular cluster calculation of electronic structure is to construct a tight binding solution from quantities that have been calculated selfconsistently in molecular clusters. This will be illustrated here on the π bands.

If $|\mu\rangle$ and $|\lambda\rangle$ are Bloch functions constructed from atomic $2p_z$ orbitals centred on the two nonequivalent sites of the two-dimensional unit cell and are given by:

$$|\lambda_{k}\rangle = \sum_{p} \exp\left(i\boldsymbol{k} \cdot \boldsymbol{R}_{p}\right)|\chi^{\lambda}(\boldsymbol{r} - \boldsymbol{R}_{p})\rangle$$

$$|\mu_{k}\rangle = \sum_{q} \exp\left(i\boldsymbol{k} \cdot \boldsymbol{R}_{q}|\chi^{\mu}(\boldsymbol{r} - \boldsymbol{R}_{q})\rangle$$
(9)

the tight binding equations for this band in the infinite solid are given by

$$\sum \left[F_{\mu\lambda}(k) - S_{\mu\lambda}(k)\epsilon_i(k) \right] C_{i\lambda}(k) = 0$$
⁽¹⁰⁾

where $F_{\mu\lambda}(k)$ is the matrix element of the effective one-electron operator between two Bloch states

$$F_{\mu\lambda}(k) = \sum_{l} \exp\left(i\boldsymbol{k} \cdot \boldsymbol{R}_{l}\right) \langle \chi_{\mu}(\boldsymbol{r}) | V | \chi_{r}(\boldsymbol{r} - \boldsymbol{R}_{l}) \rangle$$
(11)

and $S_{\mu\lambda}$ are overlap integrals between Bloch states. The matrix elements of equation (11) are calculated selfconsistently for π states by the IEXH method for different clusters, including the effects of π and σ states. The integrals of first order, $\gamma_{BN}^{(1)}$ and of second order $\gamma_{BB}^{(2)}$ and $\gamma_{NN}^{(2)}$ given by:

$$\gamma_{\rm BN}^{(1)} = \langle \chi_{\rm B}(\mathbf{r}) | V | \chi_{\rm N}(\mathbf{r} - \mathbf{R}_l) \rangle - E_0 \langle \chi_{\rm B}(\mathbf{r}) | \chi_{\rm N}(\mathbf{r} - \mathbf{R}_l) \rangle$$

$$\gamma_{\rm BB}^{(2)} = \langle \chi_{\rm B}(\mathbf{r}) | V | \chi_{\rm B}(\mathbf{r} - 2\mathbf{R}_l) \rangle - E_0 \langle \chi_{\rm B}(\mathbf{r}) | \chi_{\rm B}(\mathbf{r} - 2\mathbf{R}_l) \rangle$$

$$\gamma_{\rm NN}^{(2)} = \langle \chi_{\rm N}(\mathbf{r}) | V | \chi_{\rm N}(\mathbf{r} - 2\mathbf{R}_l) \rangle - E_0 \langle \chi_{\rm N}(\mathbf{r}) | \chi_{\rm N}(\mathbf{r} - 2\mathbf{R}_l) \rangle$$
(12)

converge reasonably with cluster size. $\gamma_{BN}^{(1)}$ ranges from -2.02 eV for borazine, to -1.95

for $B_{10}N_{10}H_{12}$ to -1.94 eV for both $B_{12}N_{12}H_{12}$ and $B_{14}N_{14}H_{14}$. $\gamma_{BB}^{(2)}$ and $\gamma_{NN}^{(2)}$ similarly converge to the values -0.836 eV and -0.104 eV, respectively, with the results for $B_{12}N_{12}H_{12}$ and $B_{14}N_{14}H_{14}$ clusters being already close.

It is plausible that the values of $-\gamma_{BN}^{(1)}$ employed by Roothaan and Mulliken (1948) to explain the optical spectrum of borazine, (2·3 eV-1·8 eV) are close to our calculated values, and that the latter reproduce binding energies as well as the one-electron spectrum reasonably, whereas noniterative LCAO methods fail to do so (Phillips 1970).

Equations (10) are solved with the above calculated matrix elements and overlap integrals calculated from Slater orbitals. Figure 5 shows the π band structure for iterated and noniterated molecular quantities. The band structure is generally similar to that obtained by scaled tight binding (Doni and Parravicini 1969) and by OPW (Nakhmanson and Smirnov 1972) methods. The π transition energy at the Q₂ point is 6.0 eV as compared with the experimental values of 6.2 eV (Choyke 1969 unpublished data; see Doni and Parravicini 1969) or 6.5 eV (Vilanov 1971).

It is evident that charge selfconsistent redistribution markedly affects the structure at the edges of the Brillouin zone, while the effect on the Γ point is smaller. The uniterated results resemble those of the free atom calculations of Doni and Parravicini (1969). The band gar, π bandwidth and ionization potential in their work were 5.4 eV, 1.2 eV and 11.8 eV, respectively, and 5.94 eV and 1.85 eV and 12.9 eV respectively, in the uniterated calculation.

As expected from the simple π calculation of §2, the results for band structure of the infinite solid, and the results for the largest planar heteropolar molecular clusters (table 3, last column) are similar. This again demonstrates the fact that for finite heteropolar hexagonal systems the approach to the properties of an infinite solid is governed by the heteropolar d term (equation 3) rather than the symmetry term g^2 , which justifies truncated crystal calculations on such systems.

4.4. Distance dependence

Since the character of the HF π MO of the employed molecular clusters is shown to simulate reasonably the character of the P_1^- level of the infinite cluster (figure 4), it is interesting to note its behaviour under compression. Interatomic distance dependence of the π work function and the $\pi\pi^*$ gap is calculated by repeating the molecular calculation for different R_{BN} distances for the D_{3h} structure $B_{12}N_{12}H_{12}$ (98.1% nitrogen character of the HF π MO and 96.6% boron character in LE π MO). The $\pi\pi^*$ gap decreases as $R_{BN}^{-0.80}$ in the EXH calculation, as $R_{BN}^{-1.8}$ in IEXH calculations, and as $R_{BN}^{-1.60}$ in INDO calculations. When charge selfconsistent methods (IEXH, INDO) are used, a stronger R_{BN} dependence results than in the noniterative EXH method. When only one iteration is allowed in IEXH, a distance dependence of $R_{BN}^{-0.73}$ results. This indicates that charge redistribution is an important mechanism in band gap compression dependence. The π work function changes as $R_{BN}^{0.46}$ in INDO.

When different molecular clusters are considered, the $R_{\rm BN}$ dependence of the gap and work function is stronger, the higher the contamination of the corresponding energy states. Thus, for instance, in the borazine molecule, with approximately 80% π nitrogen character in the HFMO, the gap distance dependence is $R_{\rm BN}^{-2.45}$ in the EXH calculation, $R_{\rm BN}^{-2.55}$ in the IEXH calculation and $R_{\rm BN}^{-2.52}$ in the INDO calculation. This dependence is very similar to the $R^{-2.5}$ dependence in tetrahedral binary crystals (Phillips 1970) for the homopolar gap, where the energy states across the gap are mixed. When the molecular cluster is large enough so that the contamination is low, a weaker $R_{\rm BN}$ dependence is evident (paper II). In tetrahedral binary crystals (such as BN, BP, etc), the distance dependence of the gap (Phillips 1970) is large because, when the direct gap occurs at a Γ point, interaction terms between the two atoms of the unit cell contribute largely to the distance dependence.

4.5. Second layer effect

The effect of a second layer is simulated by one hexagonal $B_3N_3H_6$ structure, 3.4 Å above the basal $B_{12}N_{12}H_{12}$ structure and parallel to it. The effects of this structure compared to the two-dimensional one electron states as calculated by the EXH method are small, increasing the π sub-band width by 2% and the 2s sub-band width by 1%, while the total band width increases by ~1%.

The stability of the three-dimensional structure is checked by rotating the upper hexagon with respect to the lower structure, in a way that boron atoms in the upper hexagon will be exactly above nitrogen atoms in the lower hexagon ($\phi = 0^{\circ}$) or in the middle of the B-N bond ($\phi = 30^{\circ}$), and above boron atoms in the lower structure ($\phi = 60^{\circ}$). The results of this calculation, presented in figure 7, are in agreement with



Figure 6. π band structure of boron nitride. Broken curve, uniterated results: full curve, iterated results.

the crystallographic determination (Pease 1952) of the stability of the $\phi = 0^{\circ}$ structure. When the upper hexagon is translated horizontally with respect to the lower structure to create the graphite-like structure, an increase in total energy of 0.02 eV is evident. This agrees better with the D_{3h} suggested by the Raman results (Geick *et al* 1966) on boron nitride, rather than the graphite-like structure offered as an other possibility by the same experimental results.

4.6. Energy of Frenkel pair formation

Molecular methods were shown to yield reasonable estimates for the energy of Frenkel pair formation in graphite (Moore and Carlson 1965). This property, depending only on the close atomic neighbourhood of the pair involved, is amenable to truncated crystal calculation, while other techniques are difficult.

Since the carbon atom is intermediate in its electronegativity (2.5) between boron (2.0) and nitrogen (3.0), it is interesting to compute the energy of boron and nitrogen Frenkel pair formation as compared with carbon pair formation in graphite. The energy required to remove the nitrogen atom from position 1 (figure 3) to position 2 (3.83 Å apart) or to move a boron atom in position 3 to position 4 (3.83 Å apart), was calculated by extended Huckel methods for several clusters. The results are summarized in table 7.

pair	$B_{12}N_{10}H_{12}$	$B_{12}N_{12}H_{12}$	B ₁₄ N ₁₄ H ₁₄
nitrogen pair in BN		33-31	33.35
boron pair in BN	5.98	5.99	6.03

Table 7. Energy of Frenkel pair formation in boron nitride in eV.

The calculated value for the $C_{24}H_{12}$ graphitic cluster is 25.1 eV while for $C_{28}H_{14}$ it is 25.2 eV. These values can be compared with the calculation of Moore and Carlson (1965) of 25.3 eV employing the Helmholz approximation for off-diagonal elements, and with the experimental displacement threshold (D T Eggen 1956 unpublished; see Henning and Hove 1956) of 25 eV, for graphite. No experimental results are yet available for boron nitride.

The calculated energies depend only slightly on cluster size, as expected for local properties. When the calculation for graphite is repeated for the same interatom distance as in boron nitride (1 446 Å), the energy for pair formation is 19.70 eV, which differs only slightly from the average of boron and nitrogen displacement energies of 19.64 eV, as expected from simple electronegativity arguments.

Since no experimental data exist on the displacement energy threshold in boron nitride, more detailed mappings of various displacement sites seem unjustified at this stage.

4.7. Point defects

The problem of point defects in graphite has been investigated intensively both experimentally and theoretically in the past years, while defect states in binary heteropolar crystals like boron nitride have received only little interest. In recent experimental work, carbon substitutional impurity states (Moore and Singer 1972) and nitrogen vacancy states (Khusidman and Neshpor 1968) were identified in hexagonal boron nitride. These states are claimed to be localized in the vicinity of the defect and exhibit typical ESR and thermoluminescence signals (Katzir *et al* 1972). Truncated crystal methods seem adequate for treating such localized states.

We first treat the carbon impurity state using the EXH approximation. When a carbon atom is substituted in a nitrogen site, three one-electron levels appear in the forbidden gap: two quasidegenerate carbon σ states at -12.0 eV with 40% carbon character, and one π state at -12.14 eV with 65% carbon character. The location of these states is changed only by approximately 1% when the cluster size is increased from $B_{10}N_{10}H_{12}$ to $B_{14}N_{14}H_{14}$. These states have the colouring effect of diminishing the energy difference of the lowest optical transition, a trend observed experimentally by Moore and Singer (1972) on doping boron nitride with carbon. These states could also act as luminescence trapping centres which agrees with the suggestion of Larach and Shrader (1956). The excitation of electrons from the carbon π state to the band is an internal $\pi\pi^*$ charge transfer transition from a mainly carbon state to a predominantly boron state, and should be distinguished spectroscopically from the band-to-band nitrogen to boron $\pi\pi^*$ charge transfer transition of the pure crystal. The more electronegative carbon atom placed in the centre of three boron atoms accumulates negative charge, while the positive net atomic charge of the neighbouring boron atoms decreases a little.

The nitrogen vacancy problem was treated by a molecular model with a central nitrogen atom missing. A localized state appears in the forbidden gap, 1.1 eV below the conduction edge, with its charge divided equally between the three boron atoms near the vacant site. Cluster size variation has only a small effect on this state. When allowance is made for small relaxations around the vacancy, the trapping state is changed by only some tenth of an eV.



Figure 7. Interaction energy of a boron nitride layer with one hexagonal structure parallel to it, as a function of rotation angle.

The ESR spectrum of irradiated boron nitride shows a signal arising from three equidistant boron atoms, and its temperature variation involves a barrier of 1.0 eV (Katzir *et al* 1972). Thermoluminescence measurements indicate a barrier of $1.0 \pm 0.1 \text{ eV}$ for excitation of trapped electrons. These observations are consistent with our model of a nitrogen vacancy.

A more detailed account of the use of molecular methods for point defect states in hexagonal crystals is due to be published.

5. Conclusions

In conclusion, it should be stressed that the semi-empirical methods involved cannot give completely reliable descriptions of both charges and one-electron energy spectra and only semiquantitative information can be obtained with the present semi-empirical quantum chemical methods. If a more detailed picture is required, *ab initio* methods and the introduction of explicit correlation corrections cannot be avoided. Nevertheless, the flexibility of these former methods enables one to get reasonable descriptions of a large variety of crystal properties, where *ab initio* methods are difficult.

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