A molecular calculation of electronic properties of layered crystals. II. Periodic small cluster calculation for graphite and boron nitride

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Abstract. Small (18–32 atoms) periodic clusters of two-dimensional hexagonal graphite and boron nitride are shown to represent some high-symmetry points in the Brillouin zone of the infinite crystal. Semi-empirical all-valence electron calculations are performed on these clusters and the binding energy, work function, bandwidth, band-to-band transition energy, band gap, charges and equilibrium distances are computed and compared with values obtained by tight binding and truncated crystal calculations. Favourable agreement with experimental data is obtained with selfconsistent calculations on these clusters.

1. Introduction

In a previous paper (Zunger 1974, referred to herein as I) we calculated some electronic properties of hexagonal boron nitride by applying LCAO methods to finite molecular clusters of boron and nitrogen atoms arranged hexagonally, by correlating the one-electron energy levels of the molecular cluster to points in the Brillouin zone of the crystal. When hydrogen atoms were used as boundary conditions to satisfy the free valence of the dangling bonds of the planar configuration, favourable results were obtained for some ideal crystal properties such as band gap, bandwidth, cohesion energy, equilibrium interatom distance, energy of the $\pi\pi^*$ band-to-band transition, as well as for properties of point defect states such as nitrogen vacancy and carbon impurity. It was shown that for the heteropolar case of boron nitride, finite planar clusters of 20–30 atoms could represent the limit of a large crystal π band better than in the homopolar case of graphite, where the symmetry of the finite open cluster was important. On the other hand, it was not possible to achieve these results when the hydrogen atoms satisfying the valence of the edge atoms were relaxed.

In this paper we present a different approach to calculation of electronic properties of planar hexagonal structures, based on the correlation between one-electron energies of periodic small clusters of atoms with some high-symmetry states in the Brillouin zone of the infinite crystal. This procedure is applicable to the heteropolar as well as to the homopolar case, and does not involve the use of hydrogen atoms on the boundary.

In §2 we discuss a simple tight binding model for the π bands of periodic clusters with varying number of atoms, and derive a relation between cluster size and the π work

function, bandwidth and energy gap. In § 3 we apply semi-empirical quantum chemical methods (iterative extended Huckel (Rein *et al* 1969), extended Huckel (Hoffman 1963) and INDO (Pople and Beveridge 1970)) to $\sigma + \pi$ electrons of small periodic clusters of graphite and boron nitride and calculate energy states at high-symmetry points in the Brillouin zone of these crystals. We compare the results with conventional nonself-consistent tight binding calculations, as well as with the truncated crystal method of paper I, with reference to the available experimental data. Finally we comment on some possible experiments connected with our results.

2. Tight binding model

We start by briefly considering the relation between π energy states of a small periodic cluster and the eigenvalue spectrum of an infinite periodic crystal on one hand, and the descrete one-electron energy levels of a finite nonperiodic molecular cluster on the other, for hexagonal two-dimensional structures. The tight binding scheme is employed, and the extension to the $\sigma + \pi$ states will be considered later.
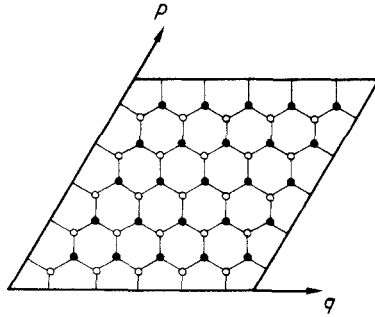

Figure 1. Two-dimensional hexagonal lattice. The dark circles represent heteroatoms in boron nitride structure.

Consider the two-dimensional hexagonal array of figure 1. We assume one atomic function per site: $\phi^A(r - R_{p,q})$ and $\phi^B(r - R_{p,q})$ for the two atoms A and B in the unit cell, respectively, where p and q number the Wigner–Seitz unit cells along the axis of the two-dimensional structure. Imposing Born's cyclic conditions, we get the one-site functions $\Phi^A_{m,n}(k_1 k_2)$ and $\Phi^B_{m,n}(k_1 k_2)$ for a lattice containing m and n unit cells (*2mn* atoms) along the two lattice directions, respectively:

$$\Phi^A_{m,n}(k_1 k_2) = \sum_{p=0}^{n-1} \sum_{q=0}^{m-1} \phi^A(r - R_{p,q}) \exp\left[2\pi i \left(\frac{k_1 p}{n} + \frac{k_2 q}{m} \right) \right]$$

$$\Phi^B_{m,n}(k_1 k_2) = \sum_{p'=0}^{n-1} \sum_{q'=0}^{m-1} \phi^B(r - R_{p',q'}) \exp\left[2\pi i \left(\frac{k_1 p'}{n} + \frac{k_2 q'}{m} \right) \right] \tag{1}$$

where $k_1 = 0, 1 \ldots n - 1$ and $k_2 = 0, 1 \ldots m - 1$. A normalized crystal state is formed by a linear combination of these auxiliary functions:

$$\Psi_{m,n}(k_1 k_2) = N_{m,n}^{-1}[\Phi^A_{m,n}(k_1 k_2) + C_{m,n}(k_1 k_2)\Phi^B_{m,n}(k_1 k_2)]. \tag{2}$$

The Hartree–Fock equations for the solid made up of $2mn$ atoms in the LCAO approximation are given by:

$$\sum[F_{m,\,n}^{A,\,B}(k_1 k_2) - S_{m,\,n}^{A,\,B}(k_1 k_2)E_{m,\,n}(k_1 k_2)] = 0 \qquad (3)$$

where $F_{m,\,n}^{A,\,B}(k_1 k_2)$ are the matrix elements of the Hartree–Fock effective one-electron operator between the states expressed by equation (1), given by:

$$F_{m,\,n}^{A,\,B}(k_1 k_2) = \sum_{r,\,s} \exp\left[2\pi i\left(\frac{k_1 r}{n} + \frac{k_2 s}{m}\right)\right]\langle\phi^A(r)\,|\,h\,|\,\phi^B(r - R_{r,\,s})\rangle \qquad (4)$$

and $S_{m,\,n}^{A,\,B}(k_1 k_2)$ is the appropriate overlap integral. When equation (3) is analytically solved for hexagonal D_{3h} or D_{6h} structure (two orders of neighbours are usually considered), the wavevector dependence of the energy $E_{m,\,n}(k_1 k_2)$ is introduced through a geometrical function

$$g_{m,\,n}^2(k_1 k_2) = 3 + 2\cos\frac{2\pi}{n}k_1 + 2\cos\frac{2\pi}{m}k_2 + 2\cos 2\pi\left(\frac{k_1}{n} - \frac{k_2}{m}\right). \qquad (5)$$

In the nearest-neighbour approximation, for instance, one gets the simple relation for the π band (Taylor and Coulson 1952)

$$E_{m,\,n}(k_1 k_2) = E_0 + \frac{-\gamma_1 S_1 g_{m,\,n}^2(k_1 k_2) \pm \gamma_1[d^2(1 - S_1^2 g_{m,\,n}^2(k_1 k_2)) + g_{m,\,n}^2(k_1 k_2)]^{1/2}}{1 - g_{m,\,n}^2(k_1 k_2)} \qquad (6)$$

where the matrix elements E_0, γ_1, S_1 were given in equation (2) of paper I. Somewhat more complicated results are yielded in the next-nearest-neighbour approximation. Similarly, when σ states are introduced, the energies in the corresponding bands are also described by the function $g_{m,\,n}(k_1 k_2)$. In an infinite cluster ($m, n \to \infty$), the function $g_{m,\,n}(k_1 k_2)$ ranges continuously from -3 to $+3$. The energies belonging to positive $g_{m,\,n}(k_1 k_2)$ values are occupied in the ground state; and form the valence band. The lowest occupied one-electron state belongs to $g_{m,\,n} = 3$ and corresponds to the Γ point in the Brillouin zone (notation of Lomer 1952), while the highest filled state corresponding to $g_{m,\,n} = 0$ is at the P point in the BZ. The saddle point Q which exhibits a Van Hove singularity in the density of states (Doni and Parravicini 1969) corresponds to $g_{m,\,n} = 1$. The gap between the two bands occurs at the point $g = 0$ and equals $(\alpha_A - \alpha_B)$ in the nearest-neighbour approximation, and

$$\Delta = (\alpha_A - \alpha_B) + \frac{3\gamma_{2A}}{1 - 3\gamma_{2A}} - \frac{3\gamma_{2B}}{1 - 3\gamma_{2B}} \qquad (7)$$

in the second- and third-nearest-neighbour approximations (notations of equation (12) in paper I).

If we denote energies of conduction states (negative $g_{m,\,n}(k_1 k_2)$ by E^* and energies of the occupied band (positive $g_{m,\,n}(k_1 k_2)$ by E^0, the gap of an $m \times n$ cluster is

$$\Delta_{m,\,n} = E_{m,\,n}^*(g_{\min}) - E_{m,\,n}^0(-g_{\min}) \qquad (8)$$

the π valence bandwidth is

$$W_{m,\,n} = E_{m,\,n}^0(g_{\min}) - E_{m,\,n}^0(g_{\max}) \qquad (9)$$

the work function, assuming Koopman's theorem, is

$$I_{m,\,n} = E_{m,\,n}^0(g_{\min}) \qquad (10)$$

and the π binding energy per atom is

$$\text{BE}_{m,n} = \frac{1}{2mn} \sum_{g_{m,n}} 2E^0_{m,n}(g_{m,n}) - E_0 \qquad (11)$$

where in the infinite crystal $g_{\min} = 0$ and $g_{\max} = 3$.

When the matrix elements of the one-electron hamiltonian appearing in equation (4) are calculated from free atom potentials (Doni and Parravicini 1969, Bassani and Parravicini 1967, Taylor and Coulson 1952, Coulson and Taylor 1952), the charge redistribution in the crystal, which is due to the electronegativity difference of the atoms in the unit cell or $\sigma - \pi$ coupling, is not taken into account. In order to get reasonable agreement with optical data, one is then forced to scale these matrix elements (Bassani and Parravicini 1967, Doni and Parravicini 1969) or to extract them from solid state and molecular experimental data (Taylor and Coulson 1952, Coulson and Taylor 1952). If on the other hand one constructs finite periodic clusters with m and n chosen to yield a sufficient number of $g_{m,n}(k_1 k_2)$ values (corresponding to high-symmetry points in the infinite crystals that are of interest to optical and dielectric data describing band structure), one can treat this cluster as a pseudomolecule and solve for its eigenvalue spectrum using selfconsistent LCAO procedures. This will not only allow for charge redistribution in the system, but will also provide a natural way of introducing $\sigma - \pi$ coupling.

It is immediately seen by inspection that if a finite periodic cluster contains the values $g_{m,n} = 0, 1, 3$ it is possible to represent the true band gap, bandwidth, work function and band-to-band transition energy by its one-electron energy levels. This behaviour is illustrated in figures 2 and 3 where these properties as a function of cluster size, for $m = n$ graphite and boron nitride clusters, are represented. α_C, α_B and α_N were taken as valence state ionization potentials (Skinner and Prichard 1953) and the matrix elements involved were calculated from the appropriate overlap integrals of Slater atomic functions, via the Mulliken approximation (Mulliken 1949). Clusters with $m = n = 3i$, $i = 1, 2 \ldots N$, always contain the values $g = 0, 3, -3$ and therefore it is possible to represent the work
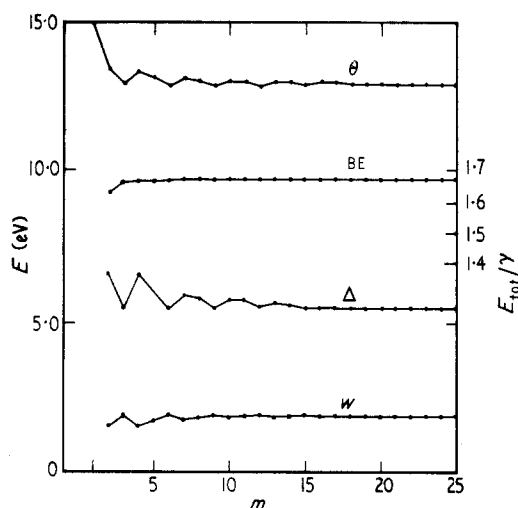

Figure 2. The dependence of ionization potential θ, binding energy BE, π band gap Δ and π bandwidth W, on the dimension of the periodic cluster, for boron nitride.
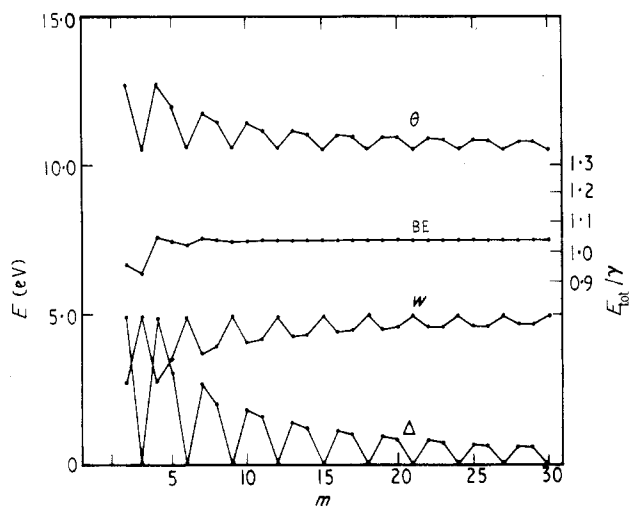
Figure 3. The dependence of ionization potential θ, binding energy BE, π band gap Δ and π bandwidth W, on the dimension of the periodic cluster, for graphite.

function, band gap and bandwidth of the infinite crystal by them, provided the atomic interaction integrals have converged to their bulk value. Similarly, clusters with $m = n = 2i, i = 2, 3 \ldots N$ contain the values $g = \pm 1$, and thus the band-to-band transition energy could be evaluated from them. It should be mentioned that each planar molecule of polycyclic boron nitride or carbon rings contains, in its one-electron energy spectrum, states that correspond to definite g values in the crystals, and thus, as shown in I, in this approximation it is possible to calculate energies in the crystal from the eigenvalue problem of such molecules.

It is evident from figures 2 and 3 that the binding energy converges quite rapidly with cluster size both in graphite and in boron nitride, while the other properties mentioned are nonmonotomic functions of cluster size over the entire range. This is due to the need to establish the maximum number of double bonds so that equivalent resonance stabilization structures could be assigned to the different clusters. The oscillations are however stronger in the homonuclear ($\delta = 0$) case of graphite, than in the heteronuclear system. This difference in the behaviour of heteronuclear and homonuclear clusters, noted also for planar nonperiodic clusters in I, is due to the importance of the heteronuclear term $d^2(1 - g^2S^2)$ which vanishes when the atoms in the unit cell are identical, as compared with the $g^2_{m, n}(k_1 k_2)$ term governed by symmetry alone. Thus, for heteronuclear finite clusters, the approach to the full $g(k_1 k_2)$ spectrum of the infinite crystal is less important in determining the energies than in homonuclear clusters.

The π electron calculation with fixed atomic potentials is unsatisfactory in the following respects:

(*a*) As noted in paper I, the σ manifold does not behave in the heteronuclear system as an unpolarized core. Charge was shown to be exchanged between σ and π systems of the atoms in boron nitride, making the boron final net charge positive, while π calculations tend to accumulate negative charge on the boron. Calculations involving $\pi + \sigma$ states are thus inevitable for such systems, although suitable parametrization of the π calculation (Taylor and Coulson 1952) can reproduce some of the experimental features. This effect

is less important in the homonuclear case of graphite, where the σ core affects the π energies to a smaller extent.

(*b*) Calculation of binding energies and equilibrium interatom distances is possible only if the σ states are included. In the same manner, as noted by Coulson and Taylor (1952), the experimental band density profile could be accounted for only if σ states are introduced, because of overlapping effects between these states.

(*c*) When fixed free atom potentials were used, it was found necessary (Bassani and Parravicini 1967) to scale the different interaction integrals appearing in the tight binding expressions by factors selected to yield the known width of the gap and the energy of the $\pi\pi^*$ transition. Since these factors were related only to experimental data on π states, the σ type interactions remained arbitrarily scaled. This procedure does not selfconsistently change the band structure, since it treats the π and σ manifolds on different footings. Unscaled calculation yields, on the other hand, a large work function and energy gaps.

(*d*) The variation of the band gap and width of different bands with interatom distance cannot be accounted for unless the effects of other than π electrons and selfconsistent charge distribution are included.

In order to calculate electronic properties of graphite and boron nitride in a self-consistent way, including all valence electrons, we make use of the fact that small ($m = n = 3, 4$) periodic clusters could be solved with all their electrons by quantum chemical selfconsistent computation methods to yield some energies at high-symmetry points, in a way that lets each atom experience a bulk crystalline environment up to second nearest neighbours. Since IEXH truncated crystal calculations on planar boron nitride clusters of increasing size (paper I) have shown that the interaction integrals γ_1, γ_{2B}, γ_{2N} converge reasonably with cluster size, it is expected that this procedure can account for the charge distribution experienced in the large crystal. Since the π and σ states for the periodic structure are treated on the same level of approximation in a selfconsistent manner, scaling factors are unnecessary and the boundary conditions of hydrogen surrounding the cluster can be relaxed.

3. Results and discussion

The results for periodic clusters of boron nitride as calculated by the charge selfconsistent IEXH method, together with experimental and tight binding results (Doni and Parravicini 1969, Taylor and Coulson 1952), are summarized in table 1. Madelung corrections were introduced in the diagonal matrix elements to account for electrostatic interaction between point charges, as suggested by Jorgensen *et al* (1967). Table 2 summarizes similar results for graphite periodic clusters. In the latter calculations the simple extended Huckel method was used for $\pi + \sigma$ electrons. This method was shown to yield a reasonable description of the electronic properties of aromatic polycyclic compounds (Hoffman 1963) and the iteration process converges within a few cycles. Transition energies at the points $g = \pm 1$ were calculated from $m = n = 4$ (32 atoms) periodic clusters, and energies at the points P and Γ were calculated from $m = n = 3$ (18 atoms) periodic clusters. The input atomic potentials employed are the same as in paper I.

The results of Greenaway *et al* (1969) on the reflectivity spectra of graphite for light polarization perpendicular to the crystal c axis indicate a peak at $4 \cdot 6 \pm 0 \cdot 2$ eV, which they ascribed to the $Q_{2g}^- - Q_{2u}^-$ transition. This is in good agreement with our calculated value of $4 \cdot 8$ eV. Several experimental investigations on reflection and absorption in graphite were analyzed by Bassani and Parravicini (1967, and references therein). They

Table 1. Calculated (two-dimensional) and experimental values for hexagonal boron nitride

Property	Tight binding	IEXH periodic cluster	Experimental
energy gap (eV)	$5\cdot4^{(a)}$, $4\cdot6^{(b)}$, $5\cdot3^{(c)}$	$3\cdot7$	$5\cdot4$–$3\cdot6^{(d-f)}$
π bandwidth (eV)	$1\cdot2^{(a)}$, $2\cdot2^{(b)}$, $3\cdot5^{(c)}$	$3\cdot8$	——
nitrogen 2S band minimum (eV)	$E_0 + 16\cdot2^{(a)}$	$E_0 + 18\cdot8$	$E_0 + 19\cdot4^{(1)}$
total bandwidth (eV)	$13\cdot6^{(a)}$, $16\cdot8^{(c)}$	$19\cdot27$	$18\cdot6^{(f)}$
work function (eV)	$11\cdot8^{(a)}$, $9\cdot4^{(c)}$	$10\cdot6$	
$\pi\pi^*$ transition energy (eV)	$6\cdot2^{(a)}$, $6\cdot3^{)c)}$	$6\cdot0$	$6\cdot2$–$6\cdot5^{(g,\,h)}$
binding energy (eV)	——	$7\cdot2$	$6\cdot6^{(i)}$
equilibrium distance (Å)	—	$1\cdot441$	$1\cdot446^{(j)}$
boron π charge	—	$0\cdot52$	$0\cdot45 \pm 0\cdot015^{(k)}$
net atomic charge (boron)	—	$0\cdot30$	—

[a] Doni and Parravicini (1969)
[b] Taylor and Coulson (1952)
[c] Zupan (1972)
[d] Larach and Shrader (1956)
[e] Rand and Roberts (1968)
[f] Formichev (1971)
[g] W J Choyke (1969 unpublished data; see Doni and Parravicini 1967)
[h] Vilanov (1971)
[i] *Janaf International Thermochemical Tables* (1965)
[j] Pease (1952)
[k] Silver and Bray (1960)
[l] Hamrin et al (1970)

concluded that the thermoreflectance peak at $6\cdot0 \pm 0\cdot2\,\text{eV}$ arises from the $\Gamma_{3g}^+ - \Gamma_{3u}^+$ transition (from highest occupied to lowest vacant σ states), thus accepting the previous assignment of Greenaway *et al* (1969). Painter and Ellis (1970) suggested that the growth of the reflectance peak of $14\cdot5\,\text{eV}$ is probably due to this $\sigma \to \sigma^*$ transition. Our results yield a value of $5\cdot96\,\text{eV}$, in agreement with Bassani and Parravicini and Greenaway's suggestion. The assignment of Painter and Ellis is dubious for one must be too near the continuum of energy for a $\sigma \to \sigma^*$ transition of this sort.

Table 2. Calculated (two-dimensional) and experimental values for graphite

Property	Theory	EXH periodic clusters	EXH modified potentials	Experimental
energy gap (eV)	0	0	0	0
π bandwidth (eV)	$5\cdot0^{(a)}$, $9\cdot8^{(b)}$, $5\cdot0^{(c)}$, $7\cdot35^{(d)}$	$4\cdot94$	$4\cdot87$	$5\cdot5 \pm 0\cdot5^{(e)}$
total bandwidth (eV)	$18\cdot5^{(b)}$, $13\cdot8^{(c)}$, $19\cdot3^{(d)}$	$20\cdot95$	$24\cdot14$	$30^{(f)}$, $31 \pm 2^{(g)}$
work function (eV)	$8\cdot95^{(c)}$, $8\cdot9^{(d)}$, $8\cdot3^{(b)}$	$10\cdot5$	$9\cdot31$	$4\cdot8^{(h)}$
$\pi\pi^*$ transition energy (eV)	$4\cdot5^{(c)}$, $4\cdot6^{(d)}$, $5\cdot15^{(b)}$	$4\cdot8$	$4\cdot6$	$4\cdot5^{(i)}$
binding energy (eV)	——	$4\cdot5$	$4\cdot7$	$5\cdot0^{(j)}$
equilibrium distance (Å)	——	$1\cdot43$	$1\cdot43$	$1\cdot42^{(k)}$

[a] Coulson and Taylor (1952)
[b] Corbato (1959)
[c] Bassani and Parravicini (1967)
[d] Painter and Ellis (1970)
[e] Chalkin (1948)
[f] Thomas et al (1971)
[g] Hamrin et al (1970)
[h] Fomenko (1966)
[i] Taft and Phillip (1965)
[j] Kanter (1957)
[k] Wyckoff (1963)

The width of the π sub-band was suggested from analysis (Coulson and Taylor 1952) of Chalkin's (1948) data to be $5\cdot5 \pm 0\cdot5$ eV, in accord with our value of $4\cdot94$ eV.

The total width of the valence band in graphite and boron nitride was measured by x-ray photoelectron emission spectroscopy (Thomas *et al* 1971, Hamrin *et al* 1970) and was found to be much larger than that suggested by earlier measurements (Chalkin 1948). Our result is larger than in previous computations, but probably still underestimates the total width.

For boron nitride, there are only a few experimental optical studies. The results of Vilanov (1971) and W J Choyke (1969 unpublished data; see Doni and Parravicini 1969) suggest that the transition at Q_2 points, between π and π^* states, occurs at $6\cdot5$ eV and $6\cdot2$ eV respectively. This agrees with our result of $6\cdot0$ eV separation at $g = \pm 1$ points. There seems to be a controversy over the experimental results for the band gap. Optical absorption measurements on thin films (Baronian 1971) suggest a $5\cdot83$ eV gap, Rand and Roberts (1968) propose a $3\cdot9$ eV gap from similar experiments, while Larach and Shrader (1956) obtained a value of $5\cdot4$ eV from reflection measurements. Formichev (1971) obtained a value of $3\cdot6$ eV from soft x-ray photoelectron emission. It is therefore impossible to comment on these experiments from our calculated results. ESCA measurements of Hamrin *et al* (1970) were able to identify the centre of the lowest 2s band, which is of nitrogen character, as being $19\cdot4$ eV from the Fermi level. Our result of $18\cdot8$ eV is thus close to this value. The total width of the valence band (including the 2S band) was measured from soft x-ray emission to be $18\cdot6$ eV (Formichev 1971). This is probably a lower limit as suggested by Hamrin *et al* (1970), and agrees well with our $19\cdot27$ eV result.

Charge selfconsistent calculation permits computation of total one-electron energies of various internuclear distances without the need of further input potential data. Thus, it is possible to calculate within the semi-empirical LCAO approximation methods employed, binding energies and the equilibrium nuclear configuration. The results of $7\cdot2$ eV and $4\cdot5$ eV for the binding energy of boron nitride and graphite, respectively, agree fairly well with the experimental thermochemical results of $6\cdot6$ eV and $5\cdot0$ eV respectively. The equilibrium interatom distances obtained were $1\cdot441$ Å and $1\cdot43$ Å for boron nitride and graphite respectively, as compared with $1\cdot446$ Å and $1\cdot42$ Å obtained experimentally.

The π bonding in boron nitride crystals was investigated by Silver and Bray (1960) by means of nuclear quadrupole resonance spectroscopy. The measured value of the quadrupole coupling constant suggests that $0\cdot45 \pm 0\cdot015$ electronic π charge is transferred from nitrogen to boron. The atomic charges are computed from one- and two-centre contributions, the latter being computed in a way that leaves unchanged the projection of the centroid of the charge onto the line connecting the two atoms involved. This complication over the common procedure of dividing the contribution of the two centres equally among the two atoms involved is needed because of differences in the size of the atomic orbitals in a heteronuclear system, thus accounting for atomic size effects on the charges. This yields a boron π charge of $0\cdot52e$ which agrees fairly well with the NQR result. The net atomic charges $Q_B = -Q_N = 0\cdot3e$ implies only small ionicity of the structure and explains perhaps the success of truncated crystal calculations (paper I), where charges were not homogenized by periodic boundary conditions. It is unfortunate that charge distribution results from this LCAO approach as it cannot be readily compared at the present time with experimental results for various effective charges on this system.

The periodic molecular method results generally in a wider valence band than in previous computations, thus decreasing the discrepancy between the measured bandwidth and previous computations. The work function is probably overestimated both

in tight binding works and in our calculation, because of the absence of explicit correlation effects. The effect of iteration towards charge selfconsistently is nevertheless in the right direction, lowering it by 15 % from the un-iterated value for boron nitride. Iteration towards charge selfconsistency decreases the band gap (from 5·4 eV to 3·7 eV), increases the π sub-band width (from 1·8 eV to 3·9 eV) and the total bandwidth (from 17·6 eV to 19·3 eV) and strongly suppresses the atomic charges of the nonconsistent computation (from $+1·1e$ to $+0·3e$ on boron). Similar behaviour was previously observed in open cluster calculations (paper I). The un-iterated results agree generally with the free atom tight binding calculation for the infinite lattice (Bassani and Parravicini 1967, Doni and Parravicini 1969).

The gross inability of extended MO calculations, with or without selfconsistency procedures, to reproduce the ionization potential of unsaturated molecules arises from the absence of nuclear field penetration effects and electron repulsion effects that are not properly considered in this scheme. This is manifested by the fact that the orbital degeneracy of $2p_x$, $2p_y$ as compared to $2p_z$ free atom states is not removed sufficiently in molecules and crystals possessing σ_h reflection symmetry when the MO approach is used (Srinivasan *et al* 1968, Messmer 1971). Analysis of these effects suggests (Armstrong *et al* 1968) that it is possible to account for these crystal field phenomena within the MO scheme if the atomic $2p_z$ potential is made less attractive than the $2p_x$ and $2p_y$ potentials. Srinivasan *et al* (1968) used such modified atomic potentials for carbon and obtained remarkable accord between EXH and SCF-MO calculations on benzene. We used their potentials in the band calculation of graphite, and the results are presented in column 4 of table 2. The overall agreement obtained is better, the differences between these results and the results of the degenerate $2p_x$, $2p_y$ and $2p_z$ calculation being mainly in the total bandwidth and work function. Since the modified potential was tested only for carbon, we did not perform such calculations on boron nitride. Preliminary results, however, indicate that removal of this orbital degeneracy increases the $\sigma - \pi$ separation at the P point, thus making the edge of the occupied band a pure π state.

The results for the periodic small clusters B_9N_9 are generally better than the corresponding results of the open molecule representation with a similar number of atoms (e.g. $B_8N_8H_{10}$, see table 3 in I), the differences being mainly in the π bandwidth, the work function and the energy gap. This is due to the fact that the open molecular representation does not closely enough approach the crystal limit of $g_{k_1 k_2}$ near the points P and Γ and due to incomplete charge homogeneity within each sublattice, in this calculation. When the bond moment population analysis is applied to the wavefunction of the open planar two-dimensional clusters, the standard deviation for boron atomic charge distribution over the cluster is 7·8 % of the mean boron net charges, and the corresponding deviation for nitrogen is 1·1 %, while in the periodically connected clusters these deviations are completely suppressed. As the number of atoms in the planar cluster increases, the results approach those of the crystal as calculated by connected clusters. For carbon clusters this is consistent with the fact that the measured density of states in the occupied band in the coronene molecule ($C_{24}H_{14}$) markedly resembles that of graphite (Thomas *et al* 1971).

A recent publication (Zupan 1972) reported a tight binding calculation for boron nitride where nitrogen and boron atomic potentials were calculated from B_3N and N_3B molecular clusters respectively. Our above mentioned analysis suggests that in that calculation the large charge nonhomogeneity expected from these small and valence unsaturated molecules could have a large effect on the resulting band structure. Suppressing these effects by considering the clusters B_3N and N_3B to have effectively 8 electrons

instead of 14 and 18 respectively, as suggested by Zupan, will interfere with the natural tendency of the hexagonal system to achieve SP^2 hybridization, thereby changing the the charge distribution.

Variation of the Slater exponents of the atomic function set employed could be used to improve the results. When variation is carried out on the exponents of the carbon 2S and 2p atomic functions in the C_{18} cluster, the binding energy reveals a minimum at $\xi = 1·56$ of 4·68 eV, where the total bandwidth increases to 21·6 eV and the work function decreases to 10·2 eV, thus improving the agreement with experiment.

In boron nitride the π energy states at the edge of the valence band and bottom of the conduction band (points P_1^-, P_2^-, respectively) are pure nitrogen and boron $2p_z$ states, respectively, thus the optical transition $P_1^- \to P_2^-$, allowed by electrical dipole, is a $\pi \to \pi^*$ internal charge transfer (CT) transition (Nagakura and Tanaka 1954), and should be observed in the UV region.

Since the π gap is formed mainly due to the difference $\alpha_B - \alpha_N$ between boron and nitrogen π energies in their crystalline bonding state (equation 7), its interatomic distance dependence is expected to be weak compared with systems where the gap occurs at the centre of the band, and is governed by nearest-neighbour interaction terms (tetrahedral binary crystals). A nonselfconsistent treatment is expected to reveal only the contribution of the second term in equation (7) to the distance dependence to the gap, while a procedure that accounts selfconsistently for the change of atomic orbital energies due to crystalline environment should reveal the full dependence. Approximate estimates of the band gap distance variation are possible from IEXH calculations on B_9N_9 periodic clusters, when the interatomic distance is varied. This yields $\Delta\pi\pi^* \sim R^{-1.6}$, where $1·40 < R < 1·50 \text{Å}$, which is a slightly weaker dependence than the result $\Delta\pi\pi^* \sim R^{-1.8}$ obtained from planar $B_{12}N_{12}H_{12}$ molecular clusters (Zunger 1972). The difference results from the fact that the valence and conduction edges in the open molecular representation are not completely pure nitrogen and boron states respectively, but contain a 2%–3% mixture of different atom states (paper I). When the calculation is repeated without the selfconsistent iterative procedure, the dependence is $\Delta\pi\pi^* \sim R^{-0.8}$, indicating that charge screening has an important effect on the gap dependence.

Higher band gap distance dependence is expected to occur in tetrahedral binary structures, where the gap contains a homonuclear contribution depending on the nearest-neighbour interaction matrix, as well as a heteronuclear term, governed by the electro-negativity difference. The homopolar energy gap, in tetrahedral systems arising from the symmetric $V_A + V_B$ pseudopotential structure factor in the AB unit cell, was shown (Van Vechten 1969) to depend on the lattice constant a as $a^{-2.5}$, while the heteropolar term is assumed to be the electronegativity difference in the AB unit cell multiplied by exp $(-k_s R)$, where k_s is the Thomas–Fermi screening constant for free electrons having density equal to that of the valence electrons, and R is the interatomic distance (Phillips 1970). In the hexagonal structure discussed here, where the gap occurs at the edge of the Brillouin zone, the homopolar term vanishes and the distance dependence is mainly governed by screening effects, and is thus small. The anomalously weak interatomic distance dependence of the band gap of hexagonal boron nitride could be investigated through optical measurements as a function of temperature and pressure, since the thermal expansion and compressibility along the in-plane axes are known.

Contrary to the situation in graphite the selfconsistent calculations on boron nitride reveal the existence of the σ band at Γ_{3g}^+ point within 0·2 eV from the π band. This contradicts previous computations (Doni and Parravicini 1969, Zupan 1972) where the σ band

was shown to lie deeper ın the band. This question could be resolved by performing polarized absorption measurements in the vicinity of the Q_2^- and P_1^- points.

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