A molecular calculation of electronic properties of layered crystals: II. Periodic small cluster calculation for graphite

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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 σ + π electrons of small periodic clusters of

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

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

and the π binding energy per atom is

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

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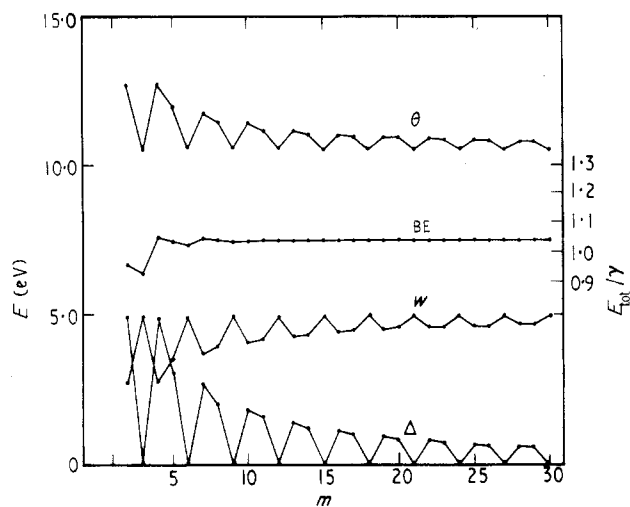
Figure 3. The dependence of ionization potential θ, binding energy BE, π band gap Δ and π bandwidth W, on the dimension of the periodic cluster, for graphite.

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

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

Property	Tight binding	IEXH periodic cluster	Experimental
energy gap (eV)	$5\cdot4^{(a)}$, $4\cdot6^{(b)}$, $5\cdot3^{(c)}$	3·7	$5\cdot4$–$3\cdot6^{(d-f)}$
π bandwidth (eV)	$1\cdot2^{(a)}$, $2\cdot2^{(b)}$, $3\cdot5^{(c)}$	3·8	——
nitrogen 2S band minimum (eV)	$E_0 + 16\cdot2^{(a)}$	$E_0 + 18\cdot8$	$E_0 + 19\cdot4^{(1)}$
total bandwidth (eV)	$13\cdot6^{(a)}$, $16\cdot8^{(c)}$	19·27	$18\cdot6^{(f)}$
work function (eV)	$11\cdot8^{(a)}$, $9\cdot4^{(c)}$	10·6	
$\pi\pi^*$ transition energy (eV)	$6\cdot2^{(a)}$, $6\cdot3^{)c)}$	6·0	$6\cdot2$–$6\cdot5^{(g,\,h)}$
binding energy (eV)	——	7·2	$6\cdot6^{(i)}$
equilibrium distance (Å)	—	1·441	$1\cdot446^{(j)}$
boron π charge	—	0·52	$0\cdot45 \pm 0\cdot015^{(k)}$
net atomic charge (boron)	—	0·30	—

[a] Doni and Parravicini (1969) [h] Vilanov (1971)

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

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 $\xi = 1 \cdot 56$ of $4 \cdot 68$ eV, where the total bandwidth increases to $21 \cdot 6$ eV and the work function decreases to $10 \cdot 2$ 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