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

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

nonmonotonic character of various electronic properties such as instability of work
function (Baetzold 1971) band gap (Baetzold 1971, Larkins 1972) valence band width

$$\alpha_{\mathrm{A}} = \langle \phi_{rs}^{\mathrm{A}} | h | \phi_{rs}^{\mathrm{A}} \rangle \qquad \alpha_{\mathrm{B}} = \langle \phi_{rs}^{\mathrm{B}} | h | \phi_{rs}^{\mathrm{B}} \rangle \qquad \beta = \langle \phi_{rs}^{\mathrm{A}} | h | \phi_{r, s+1}^{\mathrm{B}} \rangle$$

$$\delta = \tfrac{1}{2}(\alpha_{\mathrm{A}} - \alpha_{\mathrm{B}}) \qquad E_0 = \tfrac{1}{2}(\alpha_{\mathrm{A}} + \alpha_{\mathrm{B}}) \qquad S = \langle \phi_{cs}^{\mathrm{A}} | \phi_{), s+1}^{\mathrm{A}} \rangle \qquad (2)$$

$$\gamma = E_0 - \beta S \qquad d = \frac{\delta}{\gamma}.$$
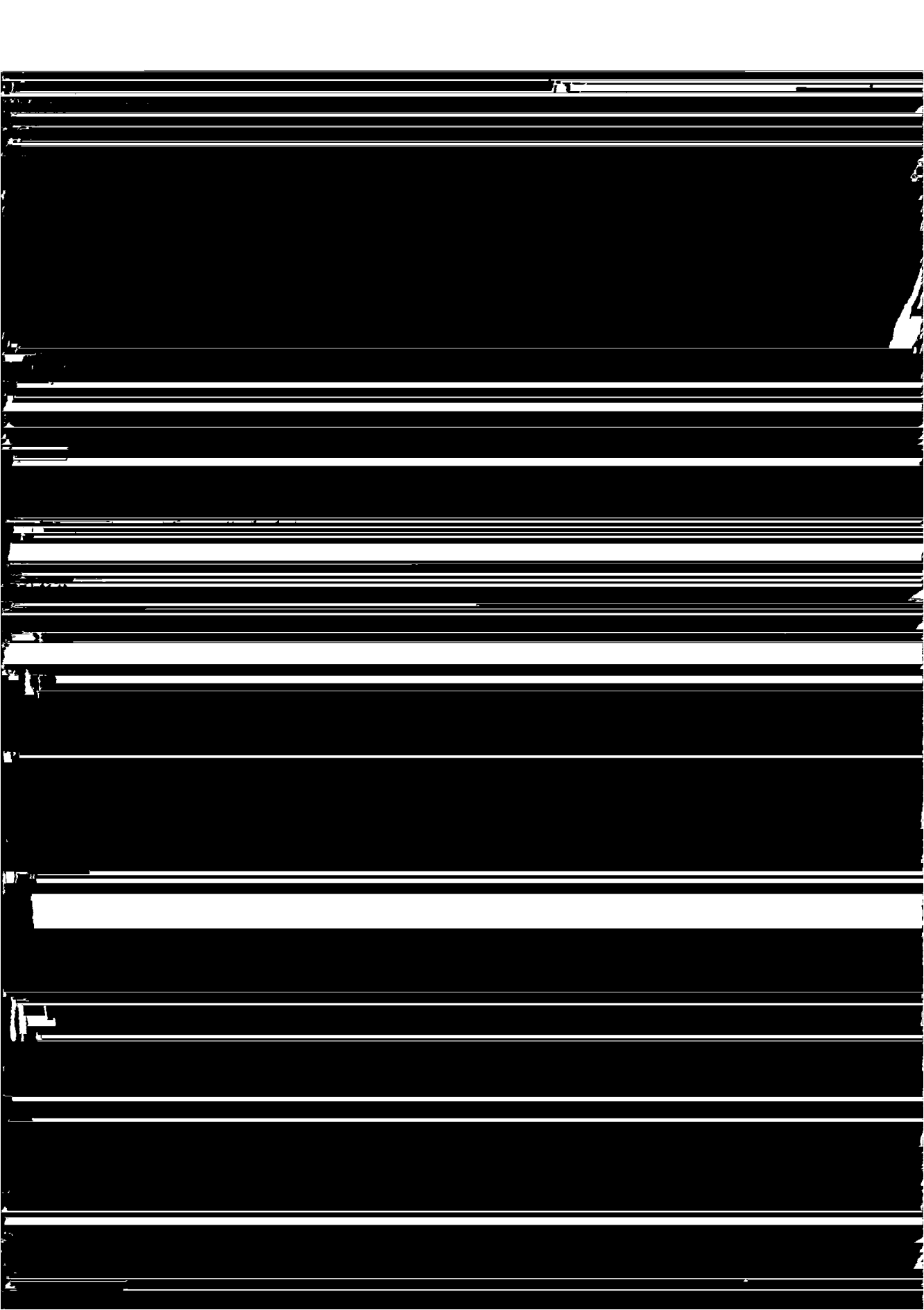
in the calculation of the electronic bands in the crystals and suggests that selfconsistent

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

Table 3. Calculated energy bands of the molecular clusters I–V by the iterative extended

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

Table 4. Experimental and theoretical values for boron nitride

band gap (eV)	5·4	reflectivity[a]	4·6	π tight binding[e]
			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)	$E_0 + 19\cdot4$	ESCA[h]	$E_0 + 16\cdot2$	$\pi + \sigma$ tight binding[f]

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
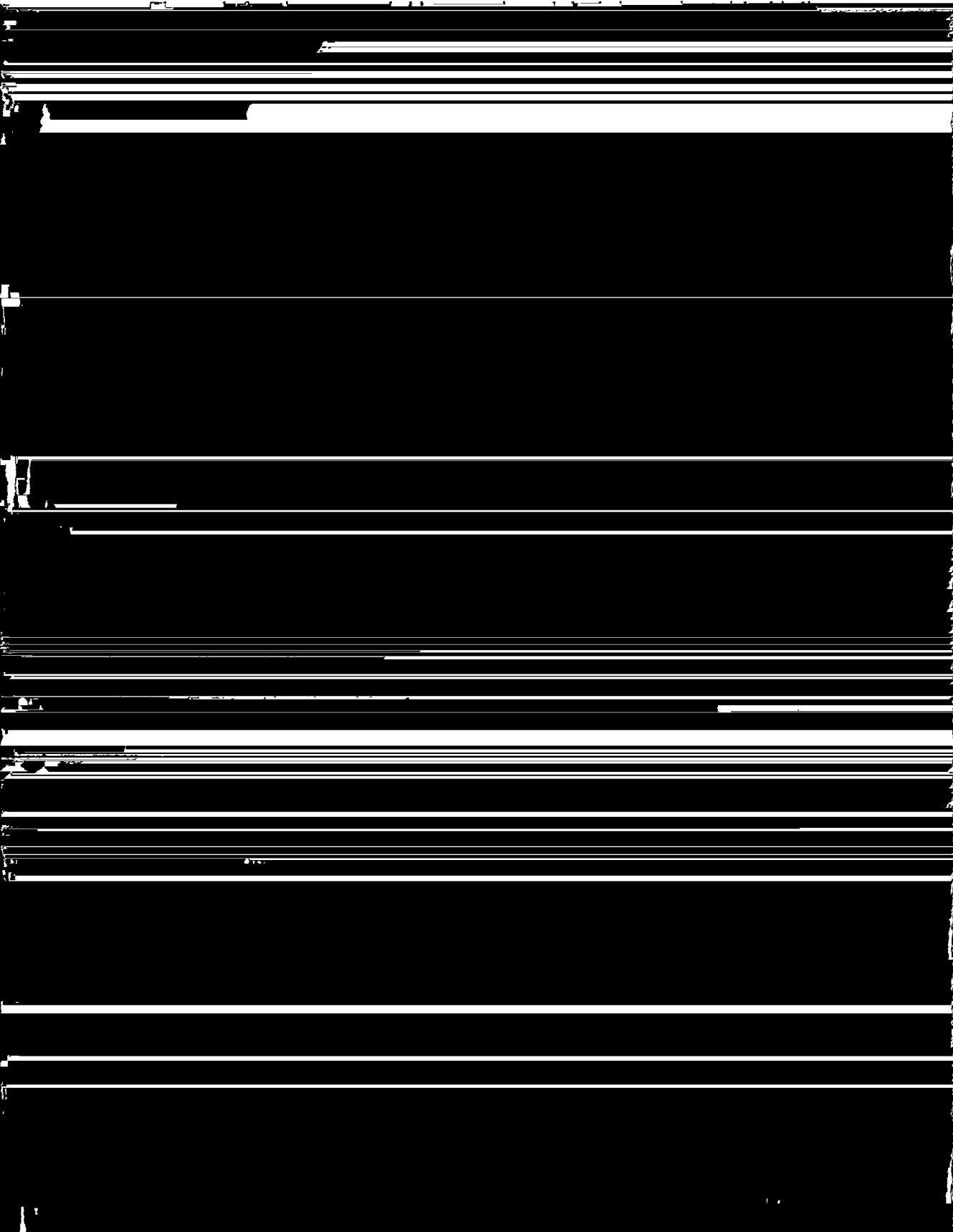
articles in Boron Nitrogen Chemistry 1964) the latter notion being mainly based on considerations involving only the π frame. These results are in line with Hoffman's suggestion (Hoffman 1964). The large effect manifested by the σ frame on the charge suggests that π electron calculations involving a '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

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

most of the charge is concentrated on boron atoms. The energy of this transition decreases as the purity of the HFπMO and LEπMO increases, the boron state (LEπMO) being the more

for $B_{10}N_{10}H_{12}$ to $-1\cdot94$ eV for both $B_{12}N_{12}H_{12}$ and $B_{14}N_{14}H_{14}$. $\gamma_{BB}^{(2)}$ and $\gamma_{NN}^{(2)}$ similarly

When the molecular cluster is large enough so that the contamination is low, a weaker R_{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, $3 \cdot 4$ 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 $\sim 1\%$.

4.6. Energy of Frenkel pair formation

gap: two quasidegenerate carbon σ states at $-12 \cdot 0$ eV with 40% carbon character, and one π state at $-12 \cdot 14$ eV with 65% carbon character. The location of these states is changed only by approximately 1% when the cluster size is increased from $B_{10}N_{10}H_{12}$

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

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