

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

This content has been downloaded from IOPscience. Please scroll down to see the full text.

1974 J. Phys. C: Solid State Phys. 7 76

(<http://iopscience.iop.org/0022-3719/7/1/016>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 128.138.65.149

This content was downloaded on 14/07/2015 at 19:30

Please note that [terms and conditions apply](#).

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

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

also noted that the convergence of symmetrical clusters ($n = 6$) is usually better than for

($m = n = 1$) 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nitride are close to these values, being 4.8 eV (Greenaway *et al* 1969) and 6.5 ± 0.3 eV (Vilanov 1971, Choyke 1969 unpublished data; see Doni and Parravicini 1969) for graphite and boron nitride respectively.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*

is the calculation of the electronic bands in the crystals and suggests that a self-consistent

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 2.5:1 (see Combs et al. 1966). The square of the ratio between charges

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

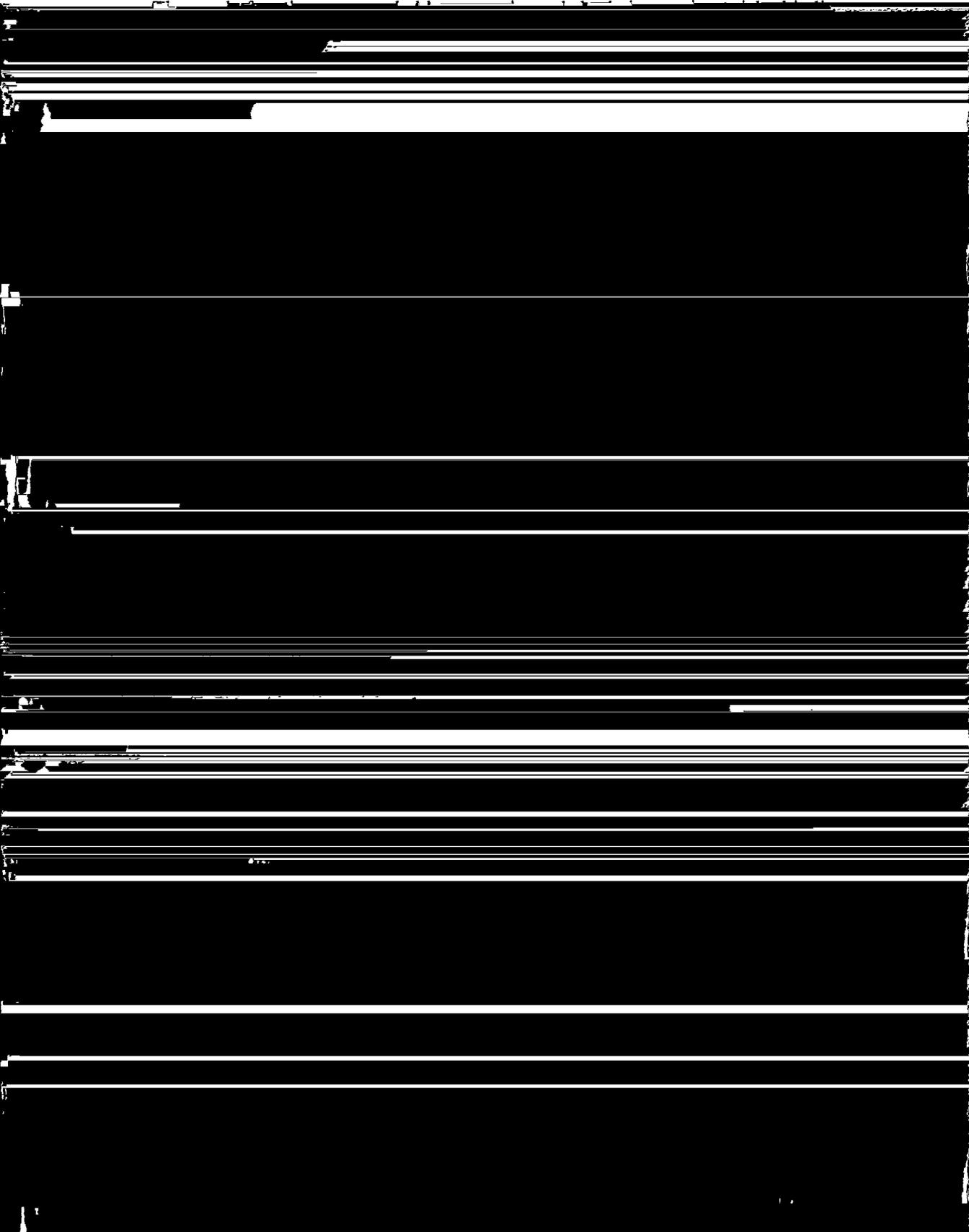
Property (eV)	B ₈ N ₈ H ₁₀	B ₁₀ N ₁₀ H ₁₀	B ₁₂ N ₁₀ H ₁₂	B ₁₂ N ₁₂ H ₁₂	B ₁₄ N ₁₄ H ₁₄
band gap	2.90	2.87	2.939	3.00	2.95
π band width	3.36	3.41	3.472	3.2	3.31
p band width	5.58	5.86	5.95	5.70	5.81
2s band width	4.94	4.29	4.40	4.40	4.42

transition energy	5.6	5.7	5.8	6.0	5.96
binding energy	7.0	7.0	7.0	8.0	8.05

Table 4. Experimental and theoretical values for boron nitride

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
valence band width (eV)	3.9	absorption ^(d)	2.95	IEXH
			13.6	$\pi + \sigma$ tight binding ^(f)
			27.8	OPW ^(g)
	18.6	x-ray emission ^(c)	17.8	EXH
2s band minimum (eV)			17.5	IEXH
	$E_0 \pm 19.4$	ESCA ^(h)	$E_0 + 16.2$	$\pi + \sigma$ tight binding ^(f)
			$E_0 + 18.4$	EXH
			$E_0 + 18.8$	IEXH
band-to-band transition energy (eV)	6.5	dielectric constant ⁽ⁱ⁾	6.6	$\pi + \sigma$ tight binding ^(f)
	6.2	dielectric constant ^(j)	6.2	EXH
			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_{c0} (Å)	1.446	crystallography ^(l)	1.48	EXH

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 ~~xxxx~~ calculations.



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

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 correspond to

most of the charge is concentrated on boron atoms. The energy of this transition decreases as the purity of the $\text{HF}\pi\text{MO}$ and $\text{LE}\pi\text{MO}$ increases, the boron state ($\text{LE}\pi\text{MO}$) being the more sensitive to charge contamination. Such internal charge transfer transitions, polarized

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

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 $\text{B}_3\text{N}_3\text{H}_6$ structure, 3.4 \AA above the basal $\text{B}_{12}\text{N}_{12}\text{H}_{12}$ 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 $\sim 1\%$.

The stability of the three dimensional structure is checked by rotating the upper

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.

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 $B_{12}N_{12}H_{14}$. These states have the colouring effect of diminishing the energy difference

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

- Kimel S, Ron A and Hornig D F 1964 *J. chem. Phys.* **40** 3351-6
Khusidman M B and Neshpor V S 1968 *Sov. Phys.-Solid St.* **10** 975-76
Kuznesof P M and Shriver D F 1960 *J. Am. chem. Soc.* **90** 1683-8
Kuznesof P M, Stafford F E and Shriver D F 1967 *J. phys. Chem.* **71** 1939-40
Larach S and Shrader R E 1956 *Phys. Rev.* **104** 68-71
Larkins F P 1971 *J. Phys. Chem. Solids* **4** 3065-76, 3077-89
Loughran E D, Mader C L and McQuiston W F 1960 Los Alamos Scientific Laboratory Report N-