PH YSICAL RE VIE% 8 VOLUME 17, N UMBER 4 15 FEBRUAR Y 1978

Ab initio self-consistent study of the electronic structure and properties of cubic boron nitride*

Alex Zunger and A. J. Freeman
Department of Physics and Astronomy, and Materials Research Center, Northwestern University, Evanston, Illinois 60201
(Received 4 May 1977)

We present the results of a first-principles fully self-consistent study of the electronic properties of cubic
boron nitride in the local-density formalism using our previously published numerical-basis-set linear combination of atomic orbitals scheme. The resulting

AB INITIO SELF-CONSISTENT STUDY OF THK ELECTRONIC... 2031

TABLE I. The pgediction of energy separation between high-symmetry points in the zone
given by various band models: 4~~ indicates the lowest point in the conduction band in the
r-X direction; %VB1 and %VB2 refer to the width of the lowest {VB1)and highest {VB2)val-
ence bands, respectively, ax)d %VB is the total width of the occupied valence band. Results
are given in eV. Asterisks denote values interpolated from the published fjLgures.

Energy
difference APWb OPWc Pseudo"

Present
exchange and
correlation

ris,.—ris,.
ris y ri, c
L3,. Li c
Xs, o Xs,c
XS,o Xi,c
J-s, o La, c

ris-S~,
%VB
%VB1
WVB2

10.8
8.4
9.9
13.8
12.7
15.0
7.6
27.5
6.8*
16.5

8.9
9,6
11.2
14.5
13o3
11.7
7.2
17.8
4.5
8.0

7.6
8.4
13.4
13.6*
9.0
11.8
3.0
23.2
0Q
12.7~

14.3
20.0
14.4
14.7
13.4
15.4
10.5
17.9
5.6
3.5

10.8
11.9
14.2
18.7
12.9
15.4
8.7
19.1
5.1
9.0

a Empirical {m)nlocal} pseudopotential, Ref. 26.
bReference 23.
'Reference 22.
~Perturbative pseudopotential, Ref. 19.

Table I presents the energies of the 1owest inter-
band transitions at high symmetry points, the width of the lowest valence bands (VBl and VB2, respectively) and the total width of the occupied bands predicted by these four models. The agree-ment between these results is seen to be generally very poor. The two nonempirical studies (OPW)" and pseudopotentia1" yield results that differ by as much as 6.'7 eV for the direct gap, V.5 eV fox the indirect gap, and 5.3 eV for the valence band width.
The

2032 ALEX ZUNGER AND A. J. FREEMAN 17

of &GNc(pmp(r)} +F"" (P p(r) +~L'Nc(r) and dePends
on the assumed set (f„„Qj for boron and nitro-
gen and on the lattice structure. The initial guess
for these populations is the neutral atom configur-
ations B' 1s'2s'2p' and N' 1s'2s'2p'. The potential
is calculated in tabular form over a set of 3500 in-

tegration points in the unit cell. Linearization" of

V„,(p, (r)) with respect to the atomic densities p (r) is avoided, and similarly, no use is made of spherical approxixnations"'" to the total potential

&'"'(p...(r)}.
We solve the band problem with this initial poten-tial in the LCAO representation using our previous-ly published numerical-basis-set discrete-varia-tional technique.

'"

We use as basis functions

Bloch states C» (k, r) formed from accurate nu-merical solutions XN" (r) to the atomic-local-den-
sity equations, again with an assumed population

and charges (f„,, Q }. We use numerical orbitals corresponding to p. =ls, 2s, 2p, 3s, and Sp for both boron and nitrogen; the addition of 3d orbital was found to introduce negligible changes in the
band structure for energies lower than 16 eV above
the valence band edge.
The Hamiltonian matrix elements in the Bloch

basis are computed by a three-dimensional Dio-phantine integration scheme" and include all the rnulticenter integrals up to an interatomic separa-tion distance of 16.5 a.u. This summation range, together with the use of 3500 Diophantine integra-tion points, assures a stability of 0.05-0.1 eV in the band eigenvalues in the energy range studied. The band Hamiltonian is solved for 10 special points in the irreducible Brillouin zone (BZ)" and the resulting crystal wave functions at these points are used to generate the output density, p„„(r). A smaller set of 6 special BZ points (I'-X-I:W-tA-Z} produced a charge density that differs by less than l%%uo from that determined by the 10-point sampling. The output crystal density p„„(r}differs, in

irr5.23 444aTf 247.69 280.72 Tf 107.37 368.62 T4.4 Tf 159.97 531. 553.44 BT /e21 455.45 Td (was)Tj Efpoints basis

determined

0. p„„(r

rsam BT 292.69 (d (formed)Tj ET BT /Xi2 10.69 Tf f 71)Tj ET 40(determined)Tj ET1.04 281.15 Td (a)Tj ffers

0.

21 Tf 77.7 422.75 T7 Td (3dT BT /om)T/Xi2 8.44 Tf 71 aTj 5 /om1 /Xi2 9.P.5 Tf 69.21 673.86 Td T /2Tf ET /X 7ET BT /Xi=T BT /Xi2 8n61 Td (1.8co.1 ET 8 BT /X3.44 Tf 71)Tj ET E251s'2s'2Tj ET (The ET BT B (sam BT 29

,

a

ALEX ZU5GER AND A. J. FREEMAN 17

e'24

—IO—

g r
LUZ
-l5

-20

yg B2P

-4
N2$

17 AB INITIO SELF-CONSISTENT STUDY OF THE ELECTRONIC... 2035

-IO
EXCHANGE QNLY EXCHANGE AND CORRELATION

2036 ALEX ZUNGER AND A. J. FREEMAN

0,50— V8I CHARGE DENS I TY

0.40
O

0.30—

--- 1

I v

— Li,v
-—XI

n v

I

0.20 —f

O.IO—

8
0':

AB INITIO SELF-CONSISTENT STUDY OF THE ELECTRONIC...

aeter admixed in along the X-S'-E directions. These trends are borne out by examining the loca-tion of the free-ion eigenvalues on the scale of the band structure (cf., Fig. 4). The N 2s eigenvalue has its energy substantially lowered in the solid (to the VB1 region) due to the attractive Madelung mell on this negative site. Similarly, a Madelung stabilization of the N 2P level lowers its energy into the VB2 bends while the positive-site 8 2s and 2P levels are pushed higher in energy (towards the conduction bands) and thus their admixture into the VB2 bands is diminished.

A description of the orbital character in the en-tire occupied manifold is given by the BZ disper-sion of

shown in Fig. 9 together with the dispersion of the
net ionic charge QN(k) =Z„-~(f~(h), where Z„ is the a-site atomic number. The striking feature

5.5

5.0

~.o„,
LLI

C9

~~

~~ x 20 +a~

O
z
0
K
I-

LIJ

~ I.5—

17 AB INITIO SELF-CONSISTENT STUDY OF THE ELECTRONIC... 2039

here, are capable of reproducing the observed
Compton profile"; free-atom ground-state func-
tions (B Is'2s'2p' and N ls'2s'2p') or the wave
functions corresponding to singly ionized atoms
produce too large values of the low-momentum
Compton components.

TABLE II. X-ray scattering factors of boron nitride; "sup" indicates the results of a superposition of spheri-cal (neutral) atomic densities while "band" indicates those from a crystalline calculation.

(h A' l) HFI~ LDF~~ HFb g LDFb ~ Expt.

1 1 1
2 0 0
2 2 0
3 1 1
2 2 2
4 0 0
3 3 1
4 2 0
5 1 1
3 3 3

4.62 4.42
1.40 1.49
4.21 4.14
2.69 2.60
0.48 0.47
3.30 3.25
2,17 2.18
0.29 0.36
1.90 1.96
1.90 1.96

5.05
1.56
4.10
2.52
0.44
3.20
2.22
0.28
1.97

4.97
1.58
4.17
2.64
0.57
3.20
2.16
0.32
1.95
1.97

4.92+0.15
1.56 a 0.05
4.17+ 0.10
2.59+ 0.10
0.50 + 0.02
3.22 x 0.10
2.17+ 0.05
0.32 +0.01
1.96 a 0.06
1.96+0.06

~Hartree-Fock superposition model, Ref. 17.
~ Hartree-Fock superposition model, Ref. 27.

D. X-ray scattering factors

X-ray scattering factors provide through the
Fourier transform of the charge density, a direct
measure of the ground-state electronic charge dis-
tribution in the solid. First-principles calculations
of this quantity for diamond and boron nitride are particularly interesting because: (i) The (222) re-Qection, called "forbidden" for diamond is zero
for a homonuclear tetrahedral compound when the
crystal density is assumed to be given by a super-position of spherical atomic densities. Its deter-
mination furnishes a direct measure of the devia-

tion of the crystal density from spherical symme-try around each atomic site. (ii) The magnitude of the (200) reflection in BN (absent in diamond) yields an important measure of the asymmetry of the charge density since it corresponds to the Chfference in the single-site atomic structure fac-
tors.

Table II presents the x-ray scattering factors obtained in the present exchange and correlation model, the observed values,

"

the results of Eu-

wema et al.~ obtained in a crystalline Hartree-
Fock model, and, for comparison, the values ob-tained by a simple superposition model.
The main conclusions that can be drawn from this

study are: (i) The difference between the values of the (222) reflection calculated in the direct cry-stal and atomic superposition models is somewhat smaller in BN than that obtained in diamond (0, 10e

and 0.14e,

"

respectively) and indicates a some-
what smaller nonspherical character of the site charge distribution in BN. (ii) The strong (200) reflection observed in BN suggests substantial charge polarization in this system. However, the rough agreement with this value obtained already from a superpositron of neutral atom densities indicates that actual large charge tmnsfer between the two sublattices (as opposed to overlap of the corresponding wave function) cannot be inferred from the size of the observed reflection. (iii) The local density calculation of the scattering factor is in very good agreement with expex iment; for al-most all reflections, the agreement is within ex-
perimental error. By contrast, the HF crystal
results do not show the same degree of agreement. It is noted however that our calculated value for the

(222) reflection is somewhat too high, indicating that our LDF representation of the crystal density is too anisotropic, relative to the superposition limit.

E. Behavior under pressure and cohesive properties

To simulate the effect of pressure, we have cal-culated the band structure for a series of 9 differ-ent lattice constants between 3.40 and 3.85 A. The

calculated results shown in Fig. 11 indicate that the
band levels can be grouped into three categories according to their behavior:
(a) The energies of the valence bands decrease substantially with decreasing lattice constant and fo11ow different slopes for the various band states. There appears to be a direct correlation between the amount of 2s character in these bands and their

pressure derivative: in the lower valence band (VB1) the pressure derivative [defined as (de/dP} = -K(de/din V)], with the volume compressibility
Z approximately 0.24 x 10 ~ dyn/cm')' ranges from
5.4 x 10 '

eV/bar at 1;,„(54%N 2s snd 46% B 2s}
to 3.6 & 10 '

eV/bar at X, „(64%N 2s, O%%d B 2s).
For the higher group of valence bands (VB2) which have substantially less 2s character (cf. Fig. 8),. the pressure derivative ranges between 2.3 & 10 and 3.6 && 10~ eV/bar. This behavior stems from

the stronger lattice constant dependence of the 2s Hamiltonian matrix elements compared with the 2P
elements. Denoting such a dependence by H„P (k}
-A R

" where p,

,

v denote Bloch orbitals and 0, P
denote atoms, we find at I n= 5.4 for H„;„,n
= 4.0 for H2,'~„and n= 4.8 for H~~z~ compared
with n ~0.5 and n =0.2 for 8%T /Xi9 9Xi9 7224 152.62 548.a85.92

ex-

2040 ALEX ZUNGER AND A. J. FREEMAN 17

0—

L 3p

I,c

"IS,c
xi,c

-l0—
ls, v
Lw,v

IL

4J -l5— K

LLi

"S,v

-20—

x(„
L I,v

constant variation of the valence band eigenvalues is substantially stronger than that

17 AB INITIO SELF-CONSISTENT STUDY OF THE ELECTRONIC...

binding energy (mainly due to the slow convergence
of the total energy integrals with the number of
Diophantine points) is 0.5 eV.] The experimental
value for this quantity is estimated to be 13 eV/
pair.

"

[In our previous