SELF-CONSISTENT LCAO CALCULATION OF THE.

AI, E X ZUWGKR

Eug(k) g

eik (Ru-Rp)

x(X,(r —R, —d) ~E~X,(r —R„—1(())

-=pe" E"(O,n),

S up(k) g

eik (Ru-RP3

x (X„(r—R, —d)~X,(r —R —d,))

—P

eik R„Su~ l((0 n)

where R, is the position vector of the origin unit cell and E,",

,

(P0,)nand S ~P(0, n) are the matrix
elements of the Hartree-Pock operator F and the unity operator, respectively.
The secular equations [Eq. (3)] are solved by applying the Lowdin orthogonal transformation' to the basis Bloch functions followed by a direct. diagonalization of the orthogonal eigenvalue equa-tions. The resulting wave functions are subjected to a Lowdin charge analysis.

"
The elements

of the charge matrix are computed by

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lifted due to the different crystal-field screening in the various axial directions. Penetration effects of an atomic orbital on a given center into the screened field of other nuclei were shown to
lower the

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Huckel method yields good results, as previously demonstrated.

"

However, when lattice imperfec-
tions are present (see II),

"
iterations towards

self-consistency substantially change the final charges and the energy

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iteration cycle due to charge rearrangement in all the oceuPied 0+@ bands in the Brillouin zone. This is a distinct improvement over both non-self-consistent all-valence electron methods"

"

and
&-electron models.

""

III. RESULTS

A. Band-structure

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TABLE I. Comparison between experimental and calculated interband transitions for graphite. Energies given in
ev. E J.c and F. ~~ c denote polarization with

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60—

m. —bands

Q2„

g

0
O

O

60—

cr- bands

0
-50 -24 -IS -12

Energy {eV)

FIG. 5, Partial density of states of graphite.

of o.-g band overlap at the zone center are given in Table III. Coulson's" analysis of the soft

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TABLE IV. Characteristic features of the valence density of states in graphite. Energies measured relative to the Fermi level, iri eV.

Exper imental
feature Energy

Theoretical
assignment
(Present work).

Energy
(present
work)

Painter
and
Ellis

Bassani and
Par ravicini

&-band peak

Top of 0
- valence band

0-band peak

Sharp peak
Local minima
SmaH peak

Flat region
Bottom of
valence band

4c

4cl

8+1d

13.8, 13.0
12-13.8
17'

17-20

Q2„saddle point
z+

Q&, saddle point

9+&„saddle point
deep near I'+3

Q+ ~+

2.5

7.2

13.1
13~ 6
16.2

17—21

21 ~ 2

45

7' 5

14.2
14.0
15 ~ 5

- 13-15

19.3, 20.7 ~

5.5

11~ 3
12.5
13.3

- 12-14

13.8

'Reference 77.
Reference 76.

K-emission spectra, Ref. 30.
X-ray photoemission, Ref. 34.

'X-ray photoemission, Ref. 33.
X-ray emission spectra, Ref. 32.
5Reference 35.

density of states, the Q'" peak is more intense. Examination of the calculated unit cell charges at the Q,'„point [(q", (k,j)+q", (k,j)] (see Appendix A) reveals 24/o 2s character and 76% 2p character. The Q' state, on the other hand, around which a high density of states is accumulated, is a pure 2P state. Using the estimated cross section ratio for 2s and 2p atomic contributions to the spectral
intensity (o„/o»= 13),'" one obtains that the Q;„
state should indeed reveal higher intensity than the Q'" peak, in agreement with experiment. Our assignment agrees with that of

mini37 Tf 120.87 643.6 Td (cell)Tj ET BT Xi9 8.06 T3 356 Tf 393r.ald (1)Tj ET BT /Xi9 i9 9.787.2 33057 533.23'd (13.)Tj ET BT /X5T

peak, The Q, isvalence should

the

Q'"

(k,

X-ray

assignment

ratiovalence

pure

peakQ,

Our

Fermi 4c

valence

on

76%

high
SmaH hand, the on

4c

state, reval point work) to peak SmaH level, the cell2P valence 35. 4cassignment peak assignment measured unit of region 3 4c

Fermi
4c

Energy(Present

the onpoint

level, 35.level,

Energy unit of

e

14.

4c

onpeak st Energy

unit

of the SmaH reveal higherpeak

Energy the

Q;„

'"

21

state, obtains the peak

other

assignmentthe

states, measured

stateson

peak

state, 5

- 12-14peak,

4coX 1 T Q m E

S s n5c

ray

k,

as2Tj ET BT /Xi9 9.i9 9.69 462.4 533 68.06 Tdk, as(of)Tj ET BT BT /Xi 9.165 5352.89 380.43 413.vel, cell

states

level, valnce 3D Tsselle a

sta (th [(q as 13. jX-ray obeVk, 071.urXXi9 6911757(on)530546405 124.2506 T ET 2T6ee2T /XT /Xi9 10Tf 385.67i9 8.2147lence opnda(Energy)Tj E4 Tf .69 52.49BT /94 4iold (1)Tj ET BT /Xi E4 Tf .4 7Tf .49BT /94 r.al 314.73 Td (a)Tj ET 9 8.84 7 Tf 1.49B8.9 480.59 Td (states)Tj ET Bi9 Tf f 9945 09 466425.54 T2„saddle Iighboro deep the estimated the '„point

touthe.of

Fermi Alphur assignmentE

ratio35.

topeak

estimated

state jEnergy onthe 4cTj ET BT /Xi9 8.T BT /43 T.47.5 23035 358valu Td (measured)Tj T7 /Xi99 Tf62i8367 34cor4.04 6d (to)Tj ET BT /Xi9 8.T Bi9 76T7 /T2.58153 378.68 Td (Fermi)Tj ET /X29 89 9 85580.4/T2.58153 3d (estimated)Tj EXi9 9.9 36992i83666425.5 ('„point)Tj ET BT /699i9 838

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l00% 2s

50%

I00%2p

FIG. 6. 2s character of the three lowest valence 0

bands along P-I -Q

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The latter energy has been calculated by Goldfarb and Jaffe'" to be 6.93 eV and by Jordan and Long-uet-Higgins' to be 7.61 eV. These yield cohesive energies E, of 8.73 and 8.05 eV, respectively. It is interesting to observe that using the two special k points for the hexagonal two-dimensional BZ calculated by Cunningham,

"

instead of the 180 k

points in the irreducible zone, we obtained an error of only 1.1% in the cohesive energy

an

638 ALEX ZU1VGER

band splitting (Er- —Er+) is a measure of the

2Q 3g

departure

640 ALE X ZUNGER 17

G. Glocker, J. Chem. Phys. /Xi1522T BT /Xi14 12.73 8.776.9 701.411 Td (Phys.)159 BT /Xi14 9.68 Tf 116.9 716.831 Td 3X1954)T BT /Xi14 8.38 T6 (X

.66d (Chem.)Tj ET BT /Xi14 8.5 Tf 1261.56268454.66d 6Phys.

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I. Shavjtt, in Methods in Computationa/ Physics, edited by B. Alder, S. Frenbach, and M. Rotenberg (Academic, New York, 1963), Vol. 2, p. 1.
S. Srebrenic, H. %einstein, and R. Paunz, Chem. Phys. Lett. 20, 81 (1973).
F. E. Harris, L. Kumar, and H. Moukhorst, Phys. Rev. B 7, 2850 (1973).
3J. Delhale and J-. M. Andre, in Proceedings of the NATO Advanced Study.Institute on'the Electronic Structure of Polymers and Molecules, Namur, 1974 (unpublished)
G. E. Bacon, Acta Cryst. 4, 558 (1951).

V. S. Fomenko, Handbook gf Thermionic I'roperties (Plenum, New York, 1966).
~ ~U. Gelius, Electron Spectroscopj, edited by D. A. Shirley (North Holland, Amsterdam, 1972), p. 314. 127C A Cou].son Valence (Oxford U. P., Oxford, 1961), p. 270.
I. J. Goldfarb and H. H. Jaffe, J. Chem. Phys. 30, 1672 (1959).
~~OP. C. H. Jordan and H. C. Longuet-Higgins, Mol. Phys. 5, 121 (1962).
~3 J. Abrahamson, Carbon 11, 337 (1973).
J. C. Phillips, Rev. Mod. Phys. 42, 317 (1970).