VOLUME 50, +UMBER 16 PHYSICAL REVIEW LETTERS 18 APRIL 1/83

One-Electron Broken-Symmetry Approach to the Core-Hole Spectra of Semiconductors

Alex Zunger
Solar Energy Research Institute, Golden, Colorado 80401, and Department of Physics,
University of Colorado, Boulder, Colorado 80309 (Received 22 November 1982)

It is shown that in contrast to band theory, a self-consistent one-electron model with
broken symmetries (crystal orbitals are not constrained to be Bloch periodic) provides a physical description of core-ionization, core-exciton, and core-to-conduction-band transition energies in semiconductors. Application to GaP shows that a hitherto unrec-ognized factor—the screening of the core-hole self-energy by the electron orbit—can explain many of the outstanding puzzles in core-hole spectra.
PACS numbers: 71.35.+z, 71.50.+t, 78.20.-e

With the recent advent of continuous-radiation

light sources in the far uv, core spectroscopy
has become a major characterization technique
for studying the electronic structure of bulk' '
and surfaces' of semiconductors. Experimental-
ly, the core-exciton binding energy b has been
defined' '

[c.f., Figs. 1(b) and l(c)] as the dif-
ference 5=Ec c&B- E,„between the core (C)-to-vacuum ionization energy E c cB~ [referred to the relevant conduction-band minimum (CBM)] and the lowest optical excitation energy F-,„from a core level to a final electron orbit (exciton state). Ec zB~ is determined by adding the value of the optical band gap E, to the spin-orbit-corrected
core-to-vacuum ionization energy Ec vB~ [ref-
erred to the valence-band maximum (VBM)], as
measured in photoemission. ' The detailed data
on a wide range of heteropolar semiconductors' '
present some intriguing puzzles. First, the measured values of 6 for cations, e.g., GaP [0.238+ 0.1 eV (Ref. 2, 4) or 0.6 eV (Ref. 1)J, InP [)0.27 eV (Ref. 3)], PbSe [1 eV (Ref. 6)], is -10
times larger than that of valence excitons or donor impurity levels which evolve from the
same conduction-band extrema. ' A broad range
of shallow-donor tight-binding" and

VOLUME 50, NUMBER 16 PHYSICAL REVIEW LETTERS 18 APRIL 1983

sistent calculation for core-hole excitations in
GaP, treating directly screening, polarization,
and relaxation effects for both the core hole and
the electron gap states. It explains the paradox-
ical features of core-hole spectra in semicon-
ductors by a hitherto unrecognized effect~he reduction 6, in the core-hole self-energy in exci-tation relative to ionization through additional relaxation-polarization by the electron orbit. Hence,

VOLUME 50, +UMBER 16 P HYSICAL REVIEW LETTERS 18 APRiL 1$8$

C
0
0.06
O
C

o.o4

0.02

0.00

-0.02

0.0 0.5 1.0 1.5 2.0

VoLUME 50) NUMBER 16 PHYSICAL REVIEW LETTERS 18 APRIL 198$

variations 5,(E) in the core-hole self-energy.
The model provides simple rules for estimating
chemical trends in 5 from information about q(F).
It explains why surface-cation core excitons have
a larger binding energy than in the bulk' in terms
of the strong cation character of the dangling-bond electron states. In contrast, this theory predicts that anion core excitons will be shallow-er (5 = li,) when the final orbital has little ampli-tude on the anion (e.g.,

the I;, state). This is
consistent with the absence of Sb (4d) core exci-tons in GaSb (Ref. 7a) and As (Sd) excitons in
GaAs, '

in contrast to the rather deep cation
core excitons in these systems. Likewise, the large excitonic shift of the X, point in InP rela-tive to GaP (Ref. 3) can be naturally explained by the larger cation content of the wave function in the former case.

I gratefully acknowledge useful discussions with D. A.spnes, M. L. Cohen, R. Enderlein, W. Harrison, and S. Kelso.

'P. Thiry, Y. Petroff, R. Pinchaux, J. R. Chelikow-sky, and M. L. Cohen, Solid State Commun. 20, 1107 (1976).
'D. E. Aspnes, C. Q. Olson, and D. W. Lynch, in Proceedings of the Thirteenth InternationaL Conference on the Physics of Semiconductors, Rome, 1976 (North-Holland, Amsterdam, 1977), p. 1000.
' D. E. Aspnes, in I estkorperprobLeme XVII, edited by J. Trensch {Vieweg, Braunschweig, 1977), p. 235. "D. E. Aspnes, C. Q. Olson, and D. W. Lynch, Phys. Rev. B 12, 2527 (1975).
S. M. Kelso, D. E. Aspnes, C. G. Olson, D. W. Lynch, R. E. Nahory, and M. A. Pollack, Jpn. J. Appl. Phys. 19, 327 (1980).
4D. E. Aspnes, S. M. Kelso, C. G. Olson, and D. W. Lynch, Phys. Bev. Lett. 48, 1863 (1982), and private
communication.

'S. M. Kelso, D. E. Aspnes, C. Q. Olson, D. W. Lynch, and D. Finn, Phys. Rev. Lett. 45, 1032 (1980). Q. Martinez, M. Schluter, and M. L. Cohen, Phys. Rev. B 11, 660 (1975).
7'D. E. Eastman and J. L. Freeouf, Phys. Rev. Lett. 34, 1624 (1975).
7 R. S. Bauer, J. Vac. Sci. Technol. 14, 899 (1977).
8L. Ley, R. A. Pollak, F. R. McFeely, S. P. Kowalc-zyk, and D. A. Shirley, Phys. Rev. B 9, 600 (1974). ~See recent reviews: M. Altarelli, J. Phys. (Paris), Colloq. 34, C4-95 (1973); F. Bassani, Appl. Opt. 19, 4093 (1980).
'OH. P. Hjalmarson, H. Buttner, and J. D. Dow, Phys. Rev. B 24, 6010 (1981).
"S.T. Pantelides, Solid State Commun. 16, 217 (1975); M. Altarelli, Phys. Rev. Lett. 46, 205 (1981).
' F. Bechstedt, R. Enderlein, and M. Koch, Phys.
Status Solidi 99(b), 61 (1980).
' A. Quattropani, F. Bassani, G. Margaritondo, and
Q. Tinivella, Nuovo Cimento B 51, 335 (1979); Q. Stri-nati, Phys. Rev. Lett. 49, 1519 (1982).
' A. Zunger, Phys. Rev. B 22, 649 (1980).
~ The local-density formalism