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d-band excitations in II-VI semiconductors: A broken-symmetry approach

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based calculations underestimate the binding energies of
the cation d-band relative to photoemission results
by about 3 eV (Ref. 27) [Table I (Refs. 22 —24, 26, 28 —31)]
(In contrast, Hartree-Fock band calculations overesti
mate the binding energy by about 2 eV.) The large LDA
error in the position of the d band has three relevant
consequences: first, the bulk photoemission peak posi-
tions are poorly explained by such calculations. Second,
the interpretation of core absorption measurements of
nanostructures and surfaces used as probes to local
structural effects is impeded, and third, the placement by
the LDA of the cation d bands too close to the VBM

leads to an artificially strong coupling with the anion p
states. This leads to an underestimation of the band gap,
and to an overestimation of exchange-coupling in mag-
netic systems.
Attempts to correct the LDA underestimation of d-band energies met with onLy partial success. ' ' ' The
model GR' calculation of Posternak et al. for ZnO
lowers the d-band energy from the LDA value of Ev~M —5.4 eV to Ev~M —6.4 eV, still considerably above
the experimental value of EvBM —7. 8 eV. The quasi-
particle calculation of Zakharov et al. on IIB-VI com-pounds uses a pseudopotential with d orbitals placed in the core. Naturally, this potential does not produce any d
band. An artificial increase in the coefticient of the LDA

exchange potential (the "Xa method") displaces the d band to deeper energies, however, at the expense of wor-sening the agreement with experiment on other proper-ties. Simple model corrections to Hartree-Fock band
theory shift the d band up (from EvtIM —10.8 eV to
EvBM —10. 1 eV in ZnS), leaving it still too deep relative to the measured value of Ev~M —9 eV.
In this paper, we present a method that systematically
corrects the LDA error in all-electron d band positions.
For Zn-based IIB-VI semiconductors, in particular, we

obtain the d-band binding energies to within 0.5—0.8 eV of the experimental values. Thus, an approximate 80%
improvement over the conventional LDA approach is
achieved.

II. BROKEN SYMMETRY
AND SELF-INTERACTION CORRECTION

The physical origin of the underestimation of core state
binding energy by the LDA is understood reasonably
well. It consists of four principal factors: (i) the ex-
istence of a spurious self-interaction '

in the LDA ei-

genUalues, which leads to the failure of Koopman's
theorem; (ii) atomic-orbital relaxations in the self-
consistent solution; (iii) solid-state effects, '

such as

hole-induced hybridization and atomic relaxation ("self-
trapping"); and (iv) many-body correlation effects that are beyond the statistical LDA description.
Effects (i) and (ii) can be described within the formal-
ism of Perdew and Zunger: The electronically relaxed
total-energy difference AE" between the system with a
core hole in state a and the system in its ground state can be written as

bELDA ~ —bELDA ~

+yLDA

~LDA( 1)+[

IILDA+ yLDA]

Here, AE „„„l is the electronically "unrelaxed"
total-energy difference computed with ground-state wave
functions for both initial and final states, X is the

correction due to electronic relaxation, II"
—=bE ~„„„I+a (1) is the non-Koopman's correc-
tion to the LDA, and e (1) denotes eigenvalues calculat-
ed self-consistently with occupancy 1. Similarly, in the
self-interaction corrected (SIC) formalism,

bESIC

~ —bESIC + BASIC a rel a unrel a

~SIC( I)+[ 11 SIC + y

SIC]

(2)

ao (Experiment)

E„(LDA)
Ed (Experiment)
Ed (Broken symmetry)
6Ed

'Reference 28.
Reference 29.
'Reference 30.
Reference 31 ~
'References 22—25.
Reference 26.

ZnO

4.566'
5.4
7 8c
8.62
3.22

ZnS

5.409"
6.37
8.98'
9.57
3.20

ZnSe

5.668'
6.76
9.38'
10.04
3.28

ZnTe

6.38
7.46
9.80'
10.33
2.87

0

TABLE I. Experimental lattice constants (in A) and average
3d-band binding energies Ed relative to the VBM (in eV) for
Zn-based IIB-VI zinc-blende compounds. Present results are
relativistic. Ed(LDA) is EvBM —e3d (1) (all d bands fully occu-
pied), while Ed (broken symmetry) is EvBM e3d (

2

), where
half of an electron is placed in one of the d bands of a (ZnS)& su-percell and the result is iterated to self-consistency. Here, 5Ed =Ed(broken symmetry) —Ed(LDA) is the shift due to lo-calization.

gESIC i BASIC( 1) ELDA( &

)

2

(3)

rather than —e" (1) used in standard one-electron
band-structure calculations. Thus, eff'ects (i) and (ii) can

be accounted for by computing self-consistently e"DA( —,

'

).

where the symbols have the same meaning as in Eq. (1),
except that all quantities are obtained from a self-
consistent solution to the SIC problem.
Perdew and Zunger showed that (a) while in the
LDA, the combined H +X" correction is very
large, in the SIC formalism, a special cancellation leads
to II ' +X ' =0. (b) The relaxed total-energy
differences satisfy b,E „I=b,E '

~ „I. (c) Finally,
Slater has shown that in the LDA,.the relaxed energy
difference can be approximated well by the eigenvalue
computed self-consistently at the intermediate occupa-

tion, i.e., b E ~ „I=—e ( —,

'

) ("transition state").
From results (a)—(c), we conclude that the ionization en-
ergy corrected for effects (i) and (ii) is

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To test the accuracy of the "transition state" method for
solids, we have calculated bE ~„I and

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eLDA(

i

)

eLDA(

I

)

)IILDA+ yLDA ~a 2 a A a

)

The non-Koopman

( II

) and electronic relaxation
(X"

) terms are large if orbital

a is localized. In this

case, the eigenvalue spectrum of the solid will exhibit

a

"splitoff" eigenstate, distinct from the states of the remaining

X

—1 states. This state is now an eigenstate of
the bulk, unlike the initial input that was constructed by placing

a hole on

a specific atomic site. In all subsequent
self-consistency iterations one places the hole in this split-off bulk eigenstate (irrespective of its degree of

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sizes for ZnO.
Using a supercell approach, one needs to maintain
charge neutrality in the unit cell. In the present calcula-
tion, we smear the extracted electron of charge q over the
unit cell, forming a uniform jellium background with
p~=q/V„&&, where V„&& is the cell volume. We have tested, in the case of ZnS with an eight atom cell, the sen-sitivity of the results to such an approximation by placing the electron, instead, in the bottom of the conduction
band. To within 0.05 eV, the two different approaches
yield identical d-state binding energy.
Finally, we find that to obtain accurate d-state binding energies, relatively large basis set kinetic energy cutofFs are needed (larger than those used for testing supercell size effects). To achieve a 0.01 eV accuracy, the neces-sary cutoffs are 24, 22, 18, 18, Ry, respectively, for ZnO, ZnS, ZnSe, and ZnTe, as inferred from d' ground-state
calculations. To determine the core-hole energies, we
used the 16 atom supercell. Corrections, due to finite cell
size and cutoff, are added. Corrections due to VBM
spin-orbit splittings of 0, 0.02, 0.13, 0.30 eV for ZnO,
ZnS, ZnSe, and ZnTe, respectively, were also added.

B. The e8'ects of atomic relaxation

We have examined the effects of atomic relaxations due to the existence of a core hole. The calculation was car-ried out for ZnO and ZnS with a 16 atom cell. The creation of the core hole leads to a reduction of the
muffin-tin charge of the Zn atom carrying the hole. As
expected, the four nearest-neighbor 0 (or S) atoms tend
to relax inwards to reduce the overall kinetic energy
(force = 0.030 Ry/A). The next shell Zn atoms also feel the presence of the core-hole (force =0.021 Ry/A) and
relax accordingly. The degree of relaxation is, however,
small: 0.013 A (or 0.64% of the bond length) for the
nearest-neighbor 0 atoms and 0.009 A for the next-
nearest-neighbor Zn atoms for ZnO. This leads to a
small relaxation energy of only 0.017 eV. The forces ex-perienced by the Zn atom in ZnS are even smaller than those for ZnO. Based on these observations, we conclud-
ed that hole-induced atomic relaxations have little effects

on the core hole binding energy of the Zn 3d states.

the oxygenlike VBM could also lead to hole localization effects. This would bring the calculated results for ZnO into a better agreement with photoemission experiments. No such calculation has been performed.
To see the effect of hybridization with the host crystal, we have plotted in Fig. 2 the change in total charge densi-ty due to self-consistent

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agreement with their LDA result. In contrast, our
broken-symmetry solution gives EvBM —8.62 eV in better
agreement with the experimental value of EvBM —7.8
V

22-25

A related subject regarding core hole is the splitoff ex-citon state below the conduction band minimum (CBM). Depending on the degree of localization of the potential created by the core hole, the energy of the splitoff state can be quite large, resulting in spatially localized defect-
like state. However, in our cases, the screened core-hole
potentials are not strong enough to create such a deep ex-
citon state. The results for ZnO and ZnS with a 32 atom

cell showed that to within 0.04 eV accuracy, there is no state such splitoff state

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