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d-band excitations in II-VI semiconductors: A broken-symmetry approach to the core hole

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Local-density approximation (LDA) band-structure calculations place the 3*d* band of zinc-blende ZnO, ZnS, ZnSe, and ZnTe at 5.4, 6.4, 6.8, and 7.5 eV below the valence-band maximum (VBM), while photoemission measurements place them at 7.8, 9.0, 9.4, and 9.8 eV below the VBM, respectively. We show that this ~3-eV LDA error can be accounted for using a "broken symmetry" band-structure approach. In this approach, a *d* core hole is placed in an impuritylike splitoff *d* subband resulting from the creation of the hole on a *particular* Zn sublattice. Self-consistent solutions to such a constrained LDA problem reveal that the final hole state is sufficiently localized to trigger a self-interaction correction of 3–4 eV, needed to explain the discrepancy with experiment. This 3–4 eV shift is reduced, by screening effects, from the 9.7-eV value in a free Zn atom. Finally, we calculated the binding energy E_{Mn} for Mn 3*d* states in ZnTe:Mn and the effective Coulomb interaction parameter U_{eff}. Significant improvements over the results of local-spin-density calculations were found. The calculated $E_{\mathrm{Mn}} = E_{\mathrm{VBM}} - 3.93$ eV and $U_{\mathrm{eff}} = 6.85$ eV are in good agreement with experiments.

I. INTRODUCTION

Wide gap IIB-VI semiconductors are being explored for optical and electro-optical applications,[1,2] largely because they have direct band gaps in the bright-color visible range, and because, unlike the alkaline-earth IIA-VI compounds (CaTe, BaSe), they can be doped and thus form electrical junctions. IIB-VI semiconductors are distinguished from IIA-VI, III-V, and elemental IV materials by having cation *d* bands *inside* the principal valence band—around 8–10 eV below the valence-band maximum E_{VBM}, and 2–4 eV above the band minimum.[3] In contrast, III-V compounds have their *d* states at much deeper energies: $E_{\mathrm{VBM}} -$ (17–20) eV,[3,4] while the Ge *d* band occurs at about $E_{\mathrm{VBM}} - 29$ eV. In classical theoretical descriptions of the electronic structure of IIB-VI compounds,[5-10] the d^{10} closed-shell orbital was assumed to be chemically inert. This view was anchored in a large body of chemical evidence,[11] suggesting that Zn, Cd, and Hg do not form high-coordination *p-d* or *s-d* bonds characteristic of the chemically active *d* orbital transition-metal compounds. Consequently, in pseudopotential descriptions,[5-10] the occupied *d* orbitals of Zn, Cd, and Hg atoms were classified as "core" and thus were not only "frozen," but were also pseudized away, leading to a band structure lacking the *d* band. Wei and Zunger[3] pointed out that even though the d^{10} orbitals do not form *bonds* in IIB-VI compounds, they do form a *band* that can significantly alter the principal sp^3 bonds via hybridization. This is so both because of (i) a "crystal potential effect" and (ii) an explicit "wave-function effect:" *first,* the d^{10} charge density does not perfectly screen the $-10/r$ nuclear attraction term. The imperfectness of the screening leads to a net *attractive* potential correction. In fact, early[12] construction of first-principles nonlocal pseudopotential for Zn showed that the *s* and *p* pseudopotentials become much deeper if the Zn 3*d* is treated as part of the valence, rather than the core. *Second,* the *d* orbitals in a molecule or a solid can mix quantum mechanically with the orbitals of the other sublattices (e.g., anion *p*-cation *d* hybridization in II-VI compounds), leading both to energy-level repulsion and to orthogonality corrections. Wei and Zunger[3] have shown that the combined potential and wave-function effects of the d^{10} orbitals lead to a large *increase* in lattice constant and bulk moduli, and to a significant *decrease* in the cohesive energy, spin-orbit splitting, and direct band gaps. While some of the "potential effects" associated with pseudizing away the *d* orbitals (e.g., the too small lattice constants) can be rectified, in part, by different construction of the pseudopotential (e.g., adding the "core correction"[13]), the "wave-function effects" cannot be accounted for without explicit inclusion of the *d bands.* Examples for such quantum wave-function effects of *d*-state mixing include the reduction of the VBM spin-orbit splitting Δ_0 in IIB-VI and chalcopyrite[3,14] compounds (*d* mixing reduces Δ_0); the occurrence of an *inverted* order of spin-up vs spin-down states (negative exchange splitting) in MnTe,[14] the inverted order of crystal-field splitting Γ_{15} and Γ_{12} states in II-VI compounds, the reduction of band gaps of chalcopyrite relative to II-VI compounds,[15] and the reversal of the order of band gaps[3] $E_g(\mathrm{ZnO}) < E_g(\mathrm{ZnS})$ relative to systems with inactive *d* bands [e.g., $E_g(\mathrm{BaO}) > E_g(\mathrm{BaS})$].

A more complete description of the electronic structure of IIB-VI semiconductors incorporates an explicit cation *d* band. Theoretical methods that include *d* states in II-VI compounds range from the early[16] all-electron extended basis set self-consistent linear combination of atomic orbitals calculations, to mixed basis methods,[17,18] linearized augmented plane wave (LAPW) methods,[3] Gaussian orbital approaches,[19,20] and the pseudopotential method with extended plane-wave basis set.[21] Unfortunately, all of these local-density approximation (LDA)

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based calculations *underestimate* the binding energies of the cation *d*-band relative to photoemission results[22–26] by about 3 eV (Ref. 27) [Table I (Refs. 22–24, 26, 28–31)] (In contrast, Hartree-Fock band calculations[32] *overestimate* 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 positions are poorly explained by such calculations. Second, the interpretation of core absorption measurements of nanostructures[33] and surfaces[34] 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,[3] and to an overestimation of exchange-coupling in magnetic systems.[35]

Attempts to correct the LDA underestimation of *d*-band energies met with only partial success.[9,20,32,36] The model *GW* calculation of Posternak *et al.*[36] for ZnO lowers the *d*-band energy from the LDA value of $E_{\rm VBM}-5.4$ eV to $E_{\rm VBM}-6.4$ eV, still considerably above the experimental value of $E_{\rm VBM}-7.8$ eV.[22–25] The quasiparticle calculation of Zakharov *et al.*[9] on IIB-VI compounds uses a pseudopotential with *d* orbitals placed in the *core.* Naturally, this potential does not produce any *d* band. An artificial increase in the coefficient of the LDA exchange potential[20] (the "$X\alpha$ method") displaces the *d* band to deeper energies, however, at the expense of worsening the agreement with experiment on other properties. Simple model corrections to Hartree-Fock band theory[32] shift the *d* band *up* (from $E_{\rm VBM}-10.8$ eV to $E_{\rm VBM}-10.1$ eV in ZnS), leaving it still too deep relative to the measured value of $E_{\rm VBM}-9$ 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.

TABLE I. Experimental lattice constants (in Å) and average $3d$-band binding energies E_d relative to the VBM (in eV) for Zn-based IIB-VI zinc-blende compounds. Present results are relativistic. E_d(LDA) is $E_{\rm VBM}-\epsilon_{3d}^{\rm LDA}(1)$ (all *d* bands fully occupied), while E_d (broken symmetry) is $E_{\rm VBM}-\epsilon_{3d}^{\rm LDA}(\frac{1}{2})$, where half of an electron is placed in *one* of the *d* bands of a $({\rm ZnS})_N$ supercell and the result is iterated to self-consistency. Here, $\delta E_d = E_d$(broken symmetry) $-E_d$(LDA) is the shift due to localization.

	ZnO	ZnS	ZnSe	ZnTe
a_0 (Experiment)	4.566[a]	5.409[b]	5.668[c]	6.38[d]
E_d (LDA)	5.4	6.37	6.76	7.46
E_d (Experiment)	7.8[e]	8.98[f]	9.38[f]	9.80[f]
E_d (Broken symmetry)	8.62	9.57	10.04	10.33
δE_d	3.22	3.20	3.28	2.87

[a] Reference 28.
[b] Reference 29.
[c] Reference 30.
[d] Reference 31.
[e] References 22–25.
[f] Reference 26.

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.[4,37–42] It consists of four principal factors: (i) the existence of a spurious self-interaction[37,38] in the LDA *eigenvalues,* which leads to the failure of Koopman's theorem; (ii) atomic-orbital relaxations in the self-consistent solution; (iii) solid-state effects,[4,37,40,41] such as hole-induced hybridization and atomic relaxation ("self-trapping"); and (iv) many-body correlation effects that are beyond the statistical LDA description.[42]

Effects (i) and (ii) can be described within the formalism of Perdew and Zunger:[38] The electronically relaxed total-energy difference $\Delta E_\alpha^{\rm LDA}$ between the system with a core hole in state α and the system in its ground state can be written as

$$\begin{aligned}\Delta E_\alpha^{\rm LDA}|_{\rm rel} &\equiv \Delta E_\alpha^{\rm LDA}|_{\rm unrel}+\Sigma_\alpha^{\rm LDA}\\ &= -\epsilon_\alpha^{\rm LDA}(1)+[\Pi_\alpha^{\rm LDA}+\Sigma_\alpha^{\rm LDA}]\ . \qquad (1)\end{aligned}$$

Here, $\Delta E_\alpha^{\rm LDA}|_{\rm unrel}$ is the electronically "unrelaxed" total-energy difference computed with *ground-state* wave functions for both initial and final states, $\Sigma_\alpha^{\rm LDA}$ is the correction due to electronic relaxation, $\Pi_\alpha^{\rm LDA} \equiv \Delta E_\alpha^{\rm LDA}|_{\rm unrel}+\epsilon_\alpha^{\rm LDA}(1)$ is the non-Koopman's correction to the LDA, and $\epsilon_\alpha(1)$ denotes eigenvalues calculated self-consistently with occupancy 1. Similarly, in the self-interaction corrected (SIC) formalism,

$$\begin{aligned}\Delta E_\alpha^{\rm SIC}|_{\rm rel} &\equiv \Delta E_\alpha^{\rm SIC}|_{\rm unrel}+\Sigma_\alpha^{\rm SIC}\\ &= -\epsilon_\alpha^{\rm SIC}(1)+[\Pi_\alpha^{\rm SIC}+\Sigma_\alpha^{\rm SIC}]\ , \qquad (2)\end{aligned}$$

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[38] showed that (a) while in the LDA, the combined $\Pi_\alpha^{\rm LDA}+\Sigma_\alpha^{\rm LDA}$ correction is very large, in the SIC formalism, a special cancellation leads to $\Pi_\alpha^{\rm SIC}+\Sigma_\alpha^{\rm SIC}\approx 0$. (b) The *relaxed* total-energy differences satisfy $\Delta E_\alpha^{\rm LDA}|_{\rm rel}\approx\Delta E_\alpha^{\rm SIC}|_{\rm rel}$. (c) Finally, Slater[43] has shown that in the LDA, the relaxed energy difference can be approximated well by the eigenvalue computed self-consistently at the intermediate occupation, i.e., $\Delta E_\alpha^{\rm LDA}|_{\rm rel}\approx -\epsilon_\alpha^{\rm LDA}(\frac{1}{2})$ ("transition state"). From results (a)–(c), we conclude that the ionization energy corrected for effects (i) and (ii) is

$$\Delta E_\alpha^{\rm SIC}|_{\rm rel}\approx -\epsilon_\alpha^{\rm SIC}(1)\approx -\epsilon_\alpha^{\rm LDA}(\tfrac{1}{2})\ , \qquad (3)$$

rather than $-\epsilon_\alpha^{\rm LDA}(1)$ used in standard one-electron band-structure calculations. Thus, effects (i) and (ii) can be accounted for by computing self-consistently $\epsilon_\alpha^{\rm LDA}(\frac{1}{2})$.

To test the accuracy of the "transition state" method for *solids,* we have calculated $\Delta E_\alpha^{\rm LDA}|_{\rm rel}$ and $-\epsilon_\alpha^{\rm LDA}(\frac{1}{2})$ for Zn core-hole excitation in ZnO and found that the difference between the two is less than 0.2 eV (2.5% of the total excitation energy of ~8 eV) for supercell size of 8 atom per cell or larger.

It is important to emphasize here that $\epsilon_\alpha^{\rm SIC}(1)$ and $\epsilon_\alpha^{\rm LDA}(1)$ can be extremely different. To illustrate this point and its physical content consider the breakdown of an LDA eigenvalue

$$\epsilon_\alpha^{\rm LDA} = \langle \chi_\alpha^{\rm LDA} | -\tfrac{1}{2}\nabla^2 + V_{\rm ps}^{\rm LDA} + V_{HXC}^{\rm LDA}[\rho] | \chi_\alpha^{\rm LDA} \rangle$$
$$\equiv \epsilon_{\rm ke}^{(\alpha)} + \epsilon_{\rm ps}^{(\alpha)} + \epsilon_{HXC}^{(\alpha)} \ , \tag{4}$$

to, respectively, orbital kinetic energy, pseudopotential, and screening (Hartree+exchange+correlation) effects. Here, χ_α and ρ are self-consistent LDA wave function and charge density, respectively, and $V_{\rm ps}$ is the LDA pseudopotential constructed from $\{\epsilon_\alpha^{\rm LDA}\}$ and $\{\chi_\alpha^{\rm LDA}\}$. In the SIC-LDA (quantities denoted by tilde), we have

$$\epsilon_\alpha^{\rm SIC} = \langle \chi_\alpha^{\rm SIC} | -\tfrac{1}{2}\nabla^2 + V_{\rm ps}^{\rm SIC} + V_{HXC}^{\rm SIC}[\tilde{\rho}] - V_H[\tilde{\rho}_\alpha] - V_X[\tilde{\rho}_\alpha] - V_C\tilde{[}\rho_\alpha] | \chi_\alpha^{\rm SIC} \rangle$$
$$\equiv \tilde{\epsilon}_{ke}^{(\alpha)} + \tilde{\epsilon}_{ps}^{(\alpha)} + \tilde{\epsilon}_{HXC}^{(\alpha)} - \delta_H^{(\alpha)} - \delta_X^{(\alpha)} - \delta_C^{(\alpha)} \ . \tag{5}$$

The first three quantities on the right-hand side of Eq. (5) have the same meaning as the respective quantities in Eq. (4), that they are calculated self-consistently with SIC wave functions,[39] while $\delta_H^{(\alpha)}$, $\delta_X^{(\alpha)}$, and $\delta_C^{(\alpha)}$ are, respectively, the self-Coulomb, self-exchange, and self-correlation corrections to orbital α. Here, $V_{\rm ps}^{\rm SIC}$ is the pseudopotential computed with self-interaction-corrected eigenvalues and wave functions.[39] For the $\alpha = 3d$ orbital of the $4s^2 3d^{10}$ Zn atom, one finds

$$\tilde{\epsilon}_{\rm ke} - \epsilon_{\rm ke} = 4.54 \text{ eV}, \quad \delta_H = -28.78 \text{ eV} \ ,$$
$$\tilde{\epsilon}_{\rm ps} - \epsilon_{\rm ps} = -1.84 \text{ eV}, \quad \delta_X = +16.48 \text{ eV} \ , \tag{6}$$
$$\tilde{\epsilon}_{HXC} - \epsilon_{HXC} = -0.84 \text{ eV}, \quad \delta_C = +0.79 \text{ eV} \ .$$

The self-interaction correction deepens the effective potential, leading to more localized self-consistent wave functions. We see that this leads to an *increase* in the (positive) orbital kinetic energy $\epsilon_{\rm ke}$ and to a *decrease* in the (negative) electron-ion pseudopotential energy $\epsilon_{\rm ps}$ and the HXC energy ϵ_{HXC}. Since the kinetic-energy term dominates, the LDA orbital energy goes *up* by 1.86 eV, due to wave function contraction. The removal of the (positive) self-Coulomb ("Hartree") energy δ_H and the removal of the (negative) self-exchange δ_X and self-correlation δ_C energies moves the orbital energy *down* by 11.59 eV. Hence, the net self-interaction correction to the eigenvalue is $\epsilon_{3d}^{\rm SIC} - \epsilon_{3d}^{\rm LDA} = -9.65$ eV, *which is ~6–7 eV too deep relative to what is needed to reconcile LDA band theory vs experiment in the solid (Table I).* This large "overshoot" of the atomic SIC effects must be partially corrected by solid-state effects on the core hole [effect (iii)]: dielectric screening in the solid replenishes part of the charge density of the hole.[4,37] Such solid-state effects can be introduced by solving variationally the SIC-LDA equations for a *solid,* as done by Svane *et al.*[44] Here we will consider a simpler and more approximate method that is able to treat self-consistently both self-interaction, as well as solid-state effects. We will ignore effect (iv) ("dynamic correlation") and attribute any difference that we find between theory and experiment to such corrections. As it will turn out, these effects amount to 0.5–0.8 eV (about 5–10% of the binding energy).

Our approach is based on the realization that the existence of a nonvanishing correction,

$$\Delta E_\alpha^{\rm SIC} + \epsilon_\alpha^{\rm LDA}(1) = -[\epsilon_\alpha^{\rm SIC}(1) - \epsilon_\alpha^{\rm LDA}(1)] + [\Pi_\alpha^{\rm SIC} + \Sigma_\alpha^{\rm SIC}]$$
$$\approx -[\epsilon_\alpha^{\rm LDA}(\tfrac{1}{2}) - \epsilon_\alpha^{\rm LDA}(1)] \ , \tag{7}$$

to the LDA band eigenvalue stems from spatial localization of state α. Bagus and Schaefer[45] have indeed realized early on that computing the Hartree-Fock 1s ionization energy of the O_2 molecule by localizing the hole on *one* atom (thus, using the $C_{\infty v}$ symmetry) produces much better agreement with experiment than extracting the electron from the canonically delocalized molecular orbital composed of both atomic sites ($D_{\infty h}$ symmetry). The same approach has been used within the LDA for diatomic molecules by Noodleman, Post, and Baerends[46] Zunger and Freeman[37] applied the notion of broken-symmetry solutions to core excitations and ionizations in a *bulk solid* (LiF), using a supercell approach, while Zunger[4] applied it to bulk GaP using a Green-function formalism. This approach has been used more recently by Norman *et al.* to calculate the core ionization in metallic cerium[47] and NiO (Ref. 48) and by Chacham *et al.* (Ref. 49) and by Machado *et al.*[50] to calculate excited states in II-VI clusters and solids, respectively.

The practical approach to the broken-symmetry solutions to core-hole excitations is based on the fact that removal of an electron (or a fraction thereof) from a distinct atomic site is analogous to creating an ("electronic") impurity state. This gives rise to a physically distinct eigenstate of the whole system. Since this state is identifiable, one can place the hole in it throughout the self-consistency iteration cycle, thus seeking a converged solution. In practice, one uses a supercell with N crystallographically identical atomic sites, constructing an initial potential (e.g., by superposing atomic functions) by placing a core hole in atomic orbital α of one atomic site, leaving the $N-1$ sites undisturbed. The extracted electron is placed in the "jellium background," to be described below. One then solves the periodic band-structure problem with this potential. According to Eqs. (1) and (3), the removal of charge from orbital α, shifts its eigenvalue $\epsilon_\alpha^{\rm LDA}(1)$ to $\epsilon_\alpha^{\rm LDA}(\frac{1}{2})$ by

$$\epsilon_\alpha^{\mathrm{LDA}}(\tfrac{1}{2})-\epsilon_\alpha^{\mathrm{LDA}}(1)=-[\Pi_\alpha^{\mathrm{LDA}}+\Sigma_\alpha^{\mathrm{LDA}}]\ . \qquad (8)$$

The non-Koopman ($\Pi_\alpha^{\mathrm{LDA}}$) and electronic relaxation ($\Sigma_\alpha^{\mathrm{LDA}}$) terms are large if orbital α is localized. In this case, the eigenvalue spectrum of the solid will exhibit a "splitoff" eigenstate, distinct from the states of the remaining $N-1$ 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 splitoff bulk eigenstate (irrespective of its degree of spatial localization), seeking a self-consistent solution under this constraint (note that the existence of a distinct splitoff state is necessary for finding a stable solution). These self-consistent iterations provide an opportunity for the eigenstate containing the hole to hybridize with other states. This mixing represents the self-consistent screening of the hole by the host states [effect (iii) of Sec. II]. This calculation can be repeated with displaced atoms around the hole, searching for a total-energy minimizing hole-induced lattice relaxation. Due to screening and relaxation effects, the calculation will converge to a core-hole eigenstate that is, in general, different from the starting solutions in which a hole was forced on a particular *atom*. For example, state α could lose part of its localization through mixing with other states, thus leading to a reduction in the $\Pi_\alpha+\Sigma_\alpha$ shift. This will then reduce the large SIC shift noted in Eq. (6) for the *free atom*. Note further that if state α is a deep state (e.g., a 1*s* core hole) the localization correction of Eq. (8) is always large, and the broken-symmetry iterations always converge to give a stable, splitoff state. The same is true for 3*d* states in Ge or III-V compounds, where the *d* band is deep. But *d* states in II-VI compounds exist *inside* the main valence band, so there, the existence of a stable splitoff solution is not guaranteed. Convergence could be slow.

The calculations were carried out using the local-density approximation as implemented by the linearized augmented plane-wave (LAPW) method[51] and the Ceperly-Alder exchange correlation as parametrized by Perdew and Zunger.[38] A zinc-blende supercell[28] and experimental lattice constants (Table I) were used in all the calculations. We assumed that the core electron is extracted with equal probability from the five lowest-energy *d* states (i.e., three Γ_{15} and two Γ_{12} states at $\bar{\Gamma}$). The energy of the *d* states thus refers here always to the average energy of the five *d* states.

III. RESULTS

A. Convergence tests—The effects of supercell size

Figure 1 shows the effects of supercell size on the splitoff Zn $3d^{9.5}$ level with the core hole and on the valence-band maximum for ZnO, ZnS, ZnSe, and ZnTe, respectively. For comparison, we also show the position of the ordinary d^{10} level (average of $\Gamma_{15}+\Gamma_{12}$), as obtained from ground-state band-structure calculations. The calculations were done using an equivalent *k*-point scheme corresponding to two special *k* points in the bulk zinc-blende zone. In this way, we avoided any energy-level fluctuation, due to different *k*-point sampling. In deriving the results in Fig. 1, we used a kinetic-energy cutoff for the plane-wave expansion of 13.6, 9.9, 14.5, 14.5 Ry, respectively, for ZnO, ZnS, ZnSe, and ZnTe. We observe the following.

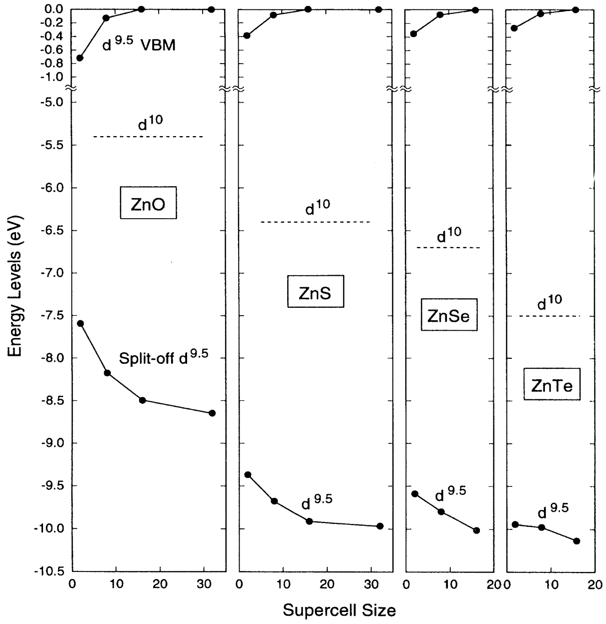

FIG. 1. The energies of the valence-band maximum (VBM) and the splitoff $d^{9.5}$ states, as a function of supercell size for ZuO, ZnS, ZnSe, and ZnTe, respectively. The energy zero is the VBM of the ground-state bulk solid. For comparison, we show also the average d^{10} band energy of the ground state.

(i) The energy of the valence-band maximum of the $d^{9.5}$ system increases monotonically with supercell size, and in all cases it converges at 16 atom cell to the value of *bulk* VBM set in Fig. 1 as the reference energy.

(ii) The average energy of the split off *d* states with the core-hole *decreases* monotonically with supercell size and converges slower than the energy of the extended (*p*-like) VBM. That this size variation is not due to direct core-hole coupling is clear from checking the magnitude of the dispersion of the splitoff *d* states within the supercell Brillouin zone, which provides a measure of the intercell interaction among the core-hole containing *d* states. For an eight atom cell, the dispersion is less than 0.005 eV. Clearly, direct core-hole interaction via wave function overlap of the splitoff states is small, consistent with the compact nature of the 3*d* orbital. However, a decrease in the core-hole *d*-state energy with increasing cell size is always accompanied by a decrease in its charge inside the Zn muffin tin. Slow convergence of the *d*-band energy (Fig. 1) may thus be caused by the fact that the screening length of the *d* core hole in II-VI compounds (a property involving also valence electrons) is not so small, but close to the dimension of 16 or 32 atom supercell.

We next tested the effect of *k*-point sampling on the core-hole energies. In particular, we carried out the calculations using 2 and 10 special *k*-point schemes. We find that the two different samplings yield less than a 0.04 eV difference in the *d* state binding energy for all the cell sizes for ZnO.

Using a supercell approach, one needs to maintain charge neutrality in the unit cell. In the present calculation, we smear the extracted electron of charge q over the unit cell, forming a uniform jellium background with $\rho_B=q/V_{\rm cell}$, where $V_{\rm cell}$ is the cell volume. We have tested, in the case of ZnS with an eight atom cell, the sensitivity 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 necessary cutoffs are 24, 22, 18, 18, Ry, respectively, for ZnO, ZnS, ZnSe, and ZnTe, as inferred from d^{10} 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 effects of atomic relaxation

We have examined the effects of atomic relaxations due to the existence of a core hole. The calculation was carried 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 O (or S) atoms tend to relax inwards to reduce the overall kinetic energy (force = 0.030 Ry/Å). The next shell Zn atoms also feel the presence of the core-hole (force =0.021 Ry/Å) and relax accordingly. The degree of relaxation is, however, small: 0.013 Å (or 0.64% of the bond length) for the nearest-neighbor O atoms and 0.009 Å for the next-nearest-neighbor Zn atoms for ZnO. This leads to a small relaxation energy of only 0.017 eV. The forces experienced by the Zn atom in ZnS are even smaller than those for ZnO. Based on these observations, we concluded that hole-induced atomic relaxations have little effects on the core hole binding energy of the Zn 3*d* states.

C. The *d*-state binding energies

Table I depicts our calculated 3*d* binding energies in ZnO, ZnS, ZnSe, and ZnTe, using the LDA approach and the symmetry-broken approach. We estimate as detailed in Sec. III A and III B that the uncertainty in the broken-symmetry calculation is 0.1 eV for ZnS, ZnSe, and ZnTe. We find (i) The large discrepancy between LDA and experiment is corrected by our approach, leaving a residual error of about 0.5–0.8 eV. (ii) The 9.5-eV core-hole shift of the *free* Zn atom [Eq. (6)] is reduced in the solid to about 3–4 eV. (iii) Our $\epsilon_\alpha^{\rm LDA}(1)-\epsilon_\alpha^{\rm LDA}(\frac{1}{2})$ shift for ZnS (3.31 eV) is larger than the value of 2.18 eV obtained by Machado *et al.*[50] using their celllular method, and is smaller than the value of 4.22 eV found by Chacham *et al.*[49] in their cluster calculation. (iv) For ZnO, we speculate that the ionization of an electron from 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 density due to self-consistent creation of a *d* hole,

$$\Delta\rho_{\rm tot}=\rho_{\rm tot}^{\rm no\ hole}(\mathbf{r})-\rho_{\rm tot}^{\rm hole}(\mathbf{r})\ , \tag{9}$$

as well as the corresponding change in the charge density of the *d* band alone,

$$\Delta\rho_d=\rho_{d\text{-band}}^{\rm no\ hole}(\mathbf{r})-\rho_{d\text{-band}}^{\rm hole}(\mathbf{r})\ , \tag{10}$$

for ZnS. The charge distributions in Fig. 2 are spherical. This is because we have placed the core hole in both Γ_{15d} and Γ_{12d} states. Clearly, the holes in Figs. 2(a) and 2(b) are highly localized on only one Zn atom. *The noticeable difference between Fig. 2(a) and 2(b) suggests that the d hole in Fig. 2(b) is largely screened by non-d states.*

Our results for ZnO offer the opportunity to compare our method with quasiparticle approaches.[9,36] The quasiparticle approach, in principle, should give exact result for the 3*d* binding energy. However, in reality, various approximations were used yielding less accurate results. Using ground-state LDA band theory, Posternak *et al.*[36] found a 3*d* binding energy of $E_{\rm VBM}-5.4$ eV, compared with $E_{\rm VBM}-6.4$ eV obtained using a model *GW* approach. Our band theory result is $E_{\rm VBM}-5.4$ eV in good

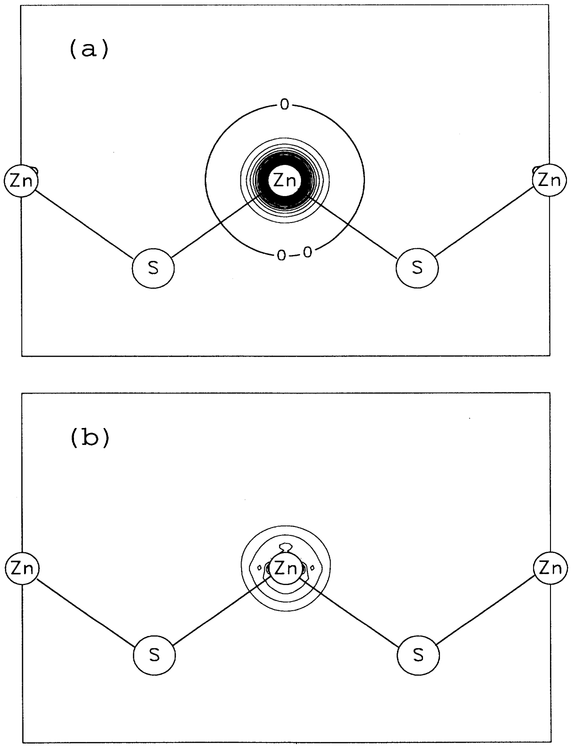

FIG. 2. Charge contours in the (110) plane ZnS for (a) bare $\Delta\rho_d=\rho_{d\text{-band}}^{\rm no\ hole}(\mathbf{r})-\rho_{d\text{-band}}^{\rm hole}(\mathbf{r})$ and (b) screened $\Delta\rho_{\rm tot}=\rho_{\rm tot}^{\rm no\ hole}(\mathbf{r})-\rho_{\rm tot}^{\rm hole}(\mathbf{r})$ splitoff *d* states for ZnS.

agreement with their LDA result. In contrast, our broken-symmetry solution gives $E_{\mathrm{VBM}}-8.62$ eV in better agreement with the experimental value of $E_{\mathrm{VBM}}-7.8$ eV.[22–25]

A related subject regarding core hole is the splitoff exciton state below the conduction band minimum[4] (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 exciton state. The results for ZnO and ZnS with a 32 atom cell showed that to within 0.04 eV accuracy, there is no such splitoff state from the CBM. Shallower exciton states with less than 0.04-eV binding energy can, of course, exist due to a Zn $3d$ core hole, but that cannot be studied by the current approach.

TABLE II. Average Mn $3d\uparrow$ state binding energy $E_d=E_{\mathrm{VBM}}-\epsilon^{\mathrm{LDA}}_{\mathrm{Mn},3d}(\frac{1}{2})$ and the effective Coulomb interaction $U_{\mathrm{eff}}=\epsilon^{\uparrow}(d^{5.5})-\epsilon^{\downarrow}(d^{4.5})$ in eV for ZnTe:Mn. Here, LSDA+Correction means a regular band calculation with an added spin-dependent empirical potential for Mn atom (see Ref. 26).

	E_d	U_{eff}
LSDA+Correction	3.36	$\Delta_x^d=5.69$
Experiment	3.75[a], 3.80[b]	6.80,[c]7.0,[d]
Present	3.93	6.85
$\Pi_\alpha^{\mathrm{LDA}}+\Sigma_\alpha^{\mathrm{LDA}}$ shift	0.57	1.16

[a] Reference 52.
[b] Reference 26.
[c] Reference 53.
[d] Reference 54.

D. d-state binding energy and effective Coulomb interaction of Mn $3d$ states in ZnTe:Mn

As an extension of the calculation on Zn $3d$ core holes, we study here d-state binding energy and the effective Coulomb interaction U_{eff} for substitutional Mn in ZnTe. Here, U_{eff} is defined as

$$U_{\mathrm{eff}}=E(d^4)+E(d^6)-2E(d^5)\ , \tag{11}$$

where the superscript n in the expression d^n is the occupation number of the Mn $3d$ orbitals. Using Slater transition state theorem,[43] Eq. (11) can be written as

$$\begin{aligned} U_{\mathrm{eff}}&=[E(d^6)-E(d^5)]-[E(d^5)-E(d^4)] \\ &\approx\epsilon^{\uparrow}(d^{5.5})-\epsilon^{\downarrow}(d^{4.5})\ , \end{aligned} \tag{12}$$

where ϵ are the one-electron eigenvalues of the localized Mn $3d$ states calculated using local-spin-density approximation (LSDA).

Before we proceed, it is useful to notice that the direct LSDA eigenvalue difference $\Delta_x^d=\epsilon^{\mathrm{LSDA},\uparrow}-\epsilon^{\mathrm{LSDA},\downarrow}=4.2$ eV for MnTe calculated in Ref. 26 cannot be compared directly to the experimental value of $U_{\mathrm{eff}}\sim 7$ eV. This is because (i) Δ_x^d contains an LSDA error reflected in the strong p-d hybridization;[35] (ii) The combined effect of the non-Koopman's correction $\Pi_\alpha^{\mathrm{LDA}}$ to the LDA eigenvalues and the correction due to electronic relaxation $\Sigma_\alpha^{\mathrm{LDA}}$, the $\Pi_\alpha^{\mathrm{LDA}}+\Sigma_\alpha^{\mathrm{LDA}}$ shift (see the discussion in Sec. II) is significant in this system. The first LSDA error was corrected in Ref. 26 by adding a spin-dependent empirical potential on Mn atom, which increases Δ_x^d by 1.5–5.7 eV. Here, we examine the second effect.

The calculation was done on ferromagnetic ZnTe:Mn. An eight-atom cell was used where one of the four Zn atoms were replaced by an Mn atom. The Mn potential used in Ref. 26 was used in the present calculation. As suggested by Fig. 1, the Zn $3d$ core state binding energy E_d is converged to within 0.2 eV in an eight-atom cell for ZnTe. We, thus, expect that increasing cell size will also increase U_{eff}, primarily from an increasing E_d, but not to exceed 0.2 eV. On the other hand, the ground state for ZnTe:Mn is antiferromagnetic, whereas our calculation employed a metastable ferromagnetic state. We estimate that U_{eff} for the true antiferromagnetic ground state is about 0.2 eV smaller than that for the ferromagnetic state.[26] An overall error of 0.1 eV is thus expected. In the calculation, we fix the atoms at their relaxed ground-state atomic positions and an equilibrium volume corresponding to $\mathrm{Zn}_{0.75}\mathrm{Mn}_{0.25}\mathrm{Te}$. As we tested earlier in Sec. III B, excitation-induced atomic relaxation has negligible effects on energies. In addition, in the calculation of $\epsilon^{\downarrow}(d^{5.5})$, the coupling between the Mn $3d\downarrow$ states and other s,p conduction states is relatively strong, thus wave-function projection was used to determine its energy position.

Table II shows the results for E_d and U_{eff} for ZnTe:Mn. The calculated binding energy for Mn $3d\uparrow$ states of VBM -3.93 eV is in good agreement with recent photoemission results of VBM-3.75 to VBM -3.80 eV.[52,26] Our theoretical binding energy is about 0.15 eV larger than experiment. This is expected from our Zn $3d$ core-hole calculations (Sec. III C). The 0.15 eV error is smaller than the 0.5–0.8 eV error for Zn $3d$ core holes, reflecting the less localized nature of the Mn $3d\uparrow$ *valence* states. The $\Pi_\alpha^{\mathrm{LDA}}+\Sigma_\alpha^{\mathrm{LDA}}$ shift, due to the d hole is, on the other hand, not negligible (0.6 eV or 18% of the LSDA binding energy). The calculated U_{eff} of 6.85 eV is also in good agreement with several experimental values of 6.80–7.0 eV.[53,54] It appears that $U_{\mathrm{eff}}=8.30$ eV determined by Franciosi *et al.*[55] is too large compared with our results and with other experiments. By comparing U_{eff} with Δ_x^d, we conclude that the $\Pi_\alpha^{\mathrm{LDA}}+\Sigma_\alpha^{\mathrm{LDA}}$ shift (1.2 eV) for U_{eff} is significant.

IV. SUMMARY

We have reviewed the causes for the large LDA errors in Zn $3d$ core-hole binding energies (i.e., the self-interaction corrections). We next showed that using a broken-symmetry band-structure approach, these large LDA errors can be systematically improved. Such a broken symmetry, implemented via the use of supercells, results in a physically distinct, spatially localized splitoff state from other Bloch d states, thereby eliminating the unwanted self-interaction energy. We found that the core-hole effects in a solid is qualitatively different from those in an atom, due to the large screening effects of valence electrons. The former is typically only a third of the latter. The *fundamental* reason why SIC should lead to more accurate occupied state energies than the uncorrected LDA was discussed by Perdew and Zunger,[38] who also demonstrated the quantitative improvement for *free atoms and ions*. The present work demonstrates that the improvements persist also for *d* state in *solid* II-VI compounds. This work thus complements the previous SIC work for solid transition metals,[56] for transition-metal oxides,[44] for LiCl and LiCl:Cu$^+$,[57] and for Si and III-V compounds.[58] All the above SIC calculations showed significant improvements over LDA.

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[27] The *d*-band energies in II-VI compounds are rather difficult to converge in terms of basis functions and charge self-consistency, since small changes in the wave-function's spatial form lead to significant changes in band energies. Thus, calculations on the same system using a fixed lattice constant ($a = 5.409$ Å in ZnS) and a fixed exchange-correlation potential lead to rather different *d*-band center energies. Furthermore, relativistic (or scalar-relativistic) corrections shift the *d* band to lower binding energies by 0.3–0.5 eV (see Table VII in Ref. 18). In ZnS, the mixed-basis method of Bernard and Zunger (Ref. 18) leads to Γ_{15d} and Γ_{12d} energies of -7.65 and -7.27 eV. The Gaussian basis set results of Schröer, Krüger, and Pollmann (Ref. 20) yield -5.84 and -5.27 eV, respectively, while the plane-wave basis calculation of Martins, Troullier, and Wei (Ref. 21) yield -6.63 and -6.16 eV. The converged, scalar relativistic LAPW results are -6.60 and -6.13 eV.

[28] ZnO crystallizes in the wurtzite structure. Here, we calculate ZnO in a zinc-blende structure by assuming that the volume of the zinc-blende ZnO is equal to that of wurtzite ZnO. The lattice parameters for wurtzite ZnO are taken from D. F. Croxall, R. C. C. Ward, C. A. Wallace, and R. C. Kell, J. Cryst. Growth **22**, 117 (1974).

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