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Ab initio electronic-structure calculations for II-VI semiconductors using self-interaction-corrected pseudopotentials

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We report results of an efficient approach for performing self-consistent *ab initio* calculations of structural and electronic properties of II-VI semiconductors which overcomes to a large extent well-known shortcomings of the local-density approximation (LDA) for these d-band compounds. Dominant atomic self-interaction corrections are taken into account by employing appropriately constructed pseudopotentials in the framework of standard LDA calculations. Our results for ZnO, ZnS, CdS, and CdSe are in excellent agreement with a whole body of experimental data.

Electronic and structural properties of II-VI compound semiconductors and their surfaces are currently moving into the focus of interest because of their paramount technological potential. Applications range from optoelectronic devices (e.g., blue lasers based on ZnSe heterostructures) to heterogeneous catalysis (e.g., oxide surfaces). For a basic understanding of the related phenomena and an optimization of materials for relevant processes ("band-structure engineering"), a quantitative knowledge of electronic and structural properties of these compounds, their surfaces, and interfaces is needed. In recent years, a number of local-density approximation (LDA) calculations of bulk[1–4] and surface[5] properties of II-VI semiconductors have been reported. They are very demanding because of the cationic d electrons. If the d electrons are treated as core electrons, calculated lattice constants badly underestimate the experimental values by as much as 13% and 18%, e.g., for wurtzite (W) structure ZnS and ZnO, respectively, while inclusion of the d electrons in the valence shell yields very accurate lattice constants.[3] But even if the d electrons are properly taken into account, the results of standard LDA calculations show distinct shortcomings. Not only is the band gap strongly underestimated, but even worse, the occupied cationic d bands reside roughly 3 eV too high in energy as compared to experiment. In consequence, their interactions with the anion p valence bands are artificially enlarged, falsifying the dispersion and bandwidth of the latter and shifting them unphysically close to the conduction bands. As a result, the LDA band-gap underestimate for the II-VI compounds is even more severe than in elemental or III-V semiconductors. For ZnO, e.g., we obtain $E_g^{\text{th}}=0.23$ eV in LDA (Ref. 3), as opposed to $E_g^{\text{exp}}=3.4$ eV.

Zakharov *et al.*[6] have recently reported plane-wave GW calculations for a number of II-VI compounds. They simply treated the d electrons as core electrons and deliberately carried out their GW calculations at the *experimental* lattice constants. This way the calculations are not more involved than those, e.g., for III-V semiconductors.[7,8] The authors obtained very good results for the anion p valence bands and for the gap energies but no assertion concerning the d-band positions could be made, of course. In particular, the Hamiltonians used in Ref. 6 are not perfectly suitable for surface structure optimizations because of the omission of the d electrons. In addition, an extension of such GW calculations to surfaces of W II-VI compounds would be computationally extremely demanding, even if the respective surface geometries were known from experiment.

In this paper, we suggest an alternative approach to treat II-VI semiconductor compounds, which approximately incorporates dominant self-interaction corrections (SIC). It is capable of overcoming the above-mentioned LDA shortcomings and is, nevertheless, computationally not more involved than the standard LDA. From the landmark contribution of Perdew and Zunger,[9] it is well known that self-interaction corrections to the LDA can be very important for a quantitative description of systems with strongly localized states such as $3d$ electrons. Straightforward application of the SIC formalism to solids leads to state-dependent effective potentials, however, which no longer obtain the translational invariance of the Bravais lattice. In consequence, full SIC calculations within density-functional formalism are extremely involved. Yet, they have recently been performed successfully by Svane and Gunnarson,[10] as well as by Szotek, Temmerman, and Winter[11] for bulk solids. The work of these authors on transition-metal oxides[10,11] has clearly revealed that SIC shifts occupied cationic d states significantly down in energy. We expect the same to be true for II-VI compound semiconductors. Now full SIC-LDA calculations for W II-VI semiconductors with four atoms per unit cell are beyond our computational possibilities and respective surface studies within SIC-LDA are entirely out of range these days. Eventually, we aim at a quantitative theory of the electronic structure of II-VI semiconductor surfaces. We, therefore, have developed an alternative approach to take care of dominant self-interaction corrections in a standard LDA calculation by employing atomic self-interaction-corrected pseudopotentials (SIC-PP's). Considering our previous LDA results for W II-VI compounds,[3] we observe that the d bands result in energy 2.7, 3.2, 2.8, and 2.8 eV too high for ZnO, ZnS, CdS, and CdSe, respectively, as compared to experiment. Thus the misplacement of the d bands in our standard LDA results is roughly 3 eV, irrespective of the different lattice constants of these compounds. We consider this to be a strong hint of the fact that it is basically the *atomic* self-interaction correction that is missing in standard LDA calculations for the II-VI compounds.[3] As a matter of fact, nonlocal, norm-conserving pseudopotentials entering standard LDA calculations are constructed employing all-electron results for atoms or ions.

But these suffer from unphysical self-interactions from the very beginning. To describe the atomic term values more accurately, we first carry out *atomic* SIC-LDA calculations employing the formalism of Perdew and Zunger.[9] These yield better term values and wave functions for the atom than a plain LDA calculation. Next we construct atomic nonlocal pseudopotentials such that they yield the same term values and, outside the core radius, the same eigenfunctions as the SIC-LDA calculation. The pseudopotentials constructed this way incorporate the dominant atomic self-interaction corrections. We then use these pseudopotentials in solid-state LDA calculations. This, admittedly, is only an approximation to a full SIC-LDA calculation for a bulk solid but it allows us to take into account dominant SIC contributions in a very efficient way. The influence of the SIC effects on the nonlocal pseudopotentials is different for different atoms and different angular momenta in the short-range region of the potential.

It should be noted at this point that the SIC-related modifications to the nonlocal pseudopotentials influence both the energy positions as well as the dispersion of the bands. A detailed account of the determination of our SIC-PP's will be given elsewhere. In our standard LDA calculations, which we carry out for reference's sake, we use for S and O the nonlocal, norm-conserving pseudopotentials of Gonze, Stumpf, and Scheffler[12] and for Zn and Cd those of Bachelet, Hamann, and Schlüter.[13] All pseudopotentials are transformed into the separable Kleinman-Bylander form.[14] The exchange-correlation potential is taken into account in the Ceperley-Alder[15] form as parametrized by Perdew and Zunger.[9] As basis sets for the wurtzite compounds we employ 160 Gaussian orbitals per unit cell with appropriately determined decay constants, and Brillouin-zone sums are carried out at six special **k** points.[16]

Let us now discuss exemplary applications of our approach. First we address the lattice constants and bulk moduli of a few compounds given in Table I. Our SIC-PP's lead to lattice constants that are slightly increased with respect to the usual LDA results. Obviously, the lattice constants calculated with our SIC-PP's are in excellent agreement with experimental data.[17] For ZnS, CdS, and CdSe, they are even closer to experiment than our standard LDA results. Also the calculated bulk moduli for the Cd compounds are considerably closer to experiment for the SIC-PP's than for the standard pseudopotentials. This general trend is in agreement with the results of Refs. 10 and 11, which also revealed a SIC-induced increase in the lattice constants and a decrease in bulk moduli. In our case these changes could be related to a weakening of the p-d hybridization due to the increased binding of the cation d levels and a concomitant weakening of the chemical bond.

Next we address the band structure of ZnO, a relevant section of which is shown in Fig. 1. The left panel shows our standard LDA result (see also Ref. 3) clearly revealing the above-mentioned shortcomings. The right panel shows the band structure as calculated with our SIC-PP. Obviously, the d bands are now shifted down in energy considerably and concomitantly the gap is opened drastically. In addition, the dispersion and bandwidth of the O $2p$ valence bands are changed significantly. The gap energy and the d-band position are grossly improved as compared to the standard LDA results. It should be noted at this point that not only the downward shift of the d bands and the related reduction in the p-d interaction opens up the gap. In addition, the change in atomic s- and p-term values resulting from the atomic SIC calculation and thus entering the pseudopotentials contribute to the effect.

TABLE I. Lattice constants and bulk moduli B of W II-VI semiconductors (in Å and Mbar), as calculated using standard pseudopotentials (PP) or using our SIC-PP's in comparison with experiment (Ref. 17).

		PP	SIC-PP	Expt.
	a	3.23	3.29	3.25
ZnO	c	5.18	5.29	5.21
	B	1.60	1.59	1.43
	a	3.71	3.83	3.82
ZnS	c	6.06	6.28	6.26
	B	1.02	0.83	0.76
	a	4.03	4.15	4.13
CdS	c	6.54	6.76	6.70
	B	0.87	0.74	0.61
	a	4.21	4.29	4.30
CdSe	c	6.86	7.02	7.01
	B	0.75	0.62	0.53

To compare the O $2p$ valence bands in more detail with angle-resolved photoelectron spectroscopy (ARPES) data[18] we show in Fig. 2 a small section of Fig. 1 from Γ to M. The standard LDA result in the left panel is obscured by the artificially high-lying d bands leading to respectively strong p-d interactions with the O $2p$ bands. Our SIC-PP results in the right panel are in much better agreement with experiment.

ZnO is special in the group of II-VI compounds in that it contains an anion from the second row of the periodic table

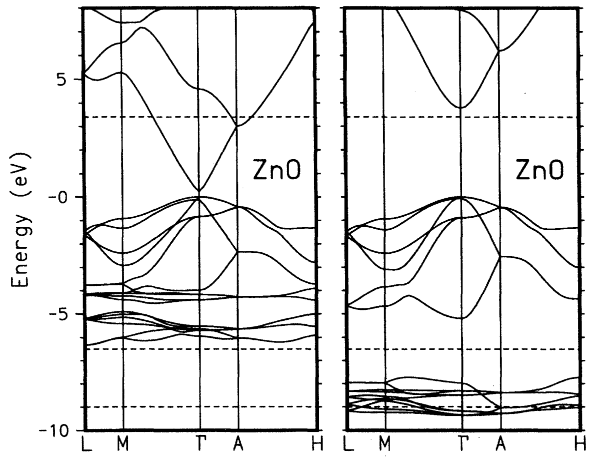

FIG. 1. LDA bulk band structure of ZnO as calculated using a standard PP (left panel) or using our SIC-PP (right panel). The horizontal dashed lines indicate the measured gap energy and d-band width.

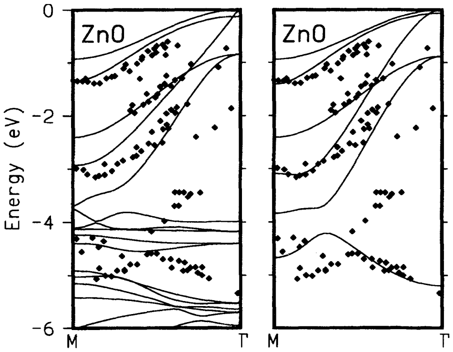

FIG. 2. Comparison of calculated and measured (Ref. 18) valence bands of ZnO. The left panel shows our standard LDA results while the right panel shows results as obtained using our SIC-PP.

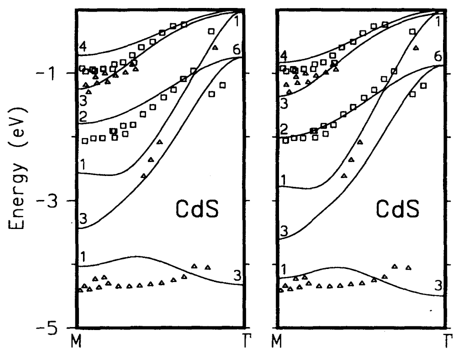

FIG. 4. Comparison of calculated and measured valence bands of W CdS. Standard LDA (left panel) and SIC-PP results (right panel) are compared with polarization and angle-resolved photoelectron spectroscopy data (Ref. 20).

without p states in the core. To make sure that the improvement of the band structure observed for ZnO is not just accidental, we have studied another more representative II-VI compound, namely, CdS. In Fig. 3 we compare a relevant section of the band structure of W CdS as calculated within standard LDA and using our SIC-PP's, respectively. ARPES data measured by Stoffel[19] at high-symmetry points are given for comparison. Again, salient shortcomings of the LDA are very obvious in the left panel. The right panel reveals that also in this case our band structure obtained with the SIC-PP is in very good agreement with the data. We note in passing that our energies of the S $3p$ valence bands are in even better agreement with the data than the GW results in Table VI of Ref. 6.

More recent high-resolution ARPES data for W CdS of Magnusson and Flodström[20] along the Γ-M line are shown in Fig. 4 in direct comparison with our results. While the standard LDA results in the left panel are hard to reconcile with the data, our SIC-PP results beautifully agree with the measured S $3p$ valence bands. The symmetry of the measured bands (△ even and □ odd with respect to the mirror plane) is in excellent accord with the calculated bands (1,3 even and 2,4 odd), as well.

We have obtained similar improvements for a number of ZB and W II-VI compounds. Characteristic band-structure data for some compounds are summarized in Table II. Obviously, in all cases the standard LDA yields much too small gap energies, places the d bands roughly 3 eV too high in energy, and concomitantly fails to yield a very accurate description of the bandwidth W_p of the anion p valence bands. Our SIC–PP approach overcomes these problems to a large extent, as is obvious from Table II. We note in passing that the gap energies of other semiconductors without semicored states are also improved.

There remains one discrepancy. In our new approach the d bands result in energy roughly 1 eV too low as compared to experiment (see Figs. 1 and 3 and Table II). This type of deviation is probably related to the fact that measured excitation energies are influenced by electronic relaxations. These can be expected to be most pronounced for the highly localized cationic semicore d states. We observe the same

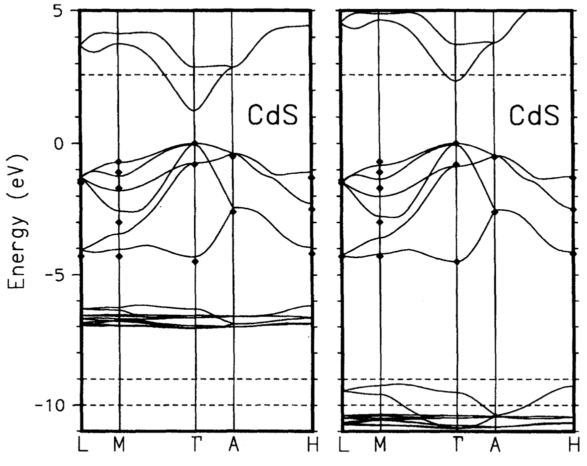

FIG. 3. Bulk band structure of W CdS as calculated within standard LDA (left panel) or using our SIC-PP (right panel) in comparison with ARPES data (Ref. 19). The horizontal lines indicate the measured energy gap and the d-band width.

TABLE II. Calculated and measured (Ref. 17) energy gaps E_g, cation d-band positions E_d, and anion p valence bandwidths W_p (in eV) of some II-VI compounds (see text).

		PP	SIC-PP	Expt.
	E_g	0.23	3.77	3.4
ZnO^{W}	E_d	-5.1	-8.9	$\sim$-7.8
	W_p	-3.99	-5.2	-5.3
	E_g	1.77	3.27	3.8
ZnS^{ZB}	E_d	-5.5	-11.2	$\sim$-9.0
	W_p	-5.14	-5.2	-5.5
	E_g	1.22	2.35	2.6
CdS^{W}	E_d	-6.8	-10.5	$\sim$-9.6
	W_p	-4.32	-4.50	-4.5
	E_g	0.51	1.27	1.8
CdSe^{W}	E_d	-7.2	-11.1	$\sim$-10.0
	W_p	-4.50	-4.74	-5.0

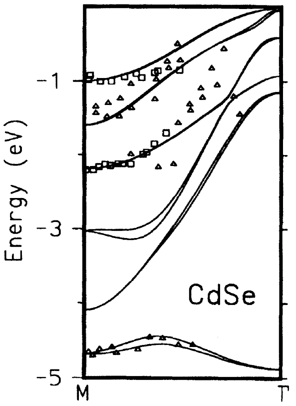

FIG. 5. Comparison of calculated and measured (Ref. 20) upper valence bands for *W* CdSe. The band structure has been calculated with our SIC-PP and spin-orbit coupling has explicitly been taken into account.

type of deviation between our *atomic* SIC-LDA results and experiment. To take such semicore-hole relaxations for atoms into account, one would have to carry out self-consistent-field calculations of energy *differences* between the ground state and the d-excited ionized states. Since the d excitation is a localized process at a particular cation site, one would have to treat it as a localized perturbation of an otherwise periodic solid. Such calculations are way beyond the scope of our current investigations.

Finally, we show in Fig. 5 a comparison of our band-structure results for the upper CdSe valence bands with ARPES data of Magnusson and Flodström.[20] Contrary to ZnO and CdS, the spin-orbit interaction is very important in CdSe. We have, therefore, carried out our calculations for CdSe including spin-orbit coupling. The agreement between our results and the data is very good, in particular, from M to $M\Gamma/2$. In addition, there is amazing agreement between the measured and calculated spin-orbit splitting of the lowest Se $4p$ valence bands near -5 eV.

In summary, we have presented exemplary results of a new and very efficient approach to accurately calculate structural and electronic properties of II-VI compound semiconductors. Since our approach is not more involved than standard LDA calculations it can easily be applied to surfaces which are currently being studied this way. It is important to note that we did not carry out full solid-state SIC-LDA calculations but rather standard LDA calculations using nonlocal pseudopotentials that incorporate atomic self-interaction corrections.

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