Quasiparticle Band Structure of CdS

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Quasiparticle band structure calculations which include the most important cationic core states in the *GW* approximation of the self-energy operator are reported for a prototype II-VI semiconductor. The most salient feature of our results for cubic CdS is the finding that the complete cationic *N* shell needs to be included in the pseudopotential and in the self-energy in order to obtain reasonable *GW* results in agreement with experiment.

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Quasiparticle band structure calculations based on the *GW* approximation of the self-energy operator as suggested by Hedin and Lundqvist [1,2] have become the "state of the art" in most advanced electronic structure calculations for semiconductors. For *s-p* bonded group IV and III-V materials this approach has been shown to yield bulk [3–8] and surface [7,9,10] quasiparticle energies with an accuracy of about 0.1 eV. In II-VI semiconductors like CdS, CdSe, ZnS, and ZnSe the Cd and Zn semicore *d* states have a very strong influence on physical properties such as the lattice constants and the fundamental band gaps, as has been shown in a number of investigations [11–16] employing the local-density approximation (LDA). Yet, so far, no *GW* quasiparticle band structure calculations including these highly localized cationic semicore *d* states have been reported for II-VI semiconductors. Only Zakharov *et al.* [17,18] have recently studied a number of II-VI compounds employing the *GW* approximation (GWA) but they treated the cationic *d* electrons as core electrons. If the *d* electrons are explicitly taken into account as valence electrons in the GWA, not only do the calculations become much more involved when plane wave basis sets are used, but, more importantly, a straightforward application of the GWA to II-VI semiconductors including cationic semicore *d* states yields relatively poor results with deviations of more than 1 eV between the calculated quasiparticle energies and experiment (see below).

In this Letter we report a systematic study of the influence of higher Cd core states on the *GW* quasiparticle band structure of CdS by treating them as valence states that are explicitly included in the calculations for the solid. We consider four different ionic Cd pseudopotentials with 2, 12, 18, and 20 valence electrons, respectively. We identify the problems that arise in GWA if only the *d* states of the semicore shell are treated as valence states and we show how these problems can be solved.

In our calculations we employ basis sets of Gaussian orbitals in both the LDA and *GW* calculations [6,7]. Thus all spatial functions are represented by relatively small sets of no more than 90 basis functions for the LDA wave functions and no more than 190 basis functions for the two-point functions occurring in the GWA. Using plane wave basis sets, the calculations would be an order of magnitude more involved [7]. In our *GW* calculations, we employ the full static RPA dielectric matrix that is extended to nonzero frequencies by a plasmon-pole model [19].

We concentrate in this Letter on the zinc blende modification of CdS, for simplicity. The electronic configuration of the Cd atom is (Kr)$4d^{10}5s^2$. Although a proper treatment of the semicore *d* states is important, as we have pointed out already, we start our systematic investigation employing a Cd^{2+} pseudopotential (PP), i.e., we treat all but the Cd 5*s* electrons as core electrons in this initial step. Actually, we use the Cd^{2+} PP of Bachelet, Hamann, and Schlüter [20]. In all calculations reported in this work the S atom is described by the S^{6+} PP of those authors.

Our results obtained with the Cd^{2+} PP do not agree very well with experiment, as was to be expected. We obtain a theoretical lattice constant of 5.05 Å which is much smaller than the experimental value of 5.82 Å [21]. The resulting LDA and GWA band structures are displayed in Fig. 1 (left panel). Dashed lines show LDA results and solid lines represent *GW* quasiparticle results. All band structure calculations reported in this work have been carried out for the experimental lattice constant for a more meaningful comparison. The LDA gap in the left panel of

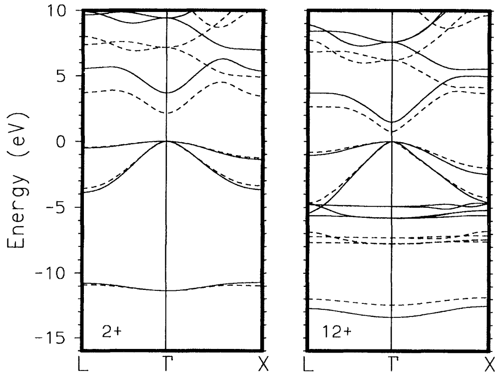

FIG. 1. Calculated band structures for cubic CdS (in eV). Dashed lines display LDA and solid lines represent *GW* quasiparticle results. The panels refer to calculations using Cd^{2+} (left panel) and Cd^{12+} (right panel) pseudopotentials.

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Fig. 1 is 2.16 eV. It is increased to 3.70 eV by the quasiparticle corrections. Compared to the experimental band gap of 2.50 eV from reflectivity or 2.55 eV from ellipsometry measurements [22], respectively, the calculated quasiparticle band gap is much too wide in this case. Characteristic results of this calculation are compiled in Table I in comparison with experimental data and respective results for the other pseudopotentials used later on. The deviations from experiment, in particular, for the lattice constant, arise from an inadequate treatment of the Cd 4*d* semicore states in the Cd^{2+} PP (see also Ref. [16]). Their atomic energy lies between the S 3*s* and the S 3*p* levels and their physical behavior in the solid differs from that in the atom. Thus they have to be included in the valence electron shell. To this end we have employed the Cd^{12+} PP of Bachelet, Hamann, and Schlüter [20] in our next step. For this potential we obtain a value of 5.61 Å for the lattice constant that is considerably closer to but still smaller than the experimental value. Concomitant, the fundamental gap is lowered and amounts to 0.78 eV in LDA, only. Similar effects on the lattice constant and on the gap energies have also been obtained by taking the core states into account employing nonlinear core-correction techniques [17].

Our band structure results obtained with the Cd^{12+} PP are shown in the right panel of Fig. 1. We observe (see also Table I) that the energetic position of the Cd 4*d* states at -7.4 eV in LDA is too high as compared to the experimental value of about -9.5 eV [23,24] (measured for the wurtzite modification). One might expect that the Cd 4*d* states are shifted to lower energies by the *GW* quasiparticle corrections. *In contrast* we find that the Cd 4*d* bands are *shifted to higher energy* by more than 2 eV in our *GW* results for the Cd^{12+} PP in marked contrast to experiment. To our knowledge, such large and obviously unreasonable upward shifts for valence states have never been found in any *GW* calculation for group IV or III-V semiconductors before. It is thus specifically related to the highly localized semicore *d* orbitals. The gap is opened indeed by 0.72 eV and now amounts to 1.50 eV but it is still much too small, as compared to experiment. More importantly, we observe that the perturbation matrix $(\Sigma - V_{\mathrm{xc}})_{mm'}$ is nondiagonal. Therefore we have evaluated its second-order energy contribution. But it yields only marginal improvements. The observed nondiagonality of the perturbation matrix is in contrast to many other *GW* calculations for group IV and III-V semiconductors. It indicates that the LDA wave functions ψ^{LDA} disagree with the quasiparticle wave functions ψ^{GWA}, in particular for the Cd 4*d* and the S 3*p* valence states. The *p*-*d* interaction between these electrons is not properly described in this particular calculation. Zakharov *et al.* [17] have observed the same deficiency for ZnS which is chemically very similar to CdS.

TABLE I. Calculated lattice constant (in Å), LDA and GWA gap energy E_g and Cd 4*d* energy E_d (in eV) of zinc blende CdS, resulting for the four different Cd pseudopotentials described in the text, in comparison with experiment. The *d* state energy has been measured for the wurtzite modification. All energies are calculated at the experimental lattice constant for a more meaningful comparison.

Cd PP	a_0	E_g^{LDA}	E_g^{GWA}	E_d^{LDA}	E_d^{GWA}
Cd^{2+}	5.05	2.16	3.70		
Cd^{12+}	5.61	0.78	1.50	-7.4	-5.2
Cd^{18+}	5.72	0.86	1.60	-7.4	-7.2
Cd^{20+}	5.73	0.83	2.45	-7.4	-8.1
exp.	5.82[a]	2.50, 2.55[b]		-9.5[c]	

[a] See Ref. [21].

[b] See Ref. [22].

[c] See Refs. [23,24].

To resolve these very basic issues of *GW* calculations including localized *d* states, we have carried out a detailed investigation of the above mentioned shortcomings and have found the quite amazing cause for these deficiencies. The unsatisfactory results of our *GW* quasiparticle calculations using the Cd^{12+} PP stem from the division of the Cd $n = 4$ core shell, i.e., the *N* shell, into 4*s* and 4*p* core electrons and 4*d* valence electrons. This division was originally motivated by the large LDA binding energy of the 4*s* and 4*p* states of about 106 and 67 eV, respectively, as compared to 11.9 eV for the 4*d* states. The fact that the 4*s* and 4*p* levels are strongly off resonant in energy with the other valence bands naturally leads to their treatment as core electrons in standard LDA calculations. It is, however, very important to note that the 4*s*, 4*p*, and 4*d* states show very similar localization properties, as can be seen in Fig. 2 where we display the 4*s*, 4*p*, 4*d*, and 5*s* radial wave functions resulting from an all-electron LDA calculation for the Cd atom. The large spatial overlap of the $n = 4$ radial wave functions causes strong interactions between these electrons. This holds in particular for the exchange interaction that does not depend on the energies of the states but only on their spatial extent. When the Cd *N* shell is separated into core and valence states in the

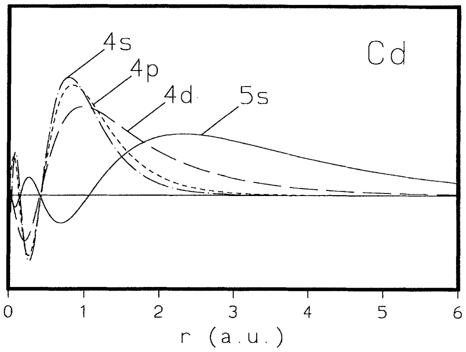

FIG. 2. Atomic 4*s*, 4*p*, 4*d*, and 5*s* wave functions, resulting from an all-electron LDA calculation for the Cd atom.

Cd^{12+} PP, the nonlinear exchange-correlation interaction is not properly described in the self-energy. Thus, neither the insensibility of lower core states to a change in chemical environment nor their strong binding energy allow the separation of the Cd N shell into 4s and 4p core and 4d valence states *in GW calculations*. We expect this conclusion to obtain in general if all valence states of a relevant shell have a very similar spatial localization.

In order to overcome the problems identified above, we have successively included the 4p and 4s electrons in the valence electron shell. First we have constructed a Cd^{18+} pseudopotential with 4p, 4d, and 5s valence states following the prescription of Hamann [25] while the 4s states remain being treated as core states. The resulting LDA band structure (left panel of Fig. 3) is nearly the same as for the Cd^{12+} PP with deviations of about 0.1 eV for the valence states and less than 0.3 eV for the conduction states (cf. Fig. 1). But for the respective GW quasiparticle band structure we observe that the unreasonably large shift of the 4d electrons to higher energies, as found for the Cd^{12+} PP, no longer occurs (see Table I and left panel of Fig. 3). Most importantly, we find that the perturbation operator $(\Sigma - V_{\mathrm{xc}})$ becomes diagonal for the Cd^{18+} PP, indicating that $\psi^{\mathrm{GWA}} = \psi^{\mathrm{LDA}}$ in this case. The nondiagonality of the perturbation operator for the Cd^{12+} PP calculation thus turns out to be an artifact of that pseudopotential. The p-d interaction with the upper valence bands was not properly described using the Cd^{12+} PP. Including the Cd 4p states as valence electrons explicitly yields a much better description of the p-d interaction. The fundamental gap, however, is still too small and amounts to 1.60 eV, only, in our quasiparticle band structure (see Table I).

Since the general arguments concerning the importance of N shell electrons in GW calculations given above hold for the 4s states equally well, there is no physical reason to leave them out of the PP in a GW calculation. Therefore, we have included the Cd 4s electrons in the valence shell, as well, constructing a Cd^{20+} pseudopotential. The resulting theoretical lattice constant for this PP amounts to 5.73 Å with a deviation of 1.5% from the experimental value. This is typical for LDA calculations using the Ceperley-Alder exchange-correlation functional. The LDA band structure for the Cd^{20+} PP is displayed in the right panel of Fig. 3. It is nearly identical to that resulting for the Cd^{18+} PP, as was to be expected. The respective GW quasiparticle band structure, however, shows that the Cd 4d levels are now shifted to lower energies by 0.7 eV with respect to the LDA results. Their final position at −8.1 eV is still somewhat too high in energy when compared to experiment. The remaining difference is closely interrelated with the very basic question to which extent GW calculations are free from electronic self-interactions. The GW band structures for the Cd^{18+} PP and the Cd^{20+} PP are in very close agreement except for the 4d states and for the lowest conduction band (see Fig. 3). The latter has predominantly Cd 5s character. Therefore, the inclusion of the Cd 4s states in the valence electron shell has a strong influence on the lower conduction band of the quasiparticle band structure, leading to an additional opening of the fundamental energy gap by 0.85 eV as compared to the Cd^{18+} PP quasiparticle band structure. The gap resulting for the Cd^{20+} PP amounts to 2.45 eV in GWA which is now in excellent agreement with the experimental values of 2.50 or 2.55 eV [22]. The deviation of 0.1 eV is in the usual range as for group IV and III-V semiconductors. Furthermore, for the Cd^{20+} PP the perturbation operator $(\Sigma - V_{\mathrm{xc}})$ remains diagonal. We have carried out, as well, test calculations for the theoretical lattice constant of 5.73 Å using all four pseudopotentials. Our results show in each case that the GW quasiparticle gap *corrections* are basically the same for both lattice constants. For the Cd^{20+} PP the LDA gap opens up by 0.11 eV so that the quasiparticle gap energy for the theoretical lattice constant of 5.73 Å amounts to 2.56 eV. We note in passing that for both lattice constants the quasiparticle correction of the valence band maximum amounts to −1.1 eV for the Cd^{20+} PP. The same value was obtained in Ref. [17].

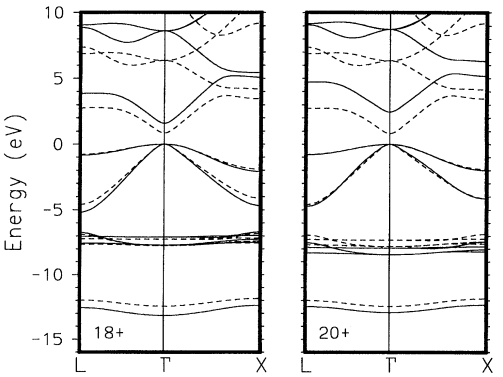

FIG. 3. Same as Fig. 1, but for the pseudopotentials Cd^{18+} (left panel) and Cd^{20+} (right panel), respectively.

Finally, we mention a most interesting result. The quasiparticle *corrections* $E_{\mathrm{GWA}} - E_{\mathrm{LDA}}$ turn out to be more or less the same for the Cd^{2+} PP and the Cd^{20+} PP as far as the S 3p valence bands and the conduction bands are concerned, as can be seen from comparing Figs. 1 (left panel) and 3 (right panel). In both cases the perturbation operator $(\Sigma - V_{\mathrm{xc}})$ is diagonal and the GW approximation works properly. For the self-energy-induced *shifts* of these bands it does not matter very much whether the *entire* Cd N shell is treated as a core or a valence shell. For the underlying LDA band structure, in contrast, we observe that the inclusion of only the Cd 5s electrons as valence electrons is insufficient. Only for the Cd^{12+} PP we obtain an LDA band structure that agrees very well with those of the Cd^{18+} PP and the Cd^{20+} PP (see Figs. 1 and 3). This is due to the fact that the 4s and 4p wave functions are nearly the same in the Cd atom and in the CdS solid as results from our calculation. Therefore the inclusion of these states as valence electrons is not necessary for LDA band structure calculations.

Under normal conditions CdS crystallizes in the wurtzite structure. Cubic CdS has been prepared by epitaxial deposition on GaAs(111) or GaP(111) single crystal slices by Cardona, Weinstein, and Wolff [22] and on InP(110) by Hofmann *et al.* [26]. The lattice constants of these substrates differ from that of cubic CdS. Those authors investigated transition energies between valence and conduction states by optical reflectivity and ellipsometry. The resulting data sets show differences of more than 1 eV (e.g., the E_0' and E_2 transitions) which could be related to substrate-induced strain effects in the CdS films. A direct comparison of our results for the bulk crystal with their film data thus is not straightforward. At least, one would need to know precisely which transitions at which **k** vectors contribute to certain measured features. For the E_0 transition this is obvious and the agreement of our calculated gap energy with the data within 0.1 eV is quite gratifying. For the other transitions which are more complicated to relate between theory and experiment we find the same type of agreement or disagreement that exists between the two data sets of Refs. [22] and [26].

In conclusion, we observe the following trends in the calculated band structure of CdS when core states are successively included in the valence electron shell. For the LDA band structure, final convergence is achieved as soon as all those electrons are treated as valence electrons whose wave functions are different in the atom and in the solid, i.e., it is sufficient to retain 5*s* and 4*d* Cd electrons in the valence electron shell. For the *GW* quasiparticle corrections, on the other hand, it is essential that all electrons of each shell are treated on equal footing, i.e., either as core electrons or as valence electrons. Since the 4*d* electrons have to be retained in the valence shell for a quantitative LDA description of the structural properties, the complete *N* shell has to be included in the valence electron shell for accurate *GW* calculations of the respective electronic structure. Including the *N* shell as valence shell, one obtains reasonable 4*d* bands, an excellent gap energy, and more accurate results, in general, because core polarization effects are included automatically. The artificial division of the *N* shell into core and valence states merely based on energetic arguments yields deviations of several eV in the quasiparticle corrections of all states.

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