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Quasiparticle band structures of six II-VI compounds: ZnS, ZnSe, ZnTe, CdS, CdSe, and CdTe

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Quasiparticle band structures of six II-VI compounds (ZnS, ZnSe, ZnTe, CdS, CdSe, and CdTe in the zinc-blende and wurtzite structures) are calculated using the *GW* approximation. Results for band structures, calculated using the *ab initio* pseudopotential method within the local-density approximation (LDA), are given along with the energies of the quasiparticle excitations at symmetry points. Comparisons are made with measured values and trends in the *GW* corrections to the LDA band structures are examined.

I. INTRODUCTION

A number of *ab initio* calculations have been performed to study structural and electronic properties of II-VI compounds.[1–5] Although the methods used in these calculations were different, all relied on the local-density approximation (LDA). The LDA is known to give reliable ground state properties of solids, hence these calculations are useful for structural studies. However, the LDA is not appropriate for describing electronic excitations. In particular, the calculated band gaps are underestimated. Although reliable band structures are available based on the empirical pseudopotential method,[6] it is still desirable to use *ab initio* calculations to provide a guide for interpreting experimental data and to test the applicability of the theory to II-VI semiconductors.

In this paper, we present the results of *ab initio* quasiparticle calculations of band structures for six II-VI compounds: ZnS, ZnSe, ZnTe, CdS, CdSe, and CdTe in both the zinc-blende and wurtzite structures. The *GW* approximation to the self-energy operator Σ is used.[7–9] This approach yields self-energy corrections for the electron energy and allows calculations of the band gap to within an accuracy approximately 0.1 eV when a random phase approximation (RPA) dielectric matrix is used, or within 0.1–0.3 eV when an appropriate model dielectric function is used.[8,9]

All calculations presented here are done at the experimental lattice parameters (see Table I). The *d* electrons are treated as core electrons. Their presence in the valence region is taken into account implicitly via nonlinear core corrections for the pseudopotentials used.[12] Some discussion of the influence of *d* electrons is given in Sec. III.

The *GW* approximation requires the input of a local field dielectric matrix. The Levine-Louie model dielectric function[9] has been used to construct the dielectric matrix in our calculations. In Sec. III we compare the results obtained for ZnS using the full RPA dielectric matrix and the model dielectric matrix.

This paper is organized as follows. Section II briefly describes the theoretical method. In Sec. III the calculated LDA and *GW* band structures are presented and compared with experimental data. A summary is given in Sec. IV.

II. THEORY

In this study, the standard plane-wave pseudopotential scheme[10,11] is used to obtain the LDA band structures and LDA wave functions which are employed as input for the *GW* calculations. The nonlocal *ab initio* pseudopotentials were generated with semirelativistic corrections. To describe some of the effects of the $3d$ core electrons of Zn and $4d$-core electrons of Cd without explicitly including them into the valence complex, the partial core corrections for exchange and correlation have been included. These corrections take into account the nonlinearity of the exchange-correlation potential in the region where core and valence charge densities overlap.[12] The core corrections are shown[13] to be important for obtaining good agreement with the experimental data for structural properties of systems with *d* electrons in the valence band. The cutoff energy for the LDA calculations is chosen to be 25 Ry. Good convergence for the electronic eigenvalues and wave functions is achieved with these cutoff energies.

TABLE I. Experimental (see Ref. 18) lattice parameters and static dielectric constants used in the calculations of the electronic band structures. The ideal value $u = 0.375$ has been used for all the wurtzite compounds. (ZB means zinc blende; WZ means wurtzite.)

Compound	$a_{\rm ZB}$(Å)	$a_{\rm WZ}$(Å)	$c_{\rm WZ}$(Å)	ϵ_∞
ZnS	5.409	3.814	6.527	5.1
ZnSe	5.668	3.996	6.626	5.4
ZnTe	6.089	4.270	6.990	5.3
CdS	5.818	4.135	6.749	5.3
CdSe	6.052	4.299	7.010	5.8
CdTe	6.480	4.57	7.47	7.3

The quasiparticle calculations are done using the Hybertsen-Louie approach[8] to the *GW* approximation. In this approach, the many-body exchange and correlation corrections to electron excitation energies are taken into account by introducing a nonlocal, energy-dependent and non-Hermitian self-energy operator Σ. The energies and wave functions for the quasiparticle excitations are obtained from the equation

$$(T + V_{\rm ext} + V_H)\Psi_{n\mathbf{k}}(\mathbf{r}) + \int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';E_{n,\mathbf{k}})\Psi_{n\mathbf{k}}(\mathbf{r}) = E_{n,\mathbf{k}}\Psi_{n\mathbf{k}}(\mathbf{r}), \quad (1)$$

where T is the kinetic energy operator, $V_{\rm ext}$ is the potential due to the ions, and V_H is the Hartree potential of the electrons. In the *GW* approximation the self-energy Σ is given by the expression

$$\Sigma(\mathbf{r},\mathbf{r}',E) = \frac{i}{2\pi}\int d\omega e^{-i\delta\omega}G(\mathbf{r},\mathbf{r}',E-\omega)W(\mathbf{r},\mathbf{r}',\omega), \quad (2)$$

where G is the full Green's function, W is the dynamically screened Coulomb interaction, and $\delta = 0^+$.

The Green's function G is first constructed using the LDA eigenfunctions and eigenvalues and then iteratively updated using the real parts of the quasiparticle energies from Eq. (1). The finite lifetime of the quasiparticles is neglected in this approach for semiconductors. To screen the Coulomb interaction, a generalized form of the Levine-Louie model dielectric matrix extended to finite frequencies by a generalized plasmon-pole model is used. This model dielectric function is known to give reliable results for various semiconductors[14] and requires only the dielectric constant ϵ_∞ as an input. The experimental values for the dielectric constants which have been used in our calculations are given in Table I. The results of the calculations are not very sensitive to the choice of ϵ_∞ since ϵ_∞ is responsible mostly for long-range screening.[14] To check the applicability of the model dielectric function in the case of the II-VI compounds, we also performed calculations employing the full RPA dielectric functions for ZnS in the zinc-blende structure. See the discussion of the results in Sec. III.

Once the self-energy operator Σ is constructed, the quasiparticle energies are calculated as

$$E^{qp}_{n,\mathbf{k}} = \epsilon^{\rm LDA}_{n,\mathbf{k}} + \langle n,\mathbf{k}|\Sigma - V^{\rm LDA}_{\rm xc}|n,\mathbf{k}\rangle, \quad (3)$$

where $V^{\rm LDA}_{\rm xc}$ is the LDA exchange-correlation potential. Here we make use of the fact that the quasiparticle wave functions are extremely well approximated by the LDA wave functions.[8]

A number of numerical cutoffs are involved in the calculations. The dielectric matrix is truncated at $|\mathbf{q}+\mathbf{G}| = 3.1$ (a.u.)$^{-1}$. For the zinc-blende (wurtzite) structure, 10 (8) special $\mathbf{k}$ points[15] in the irreducible part of the Brillouin zone have been chosen to perform the integration, and 100 (150) bands are taken into account in the calculation of the matrix elements of Σ. With these parameters we estimate the convergence errors of quasiparticle energies to be less than 0.1 eV.

III. RESULTS

The experimental values of the lattice parameters have been chosen for the calculations. It is important to note that the *GW* method is not a correction to the LDA approach but rather an independent approximation which is usually computed assuming experimental lattice parameters. Using LDA wave functions is technically very convenient since they are, in general, a good approximation to the quasiparticle wave functions.[8] The LDA eigenvalues are also used as a first-iteration values for the quasiparticle energies. Applying the *GW* method to the systems with *d* electrons in the valence band still encounters some difficulties which we will discuss later in this section.

The calculated LDA band structures (Figs. 1 and 2) are consistent with the previously published results. The LDA pseudopotential calculations treating *d* electrons as valence electrons give smaller gap values due to *p*-*d* hybridizations of the upper valence band with the *d* states which results in its repulsion upward causing a reduction in the gap. The introduction of the core corrections into the *sp*-only pseudopotential reduces the gaps slightly (from 2.47 eV to 2.37 eV for cubic ZnS in our calculations) but not enough to reproduce the calculations with the valence *d* electrons (1.84 eV for cubic ZnS).[2] The localized character of the *d* electron wave functions makes it difficult to treat them within the framework of the plane wave basis expansion since they require much higher plane wave cutoffs and moreover the LDA usually underestimates the binding energy of the *d* electrons and overestimates *p*-*d* hybridization.

The influence of the cation 3*d* levels on the valence *s* and *p* bands has been studied in detail by Wei and Zunger.[16] Recent calculations[1,2,16] within the LDA confirm the presence of strong *p*-*d* coupling when 3*d* levels are taken out of the core. This effect is responsible for a reduction of the gap discussed above and for the appearance of strong *d* character at the top of the valence band. However, this strong *p*-*d* interaction is mainly due to the fact that the LDA underbinds the 3*d* levels. Consequently, the 3*d* levels are calculated to be too close to the top of the valence band and the *p*-*d* coupling is overestimated within the LDA. The self-energy calculations performed for ZnS,[17] including the Zn 3*d* levels in the valence shell, show that the LDA wave functions for the top of the valence band (contrary to other semiconductors) are in disagreement with the corresponding quasiparticle wave functions. This can be demonstrated by calculating the nondiagonal matrix elements of the self-energy operator. When the 3*d* level are kept in the core, we find that at the Γ point this operator is almost diagonal. This confirms that in this case the LDA and quasiparticle *s*-*p* wave functions are in good agreement. However, when 3*d* levels are included into the valence complex together with *s* and *p* valence electrons, the zinc six-fold 3*d* com-

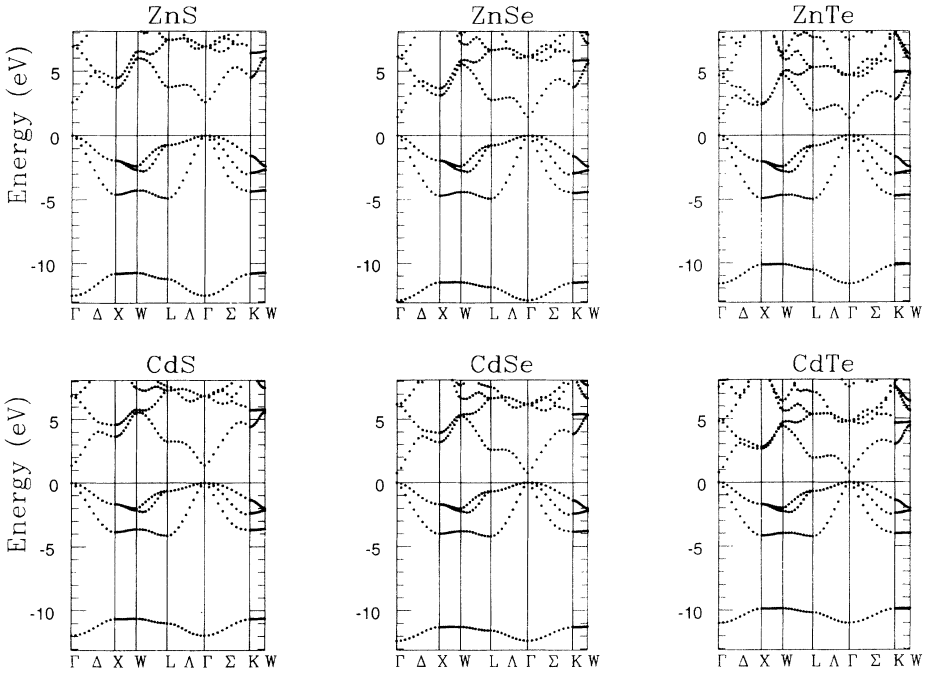

FIG. 1. Calculated LDA band structures in the zinc-blende structure at the experimental volume.

plex strongly couples with the threefold degenerate $3p$ highest occupied orbital level of sulfur. Consequently, an evaluation of the self-energy in this case requires a very time consuming self-consistent calculation of the full self-energy matrix, in the basis of the LDA wave functions including enough conduction states to converge the valence and lowest unoccupied orbital states.

In order to quantify the exact amount of d character in the valence-band maximum (VBM) states, without following the self-consistent scheme described above, we added a short-range attractive potential δV_d in the nonlocal d channel of the Zn pseudopotential. We use this "ansatz" pseudopotential to perform an LDA calculation. By adjusting the strength of δV_d, the $3d$ levels are moved down to their experimental position (10 eV below the top of the valence band). An analysis of the LDA wave functions obtained in this calculation shows that the d character of the VBM states is strongly reduced and the gap obtained is $E_g = 2.31$ eV. This value is nearly equal to the one obtained in the present calculations with the

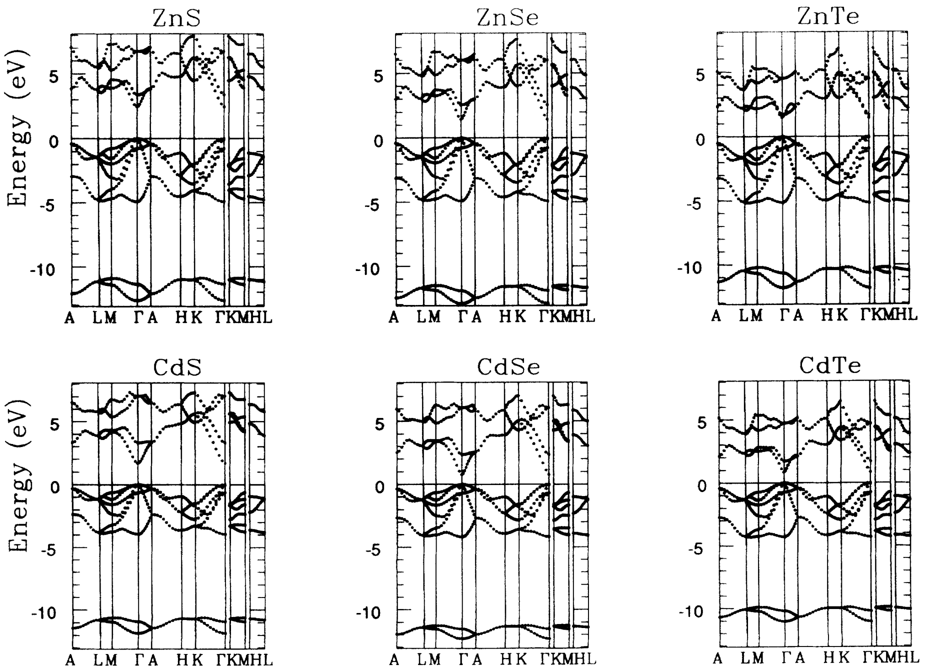

FIG. 2. Calculated LDA band structures in the wurtzite structure at the experimental volume.

TABLE II. Calculated LDA and *GW* energies (in eV) at symmetry points for the zinc-blende compounds.

	ZnS		ZnSe		ZnTe		CdS		CdSe		CdTe	
	LDA	*GW*	LDA	*GW*	LDA	*GW*	LDA	*GW*	LDA	*GW*	LDA	*GW*
Γ_{1v}	-12.63	-13.42	-12.92	-13.49	-11.64	-12.07	-11.95	-12.55	-12.36	-12.71	-11.00	-11.07
Γ_{15v}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Γ_{1c}	2.37	3.98	1.45	2.84	1.33	2.57	1.37	2.83	0.76	2.01	0.80	1.76
Γ_{15c}	6.83	8.74	6.12	7.67	4.66	5.91	6.87	8.65	6.18	7.60	4.82	5.80
L_{1v}	-11.35	-12.15	-11.88	-12.44	-10.55	-10.95	-10.98	-11.61	-11.57	-11.91	-10.18	-10.25
L_{1v}	-4.90	-5.20	-4.92	-5.23	-4.98	-5.31	-4.14	-4.33	-4.22	-4.42	-4.24	-4.41
L_{3v}	-0.73	-0.78	-0.76	-0.81	-0.82	-0.88	-0.65	-0.68	-0.68	-0.71	-0.70	-0.73
L_{1c}	3.60	5.28	2.74	4.14	1.91	3.07	3.25	4.82	2.56	3.87	1.91	2.84
L_{3c}	7.29	9.17	6.63	8.18	5.26	6.52	7.30	9.02	6.65	8.04	5.36	6.33
X_{1v}	-10.92	-11.71	-11.52	-12.07	-10.13	-10.52	-10.66	-11.29	-11.30	-11.65	-9.88	-9.96
X_{3v}	-4.49	-4.89	-4.70	-5.03	-4.92	-5.27	-3.85	-4.05	-4.01	-4.22	-4.18	-4.36
X_{5v}	-1.94	-2.06	-1.96	-2.08	-2.02	-2.16	-1.66	-1.74	-1.70	-1.78	-1.72	-1.78
X_{1c}	3.55	5.14	3.09	4.41	2.38	3.47	3.64	5.08	3.17	4.37	2.63	3.46
X_{3c}	4.34	6.03	3.64	5.01	2.42	3.53	4.58	6.17	3.92	5.20	2.77	3.64

$3d$ levels in the core (2.37 eV). This shows that, at least for the Γ point, it is a good approximation to treat the s and p levels without considering the coupling with the $3d$ levels. We also note that the matrix elements of the short-range δV_d potential on the s and p eigenstates are negligible since the potential is localized in the core region of the Zn atoms. So these levels feel the "true" ionic Zn pseudopotential despite the addition of δV_d.

The results of our LDA and *GW* band structure calculations for some of the high symmetry **k** points are given in Tables II and III. The *GW* calculations open the gap and increase both the valence and conduction bandwidths with respect to the corresponding LDA calculations. Because of the nonlocal and energy dependent character of the self-energy operator Σ these corrections to LDA eigenvalues are also energy dependent. This dependence for the zinc-blende compounds is illustrated in Fig. 3.

The *GW* corrections to the LDA eigenvalues are almost linear in energy and **k** independent for the upper valence bands. Our calculations for eight different **k** points (some of which are not symmetry points) in the Brillouin zone of cubic ZnSe also reproduce this behavior. This fact can be used to calculate the self-energy corrections for the upper valence band LDA eigenvalues without actually performing the *GW* calculations for all the **k** points.

As we go from more ionic to less ionic compounds, the self-energy corrections to the LDA energies decrease. This result can be expected since the LDA is, in principle, exact for the homogeneous electron gas and higher ionicity means less homogeneous charge densities and larger local field effects. The slope of the corrections also changes slightly, and the corrections are the smallest for the valence and the conduction bands of CdTe, which is the closest to the homogeneous case among the compounds considered. If we consider *GW* corrections to the top valence and the lowest conduction bands, we note that for the row of compounds with the same cation, ionicity change mostly affects corrections for the valence anion s and p band. For the compounds with the same anion but different cations both the corrections to the valence and to the conduction bands are affected. The cor-

TABLE III. Calculated LDA and *GW* energies (in eV) at symmetry points for the wurtzite compounds.

	ZnS		ZnSe		ZnTe		CdS		CdSe		CdTe	
	LDA	*GW*	LDA	*GW*	LDA	*GW*	LDA	*GW*	LDA	*GW*	LDA	*GW*
Γ_{1v}	-12.66	-13.65	-12.39	-13.56	-11.81	-12.28	-11.89	-12.53	-12.32	-12.70	-11.06	-11.23
Γ_{3v}	-11.37	-12.34	-11.93	-12.54	-10.66	-11.10	-10.95	-11.64	-11.54	-11.93	-10.21	-10.38
Γ_{3v}	-4.95	-5.35	-4.93	-5.31	-5.15	-5.55	-4.10	-4.32	-4.18	-4.44	-4.30	-4.53
Γ_{6v}	-0.78	-0.85	-0.77	-0.84	-0.92	-1.00	-0.65	-0.69	-0.69	-0.74	-0.75	-0.80
Γ_{1v}	-0.07	-0.09	-0.10	-0.10	-0.07	-0.09	-0.06	-0.06	-0.06	-0.05	-0.06	-0.08
Γ_{5v}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Γ_{1c}	2.45	4.08	1.43	2.75	1.48	2.67	1.36	2.79	0.75	1.91	0.85	1.80
Γ_{3c}	3.39	5.06	2.55	3.89	1.68	2.73	3.02	4.54	2.34	3.55	1.71	2.58
Γ_{3c}	6.74	8.66	6.02	7.48	4.49	5.37	6.79	8.50	6.06	7.38	4.71	5.65
M_{1v}	-11.39	-12.35	-11.90	-12.50	-10.68	-11.11	-10.97	-11.90	-11.55	-11.94	-10.23	-10.39
M_{3v}	-10.92	-11.88	-11.53	-12.13	-10.22	-10.64	-10.64	-11.32	-11.28	-11.66	-9.91	-10.07
M_{1v}	-4.70	-5.09	-4.78	-5.14	-5.07	-5.46	-3.91	-4.11	-4.04	-4.27	-4.25	-4.49
M_{3v}	-3.98	-4.31	-4.14	-4.45	-4.37	-4.70	-3.34	-3.50	-3.50	-3.69	-3.69	-3.89
M_{1v}	-3.01	-3.25	-3.00	-3.22	-3.22	-3.48	-2.44	-2.57	-2.51	-2.66	-3.61	-3.79
M_{2v}	-1.96	-2.12	-1.94	-2.10	-2.13	-2.30	-1.64	-1.72	-1.68	-1.78	-1.76	-1.86
M_{3v}	-1.57	-1.68	-1.59	-1.68	-1.79	-1.92	-1.23	-1.28	-1.27	-1.35	-1.39	-1.49
M_{4v}	-0.77	-0.84	-0.81	-0.88	-0.89	-0.96	-0.65	-0.68	-0.67	-0.72	-0.73	-0.77
M_{1c}	3.90	5.55	3.26	4.54	2.16	3.13	3.92	5.50	3.36	4.63	2.50	3.30
M_{3c}	4.55	6.32	3.70	5.10	3.01	4.15	4.05	5.55	3.43	4.59	2.81	3.76
M_{3c}	5.29	6.98	4.85	6.18	4.14	5.18	5.17	6.65	4.82	5.99	4.14	4.97
M_{1c}	7.29	9.23	6.63	8.11	5.22	6.37	6.55	8.29	6.29	7.73	5.34	6.27

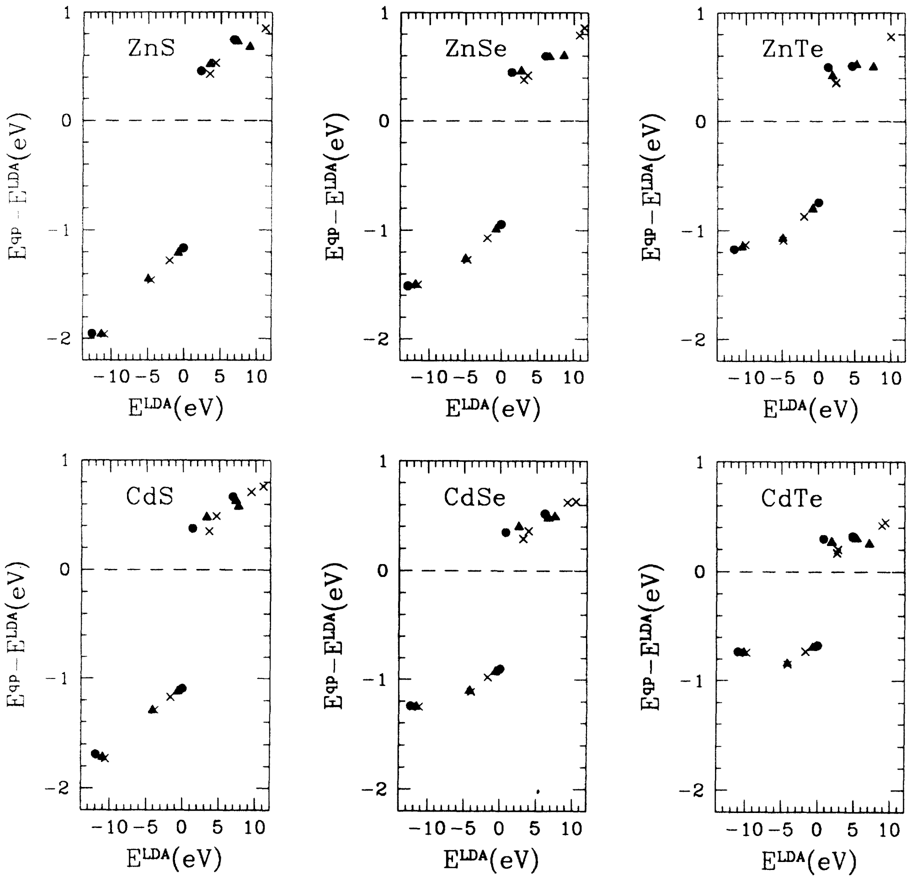

FIG. 3. The *GW* corrections to the LDA energies for the zinc-blende compounds at different symmetry points (circles correspond to Γ, crosses to *X*, and triangles to *L*).

rections to the conduction bands have much more complicated character than the corrections to the valence bands. They show clear **k**-dependent behavior.

The self-energy corrections for the wurtzite compounds are very similar to those found for the zinc-blende compounds. This can be explained by the fact that the self-energy operator is a short-range operator and the differences between these two structures only appear when we consider the third nearest neighbor atomic positions.

The calculated gaps and their experimental values are given in Tables IV and V.

The LDA calculations underestimate the gaps by 30–50 %. The *GW* calculations results are in a fairly good agreement with experiment. Note that since we do not include spin-orbit splitting in our calculations, the calculated values correspond to the energy differences between the lowest conduction band and the center of gravity of the two split upper valence bands. The spin-orbit splitting is small (less than 0.07 eV) for the sulfides but it is approximately 0.4 eV for the selenides and 1.0 eV for the tellurides. After taking into account the spin-orbit split-

TABLE IV. Calculated and experimental (see Ref. 18) band gaps for the zinc-blende compounds (eV). When two values are given for the experimental gap, they correspond to transitions from the spin-orbit split upper valence bands to the conduction band. The number in parentheses is the energy difference between the center of gravity of the spin-orbit split upper valence bands and the conduction band.

Compound	LDA	*GW*	Expt.
ZnS	2.37	3.98	3.78, 3.85 (3.80)
ZnSe	1.45	2.84	2.82, 3.24 (2.96)
ZnTe	1.33	2.57	2.39, 3.36 (2.71)
CdS	1.37	2.83	2.55
CdSe	0.76	2.01	1.90
CdTe	0.80	1.76	1.60, 2.55 (1.92)

TABLE V. Calculated and experimental (see Ref. 18) band gaps for the wurtzite compounds (eV). When two values are given for the experimental gap, they correspond to transitions from the spin-orbit split upper valence bands to the conduction band. The numbers in parentheses are the energy difference between the center of gravity of the spin-orbit split upper valence bands and the conduction band.

Compound	LDA	*GW*	Expt.
ZnS	2.45	4.03	3.91, 3.94 (3.92)
ZnSe	1.43	2.75	2.87
ZnTe	1.48	2.67	
CdS	1.36	2.79	2.58, 2.60 (2.59)
CdSe	0.75	1.91	1.83, 2.26 (1.97)
CdTe	0.85	1.80	1.60

ting by calculating the position of the center of gravity for the split valence bands, we find that the experiment gap values lie within the accuracy range (0.1–0.3 eV) of the calculated values.

Since the positions of the levels and the transition energies are affected by the spin-orbit splitting, the comparison of our results with the experimental values without making the corrections for the spin-orbit splitting is possible only for the sulfides. When comparing the results of the *GW* calculations with the experimental values, it is necessary to consider that the one particle Green's function approach gives the energies of the excitations corresponding to one particle being removed from or added to the system (see the discussion in Ref. 14). Hence we would expect the best agreement of our calculations with results from photoemission and inverse photoemission experiments.

In Table VI we compare the calculated quasiparticle energies at symmetry points with the angle resolved photoemission spectroscopy data[18] for hexagonal CdS. The agreement of our results with experiment is very good except for the M_{3v} state. But we note that the M_{1v} state has not been identified in the experiment. This suggests that the M_{1v} and M_{3v} levels may have not been resolved.

The results of our calculations are also consistent with the experimental values for gaps at symmetry points other than Γ. These gaps for some of the cubic compounds are given in Table VII. Again after taking into account the spin-orbit splitting we find that the experimental values are within the accuracy range of our calculation (except for the X point of ZnS).

Treating of the lowest s-like valence band is difficult both theoretically and experimentally. The energy of this band is very close to the energies of the d bands which are not included into the valence complex in our calculations. Thus, our LDA eigenstates and eigenvalues for the lowest valence band are not very reliable. The quasiparticle calculations may introduce additional errors into the calculated energies for this band since we use the calculated LDA wave functions in construction of the self-energy operator. Besides the generalized plasmon-pole approximation is less valid for describing the dynamical screening for this band and the infinite lifetime approximation used in our calculations fails for the higher-energy excitations. We therefore do not expect our results for the lowest valence band to reproduce as well the experimental values. Comparing our results with the experimental data, we find that the binding energy of the localized anion s state is underestimated by 1–1.5 eV.

TABLE VI. Calculated and experimental valence-band energies (in eV) at high symmetry points for CdS in the wurtzite structure referred to the top of the valence band.

	GW	Exp		*GW*	Exp
Γ_{3v}	-4.32	-4.5	M_{1v}	-4.11	-4.3
Γ_{6v}	-0.69	-0.8	M_{3v}	-3.50	-3.0
Γ_{5v}	0.00	0.0	M_{1v}	-2.57	not identified
$L_{1v}+L_{3v}$	-4.15	-4.3	M_{2v}	-1.72	-1.7
$L_{2v}+L_{4v}$	-1.27	-1.5	M_{3v}	-1.28	-1.1
$L_{1v}+L_{3v}$	-1.24	-1.4	M_{3v}	-0.68	-0.7
$A_{1v}+L_{3v}$	-2.60	-2.6			
$A_{5v}+L_{6v}$	-0.36	-0.5			

In this work we neglect the effects arising from core polarization and treat core-valence exchange and correlations at the LDA level only. Although relaxation effects could be important for the materials with shallow cores,[19] the validity of this approximation is confirmed by the good agreement of our calculated quasiparticle energies with the experimental values. To illustrate how the approximations made in our calculations influence the results, we calculated the quasiparticle energies with and without core corrections using the full RPA and the model dielectric functions for ZnS in the zinc-blende structure. The results are given in Table VIII.

From Table VIII we conclude that the core corrections are more important for the conduction bands than for the valence bands. Since the overlap with the core charge density is larger for the states with s character than for the states with p character, we expect that the nonlinear core corrections should be larger for s-like states. The lowest valence band is an exception, since its wave function is very close to the atomic wave function (the dispersion of this band is rather small); thus, this band is almost unaffected by introducing the core corrections. The core corrections are important for the lowest conduction band which has mostly s character and consequently these corrections influence the size of the band gap. For example, for Γ_{1c} the change in the energy due to the core corrections are 0.1 eV for the LDA and 0.25 eV for the *GW* calculations and thus cannot be neglected.

Table VII also illustrates that the quasiparticle energies obtained using the model dielectric matrix are in a good agreement with the results of the calculation with the full RPA dielectric matrix. The quasiparticle energies relative to the valence-band edge energies are within 0.1–

TABLE VII. Calculated quasiparticle values and available experimental (see Ref. 18) data for the gaps at X and L (in eV) for the zinc-blende compounds. When two experimental values are given, they correspond to transitions from the spin-orbit splitted highest valence band to the lowest conduction band.

	ZnS		ZnSe		ZnTe		CdTe	
	GW	Expt.	*GW*	Expt.	*GW*	Expt.	*GW*	Expt.
$L_{3v}-L_{1c}$	6.06	5.81	4.95	4.91,5.14	3.95		3.57	3.41,4.02
$X_{5v}-X_{1c}$	7.20	6.6	6.49	6.42	5.63	5.41	5.14	

TABLE VIII. Comparison of the LDA eigenvalues, the quasiparticle energies (in eV) calculated using the model dielectric function, and the quasiparticle energies from the full calculations with and without the core corrections for ZnS in the zinc-blende structure.

Level	Without core correction		With core correction		
	LDA	*GW*-RPA	LDA	*GW* model	*GW*-RPA
Γ_{1v}	-12.61	-12.71	-12.63	-13.42	-12.73
Γ_{15v}	0	0	0	0	0
Γ_{1c}	2.47	4.22	2.37	3.98	3.97
Γ_{15c}	6.82	8.91	6.83	8.74	8.87
X_{1v}	-10.89	-11.06	-10.92	-11.71	-11.08
X_{3v}	-4.61	-4.82	-4.59	-4.89	-4.80
X_{5v}	-1.93	-2.00	-1.94	-2.06	-2.01
X_{1c}	3.66	5.45	3.55	5.14	5.30
X_{3c}	4.40	6.31	4.34	6.03	6.20
L_{1v}	-11.33	-11.48	-11.35	-12.15	-11.50
L_{1v}	-4.89	-5.10	-4.90	-5.2	-5.11
L_{3v}	-0.74	-0.76	-0.73	-0.78	-0.78
L_{1c}	3.66	5.53	3.60	5.28	5.43
L_{3c}	7.33	9.38	7.29	9.17	9.29

0.2 eV of the results from the full theory. The model dielectric matrix usually slightly underestimates the screening in the intermediate range of q and overestimates it in the high-q region.[14] This is also true for our calculations as illustrated by Fig. 4. Less efficient screening pushes the energies of the valence states further down. This effect is the largest for the lowest Γ_{1v} valence band where the discrepancy between the full and the model calculations is around 0.6–0.7 eV. Since the model dielectric matrix is constructed using the local-density-functional approach, we may expect even better agreement between the model and full RPA calculations for the compounds less ionic than ZnS.

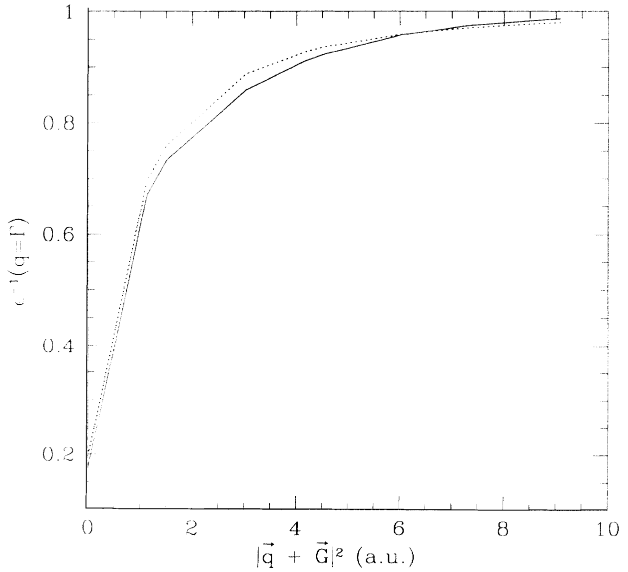

FIG. 4. Comparison of the diagonal elements of the model (broken line) and the RPA (solid line) inverse dielectric matrices for cubic ZnS at Γ.

IV. CONCLUSION

The quasiparticle band structures of six II-VI compounds (ZnS, ZnTe, ZnTe, CdS, CdSe, CdTe) have been obtained using the *GW* approximation for the self-energy operator. In our calculations we treat d electrons as core electrons. The generalized Levine-Louie model dielectric function is used for screening. Satisfactory agreement between the calculated quasiparticle energies and experimental spectroscopic data is obtained. This agreement together with the results of the full RPA calculation for ZnS confirms the validity of the approximations made. The results of our calculations demonstrate the applicability of the *GW* approximation to the quasiparticle band structure calculations for a wide class of II-VI compounds.

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