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Electronic structure of II^B-VI semiconductors in the *GW* approximation

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A series of *GW* calculations for zinc-blende Zn, Cd, and Hg chalcogenides (S, Se, and Te) is presented. The resulting quasiparticle gaps are 0.3–0.6 eV smaller than in experiment. The cation semicore states remain similarly underbined as in previous *GW* calculations for II^B-VI materials. It is shown that application of the plasmon-pole model for screening leads to systematic and qualitative errors: the band gaps result larger and the occupied band widths undergo expansion, instead of contraction. Several steps, like including off-diagonal matrix elements of the self-energy, updating eigenvalues in the Green's function and screening, and using the special vertex corrections, are examined. We also propose a scheme to treat core corrections in the case when Zn^{2+}, Cd^{2+}, or Hg^{2+} pseudopotentials are used in a *GW* calculation.

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I. INTRODUCTION

The II^B-VI semiconductors are a special class of materials. The zinc-, cadmium-, and mercury chalcogenides show a large spectrum of properties, making them good candidates for modern optoelectronic and spintronic applications. From the theoretical standpoint they are very interesting and challenging materials as well. Many of their special properties are largely determined by the interaction between the localized semicore *d* electrons with the valence *sp* electrons. Due to this *sp-d* interaction the *ab initio* description of II^B-VI compounds is more complex than for group-IV or -III-V semiconductors and in some sense less satisfactory. For example, energy gaps between occupied and empty bands provided by the local-density approximation (LDA) of the density-functional theory[1] (DFT) deviate much more from experiment than is usually the case. Similarly, the shallow semicore *d* levels are strongly underbined within the LDA. LDA calculations for these materials have been available for a long time, and the problems were recognized and analyzed in detail by Wei and Zunger.[2] It is well known, however, that the LDA band structure, as well as presumably any Kohn-Sham band structure, need not correspond to physical, one-particle excitations in the system, so the problems with the LDA are in a sense understood. On the other hand, an interesting question is whether the description of electronic excitations by the *GW* approximation[3–9] were as successfull for II^B-VI compounds as it turned out to be for standard semiconductors.

Partially, an answer to this question is given by a few already existing calculations for II^B-VI compounds: the calculations of Aryasetwan and co-workers[10,11] for ZnO, ZnS, and ZnSe, of Rohlfing *et al.*[12,13] for CdS and ZnS, of Rohlfing and Louie[14] for HgSe, and very recently, of Luo *et al.*[15] for ZnS and ZnSe. Zakharov *et al.*[16] have applied the *GW* approximation to the case of all zinc and cadmium chalcogenides in their zinc-blende and wurtzite phases. In their calculation, however, the important for physics of these compounds semicore *d* states have not been explicitly considered and kept rigidly in the core. It is interesting to note that all these calculations differ in the way the *GW* approximation is applied and also differ in the obtained results. In addition, in a very recent *GW* calculation for several materials by Kotani and van Schilfgaarde[17] it was claimed that the application of the *GW* method including all electrons, as opposed to pseudopotentials, leads to a systematic lowering of the calculated gaps, thus spoiling the usually good-quality results of the *GW*-pseudopotential calculations. This finding seems to be in accordance with the most recent all-electron and *self-consistent* application of the *GW* scheme to Si and Ge by Ku and Eguiluz.[18] These authors report on the opposite effect of core electrons and self-consistency on the band gap in Si and Ge and suggest the universality of this phenomenon.

In this situation, in order to draw more general conclusions, it is important to work out a large database of results obtained with the same methodology and technicalities for all II^B-VI compounds. For this reason we present in this paper *GW* calculations for ZnS, ZnSe, ZnTe, CdS, CdSe, CdTe, HgS, HgSe, and HgTe in the zinc-blende modification. Our calculations are based on pseudopotentials. However, using Zn^{20+}, Cd^{20+}, and Hg^{20+} pseudopotentials—i.e., explicitly including the most important core electrons—namely, *s*, *p*, and *d* electrons from the $n=3$, $n=4$, and $n=5$ shells of Zn, Cd, amd Hg atoms, respectively—ensures being not far from the all-electron limit. The mixed-basis expansion for Bloch orbitals is used without any shape approximation to the Kohn-Sham potential. The screened Coulomb interaction $W(\omega)$ is calculated within the random phase approximation (RPA) with an explicit ω dependence. The results are compared then with ones obtained using the plasmon-pole (PP) approximation.[4,6] The role of the exchange-correlation contribution to screening, as described by the time-dependent LDA, is shortly discussed. The effect of the off-diagonal matrix elements of the self-energy is also examined. As usual, our calculations are not self-consistent in the *interacting* Green's function; however, the first step towards self-consistency is examined. It consists in updating the quasiparticle energies in the construction of the Green's function and response.

Our results show that with the exception of β-HgS, the *GW* energy gaps between conduction and valence states are 0.3–0.6 eV smaller than in experiment. Imposing a limited self-consistency by updating the eigenvalues increases the gaps by 0.1–0.4 eV, thus leading to a rather good agreement with experiment. Our results concerning the binding energy of semicore states agree with previous observations[10–13,15,17] that the *GW* theory, although performing better than the LDA, still underbinds theses states. When the plasmon-pole approximation is used instead of the full, ω-dependent, RPA screening, systematic trends are noted: (i) *GW* energy gaps get larger, (ii) semicore states are more bound, and (iii) occupied bandwidths undergo an opposite shift than is obtained with the full, frequency-dependent screening.

In the next section a short presentation of our implementation of the *GW* scheme is given together with some technicalities. In Sec. III the results are presented and compared with experiment. In Sec. IV the first steps towards self-consistency, vertex corrections, and the role of the off-diagonal matrix elements of self-energy are discussed. In Sec. V the results of an approach using Zn^{2+}, Cd^{2+}, and Hg^{2+} pseudopotentials are presented.

II. *GW* APPROXIMATION

The band structure of a solid is the energy-quasimomentum dependence of one-particle excitations—i.e., of electrons or holes created in the system—e.g., in the inverse-photoemission or photoemission process. It is described by poles of one-particle Green's functions Fourier transformed to the energy-momentum domain. Green's functions are obtained solving the Dyson equation, in which the electron-electron interaction is contained in two terms: the electrostatic, Hartree potential and the non-Hermitian, energy-dependent, and spatially nonlocal operator, called the self-energy. The complexity of obtaining the *interacting* Green's functions—i.e., the Green's functions when the electron-electron interaction is described more realistically than in the one-particle approximation—comes from the complexity of calculation of self-energies. This is made managable only using approximations. The most popular approximation applied in the *ab initio* framework is the *GW* approximation.[3,4] In this scheme the self-energy is represented by a product of the Green's function G and the dynamically screened interparticle (Coulomb) interaction $W = \epsilon^{-1} 1/r$:

$$\Sigma = iGW. \tag{1}$$

ϵ^{-1} is the inverse, longitudinal, RPA, electronic, dielectric function of the system.

First applications of the *GW* approximation to real solids date back to the works of Strinati *et al.*,[5] Hybertsen and Louie,[6] and Godby *et al.*[7] Since then, it has been applied to many materials; the results are described in two recent reviews.[8,9] In most cases the "standard" put forward by the Hybertsen-Louie calculation[6] was followed—the *GW* approximation is applied perturbatively on top of the zeroth-order, LDA band structure, within the pseudopotential framework, using plane-wave expansion of Bloch functions and interactions and modeling the energy dependence of ϵ^{-1} by the plasmon-pole approximation.[4,6] The work of Zakharov *et al.*[16] for zinc and cadmium chalcogenides is based on the same methodology, with the exception that the screening was approximated by a model function and the Green's function entering Eq. (1) was iteratively updated. The authors used Zn^{2+} and Cd^{2+} pseudopotentials and the semicore *d* states were ignored in their *GW* calculation. Since then, a few more rigorous calculations for II^B-VI compounds have appeared, with an explicit account of the semicore *d* states. In particular, Rohlfing *et al.*[12] have shown for the case of cubic CdS that when the semicore Cd 4*d* states are treated as valence states in a *GW* calculation, it is mandatory to include also more deep core states from the same $n=4$ shell. This is an important and general conclusion concerning not only CdS and other II^B-VI materials, but valid for all cases where localized *d* orbitals must be treated explicitly.[19]

Similarly to Rohlfing *et al.*,[12] our implementation of the *GW* scheme for II^B-VI compounds is based on the cation 20+ (Zn^{20+}, Cd^{20+}, Hg^{20+}) and anion 6+ (S^{6+}, Se^{6+}, Te^{6+}) LDA pseudopotentials.[20] The zeroth-order, LDA band structure is obtained using the mixed-basis set composed of localized gaussians of *s*, *p*, and *d* symmetry at cation sites and plane waves with a cutoff of 30 Ry. We believe that such a basis describes well both the localized core and semicore *s*, *p*, and *d* states as well as the highly excited conduction bands. This is an important prerequisite of a *GW* calculation because of the slow convergence of the *GW* self-energy with respect to the contribution of highly excited states.[21,22] The frequency-dependent RPA screened Coulomb interaction $W(\omega)$ is calculated in Fourier space at the Monkhorst-Pack[23] *k* mesh of 32 points in the Brillouin zone. The Coulomb singularity is integrated out using the Gygi-Baldereschi method.[24] The calculations follow our previous implementations of the *GW* scheme.[21,25,26] As usual, the Dyson equation is solved in the diagonal approximation—i.e., projecting all relevant quantities on the particular state of interest ϕ_{kn} (k is the wave vector and n is the band index):

$$E^{QP} = E_{kn}^{LDA} + \langle \phi_{kn} | \Sigma(E^{QP}) - V_{xc}^{LDA} | \phi_{kn} \rangle. \tag{2}$$

E^{QP}, E_{kn}^{LDA}, and V_{xc}^{LDA} are the quasiparticle energy, LDA Kohn-Sham energy, and LDA exchange-correlation potential respectively. Equation (2) can be solved for E^{QP} iteratively or, for not large quasiparticle shifts $E^{QP} - E_{kn}^{LDA}$, analytically, through the linearization of the self-energy around E_{kn}^{LDA}:

$$E^{QP} = E_{kn}^{LDA} + Z \langle \phi_{kn} | \Sigma(E_{kn}^{LDA}) - V_{xc}^{LDA} | \phi_{kn} \rangle. \tag{3}$$

Z is the renormalization constant:

$$Z = \left(1 - \frac{d\langle \phi_{kn} | \Sigma(E_{kn}^{LDA}) | \phi_{kn} \rangle}{dE} \right)^{-1}. \tag{4}$$

The spin-orbit (SO) interaction is included perturbatively after the LDA self-consistency or *GW* self-energy has been obtained.

It was found out by Rohlfing *et al.*[12] for CdS that using the Cd^{12+} pseudopotential—i.e., explicitly including the Cd 4*d* states and keeping rigidly in core the Cd 4*s* and Cd 4*p* states—significantly deteriorates the results. The underbound in the LDA Cd 4*d* states get even less bound in the *GW* calculation. On the other hand, putting the whole $n=4$ shell of Cd into the core—i.e., working with Cd^{2+} pseudopotential (and following the "standard" of the Hybertsen and Louie[6])

TABLE I. ZnS, ZnSe, and ZnTe in the zinc-blende structure: one-electron energies (in eV) at Γ, *X*, and *L* points. (LDA) Kohn-Sham-LDA results, (*GW*) *GW*-RPA calculations with full, frequency-dependent screening, and (*GW*-PP) *GW*-RPA using the plasmon-pole model of screening. Spin-orbit interaction not included.

	ZnS			ZnSe			ZnTe		
	LDA	*GW*	*GW*-PP	LDA	*GW*	*GW*-PP	LDA	*GW*	*GW*-PP
Γ_{1c}	1.84	3.41	3.50	1.02	2.37	2.46	1.04	2.27	2.39
Γ_{15v}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Γ_{12d}	−6.02	−6.59	−6.68	−6.33	−6.98	−7.04	−6.82	−7.48	−7.46
Γ_{15d}	−6.50	−7.01	−7.18	−6.69	−7.30	−7.42	−7.05	−7.68	−7.70
Γ_{1v}	−13.08	−12.57	−13.32	−13.23	−12.90	−13.66	−11.83	−11.52	−12.26
X_{1c}	3.19	4.59	4.62	2.79	3.92	3.94	2.11	3.11	3.20
X_{5v}	−2.25	−2.24	−2.42	−2.20	−2.20	−2.38	−2.20	−2.19	−2.35
X_{3v}	−4.69	−4.66	−4.91	−4.86	−4.79	−5.09	−5.11	−4.96	−5.27
X_{1v}	−11.79	−11.37	−12.02	−12.15	−11.89	−12.51	−10.63	−10.41	−10.97
L_{1c}	3.06	4.71	4.80	2.31	3.68	3.76	1.61	2.72	2.82
L_{3v}	−0.88	−0.89	−0.94	−0.88	−0.88	−0.94	−0.91	−0.91	−0.97
L_{1v}	−5.39	−5.18	−5.66	−5.31	−5.12	−5.60	−5.27	−5.09	−5.50
L_{1v}	−12.12	−11.68	−12.35	−12.43	−12.15	−12.80	−10.95	−10.71	−11.30

results for CdS—according to Rohlfing *et al.*[12]—in an energy gap unusually—about 1.2 eV—bigger than the experimental gap. This is in contrast with the calculation of Zakharov *et al.*,[16] whose gap for zinc-blende CdS was only 0.3 eV bigger than in experiment. Our results support the observation of Rohlfing *et al.*[12] We will address this point in Sec. V and will also suggest that one should take a careful care of core density corrections in that case in order to get resonable results.

All calculations have been done using the experimental, zinc-blende lattice constants, which are 10.214, 10.713, and 11.504 a.u. for ZnS, ZnSe, and ZnTe; 11.017, 11.497, and 12.245 a.u. for CdS, CdSe, and CdTe; and 11.057, 11.497, and 12.210 a.u. for HgS, HgSe, and HgTe, respectively.

III. RESULTS

In Tables I–III the LDA-Kohn-Sham and *GW* energies of a few states at the Γ, *X*, and *L* points are given for zinc-blende Zn, Cd, and Hg chalcogenides respectively. The *GW* results are obtained with the frequency-dependent, RPA-type screening of the electron-electron interaction (column denoted "*GW*"). For comparison, the results obtained with the plasmon-pole approximation based on the static limit of the screening matrices are also presented (column "*GW*-PP").[27] The results in Tables I–III are obtained using scalar-relativistic pseudopotentials—however, without including the spin-orbit interaction. We present these results in order to

TABLE II. Same as Table I for CdS, CdSe, and CdTe in the zinc-blende structure.

	CdS			CdSe			CdTe		
	LDA	*GW*	*GW*-PP	LDA	*GW*	*GW*-PP	LDA	*GW*	*GW*-PP
Γ_{1c}	0.82	2.13	2.23	0.29	1.38	1.48	0.49	1.51	1.64
Γ_{15v}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Γ_{12d}	−7.24	−7.88	−7.95	−7.49	−8.21	−8.25	−7.92	−8.65	−8.62
Γ_{15d}	−7.72	−8.29	−8.44	−7.88	−8.53	−8.64	−8.19	−8.88	−8.92
Γ_{1v}	−12.35	−11.84	−12.56	−12.60	−12.25	−12.97	−11.21	−10.91	−11.59
X_{1c}	3.30	4.54	4.59	2.92	3.90	3.95	2.43	3.22	3.29
X_{5v}	−1.95	−1.92	−2.08	−1.90	−1.89	−2.05	−1.90	−1.91	−2.05
X_{3v}	−4.11	−3.94	−4.22	−4.20	−4.07	−4.36	−4.42	−4.30	−4.57
X_{1v}	−11.76	−11.37	−11.97	−12.09	−11.86	−12.41	−10.67	−10.52	−11.04
L_{1c}	2.70	4.13	4.25	2.11	3.27	3.39	1.59	2.57	2.70
L_{3v}	−0.78	−0.78	−0.83	−0.77	−0.78	−0.83	−0.79	−0.81	−0.85
L_{1v}	−4.57	−4.37	−4.76	−4.51	−4.37	−4.75	−4.53	−4.42	−4.76
L_{1v}	−11.90	−11.48	−12.11	−12.21	−11.95	−12.54	−10.79	−10.60	−11.16

TABLE III. Same as Table I for HgS, HgSe, and HgTe in the zinc-blende structure.

	HgS			HgSe			HgTe		
	LDA	*GW*	*GW*-PP	LDA	*GW*	*GW*-PP	LDA	*GW*	*GW*-PP
Γ_{15c}	5.84	6.77	6.79	5.37	6.20	6.21	4.15	4.79	4.81
Γ_{15v}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Γ_{1c}	−0.65	+0.03	+0.05	−1.14	−0.51	−0.49	−0.90	−0.31	−0.25
Γ_{12d}	−6.20	−6.48	−6.46	−6.39	−6.82	−6.83	−6.77	−7.21	−7.19
Γ_{15d}	−7.12	−7.29	−7.45	−7.14	−7.46	−7.62	−7.31	−7.68	−7.77
Γ_{1v}	−13.23	−12.76	−13.61	−13.42	−13.03	−13.82	−12.02	−11.71	−12.48
X_{1c}	3.08	3.95	4.08	2.66	3.43	3.53	1.79	2.39	2.45
X_{5v}	−2.37	−2.35	−2.58	−2.32	−2.30	−2.51	−2.29	−2.29	−2.50
X_{3v}	−4.94	−4.88	−5.00	−5.13	−5.11	−5.26	−5.48	−5.46	−5.64
X_{1v}	−12.47	−12.15	−12.81	−12.76	−12.51	−13.10	−11.23	−11.07	−11.63
L_{1c}	1.41	2.28	2.32	0.94	1.72	1.74	0.56	1.20	1.23
L_{3v}	−0.99	−1.01	−1.08	−0.98	−0.99	−1.07	−0.99	−1.01	−1.11
L_{1v}	−5.62	−5.49	−5.88	−5.58	−5.45	−5.81	−5.55	−5.48	−5.81
L_{1v}	−12.66	−12.30	−13.01	−12.93	−12.64	−13.29	−11.44	−11.24	−11.85

allow for a better comparison with other calculations, which are usually published without the account of the SO. Including the spin-orbit splitting enables a comparison with experiments. This is done in the Tables IV–VI in the column denoted "*GW*." The presented value of the binding energy of cations' semicore *d* states ($\overline{E}_d$) is the average value over all spin components at the Γ point. For mercury chalcogenides the spin-orbit splitting at the valence-band maximum (Δ_o) is also shown [$\Delta_o = E(\Gamma_8) - E(\Gamma_7)$].

The LDA results presented in Tables IV–VI confirm the well-known fact that the LDA energy gaps of II^B-VI compounds deviate much more from experiment than is the case for III-V or the group-IV semiconductors. For example, the LDA absolute energy gaps amount to only 10% or 13% of the experimental values for CdSe and CdTe, respectively. In the case of mercury chalcogenides, the negative experimental gaps of the order of −0.2 to −0.3 eV are exceeded several times in the LDA theory (−1.23 eV and −1.17 eV for HgSe and HgTe, respectively).[28] Another characteristic result of the LDA approach is the strong underbinding of the cations' semicore *d* states. Both effects are related and were analized in detail in the Ref. 2. In the *GW* approach the energy gaps are represented much better than in the LDA, as can be seen in Tables IV–VI. It should be noted, however, that the agreement with experiment is less satisfactory than was the case in other semiconductors, which do not possess semicore states. The binding energies of semicore *d* states, although being shifted towards experimental values, still deviate pronouncely from experiment. The quasiparticle shift is highly not sufficient for the semicore states and—as was shown previously by Rohlfing *et al.*[12]—results mainly from the

TABLE IV. Absolute energy gap (E_g) and the average position of semicore *d* states at Γ with respect to the VBM ($\overline{E}_d$) for zinc-blende ZnS, ZnSe, and ZnTe. Comparison of LDA and various *GW* calculations with experimental results (Ref. 32). Spin-orbit interaction included perturbatively. *GW* corresponds to *GW*-RPA type of self-energy with *G* and *W* given by the LDA calculation. $G'W'$ corresponds to *GW*-RPA with *G* and *W* recalculated by updating the eigenvalues. $GW\Gamma$ denotes the results obtained with the LDA vertex function included [Eq. (8)]. $G'W'\Gamma$ corresponds to the LDA vertex function and updated eigenvalues in *G* and *W* in the same time. All values in eV.

	LDA	*GW*	$G'W'$	$GW\Gamma$	$G'W'\Gamma$	Expt.
ZnS						
E_g	1.82	3.38	3.80	3.56	3.99	3.84
$\overline{E}_d$	−6.33	−6.87	−7.49	−7.41	−8.02	−8.97
ZnSe						
E_g	0.88	2.24	2.58	2.33	2.68	2.82
$\overline{E}_d$	−6.68	−7.31	−7.82	−7.86	−8.37	−9.37
ZnTe						
E_g	0.74	1.98	2.26	1.97	2.27	2.39
$\overline{E}_d$	−7.26	−7.90	−8.43	−8.50	−9.03	−9.80

TABLE V. Same as Table IV for zinc-blende CdS, CdSe, and CdTe. All values in eV. Experimental results from Ref. 32.

	LDA	*GW*	$G'W'$	$GW\Gamma$	$G'W'\Gamma$	Expt.
CdS						
E_g	0.80	2.11	2.47	2.26	2.63	2.48
$\overline{E}_d$	−7.55	−8.15	−8.56	−8.59	−8.99	−9.20
CdSe						
E_g	0.17	1.25	1.56	1.34	1.66	1.70
$\overline{E}_d$	−7.85	−8.53	−8.98	−8.97	−9.40	−9.73
CdTe						
E_g	0.21	1.22	1.47	1.25	1.51	1.61
$\overline{E}_d$	−8.37	−9.08	−9.52	−9.53	−9.96	−10.50

TABLE VI. Same as Table IV for zinc-blende HgS, HgSe, and HgTe. All values in eV. Experimental results for HgS from Ref. 29 and for HgSe and HgTe from Ref. 32. $\Delta_o=\Gamma_8-\Gamma_7$ is the spin-orbit splitting at VBM. Negative values of Δ_o for HgS mean that the Γ_7 state is above the Γ_8 state.

	LDA	GW	$G'W'$	$GW\Gamma$	$G'W'\Gamma$	Expt.
HgS						
E_g	−0.62	0.06	0.13	0.12	0.28	−0.11
Δ_o	−0.12	−0.12	−0.13	−0.13	−0.13	
$\overline{E_d}$	−6.74	−7.03	−7.32	−7.41	−7.64	
HgSe						
E_g	−1.23	−0.60	−0.50	−0.50	−0.40	−0.20
Δ_o	0.23	0.23	0.23	0.23	0.23	0.45
$\overline{E_d}$	−6.95	−7.31	−7.54	−7.66	−7.86	−8.09
HgTe						
E_g	−1.17	−0.57	−0.48	−0.55	−0.45	−0.30
Δ_o	0.80	0.80	0.80	0.80	0.80	1.08
$\overline{E_d}$	−7.38	−7.79	−8.02	−8.16	−8.39	−8.58

strong exchange interaction with core electrons in states with the same principal quantum number.

The case of the cubic HgS—so-called β-HgS—needs a comment. The natural stable form of HgS is a trigonal, cinnabar structure. The zinc-blende structure of HgS is stabilized under a few percent admixture of transition metals, which replace Hg ions in the lattice. The experimental result of −0.11 eV for the energy gap of β-HgS quoted in Table VI has been obtained for samples with 2% content of transition metals (Fe, Co, Mn).[29] The energy gap E_g in Table VI is assigned to the energy difference between the Γ_6 and Γ_8 states; therefore, it results as negative within LDA theory for β-HgS and both other mercury chalcogenides. However, in the LDA, β-HgS is an open-gap insulator with an "exotic" electronic structure: unlike the usual situation with the Γ_7 state below the Γ_8 one, the ordering of both states is reversed. In the LDA, Γ_8 and Γ_7 built the valence-band maximum (VBM) and the conduction-band minimum (CBM), respectively. For this reason the spin-orbit splitting of β-HgS in Table VI is reported with the minus sign ($\Delta_o=-0.12$ eV) and the "true" LDA absolute energy gap in β-HgS is +0.12 eV. This change of the sign of Δ_o is an extreme manifestation of the common to the LDA description of all II^B-VI compounds decrease of Δ_o at the VBM. As analyzed by Wei and Zunger,[2] it results from the unphysically strong (in the LDA) hybridization of the cations' semicore d states with anions p orbitals. The results for HgSe and HgTe in Table VI show that the calculated Δ_o is of ~0.2 eV smaller than the experimental value. In the case of β-HgS the 0.2 eV reduction of Δ_o results in a change of its sign. In the GW theory the Γ_6 level gets shifted upwards and the energy gap E_g becomes slightly positive for β-HgS ($E_g=0.06$ eV). However, because within the perturbative application of the GW theory LDA wave functions of zeroth order remain unchanged, the spin-orbit splitting Δ_o does not change essentially either. As a result, the true absolute energy gap of β-HgS is in the GW theory still "exotic": it is positive, amounts to 0.06 eV and is built by the Γ_6 and Γ_7 levels as VBM and CBM, respectively.

The unusual energy-level sequence in both LDA and GW descriptions of β-HgS is an artifact of the overemphasized in LDA *sp*-*d* hybridization, which is not romoved in the perturbatively applied GW theory. However, it seems to be also the reason for the rather moderate successes of the GW description of all other II^B-VI compounds. A question arises then: what should be improved? Should one include also off-diagonal elements of the self-energy in order to decouple the p and d states? Or should one apply the GW theory self-consistently and/or with the account of physically important and computationally managable vertex corrections? A short discussion of these points will be given in the next section.

At the end of this section we would like to comment on the validity of the plasmon-pole approximation in the GW calculations. Using the plasmon-pole models for the frequency dependence of screening makes the calculations significantly more efficient. This is for two reasons. First, one avoids time-consuming calculations of the dynamical-response functions at a dense mesh of frequences. In the plasmon-pole model it is sufficient to calculate response matrices at zero frequency only. Second, when the plasmon-pole model is used, the energy integration present in the formula for the GW self-energy is done analytically. It is therefore interesting to know whether the significant gain in the computational effort is shadowed or not by a loss of accuracy. Tables I–III point out at a few clear trends.

(i) The absolute energy gaps in the GW-PP calculations are always ~0.1 eV bigger than in a full-GW calculation. The difference grows for higher conduction bands.

(ii) The binding energy of semicore d states is also ~0.1 eV bigger in the GW-PP approximation.

(iii) The most interesting fact, however, is that occupied valence *sp* states undergo opposite quasiparticle shifts in the full-GW- and GW-PP calculations. The full-GW shifts lead to a contraction of valence bands, whereas the GW-PP shifts lead to the expansion with respect to the LDA results. The difference between both calculations is about 0.6–0.8 eV at the bottom of the valence band.

All these facts mean that the quasiparticle shifts of the LDA energies are bigger when the PP model is applied than with the full response functions. In addition, the difference between shifts calculated with two screening methods is particularly large for the valence-band minimum. Since the quasiparticle shifts result from a competition between the widening efect of the pure exchange diagram and the opposite efect of the correlation part of the self-energy and because the exchange part is the same for both screening models, the differences point to the fact that the correlation part of the self-energy is weaker with the PP model than without it. It is so, because the PP models put too big a spectral weight in the response to the plasmon type—i.e., higher-energy excitations on the cost of the lower-energy, electron-hole excitations. Because the correlation part of the self-energy of the valence-band minimum is largely built up from the virtual transitions to energetically close semicore d states, this shifting of spectral weight leads to dramatic consequences.

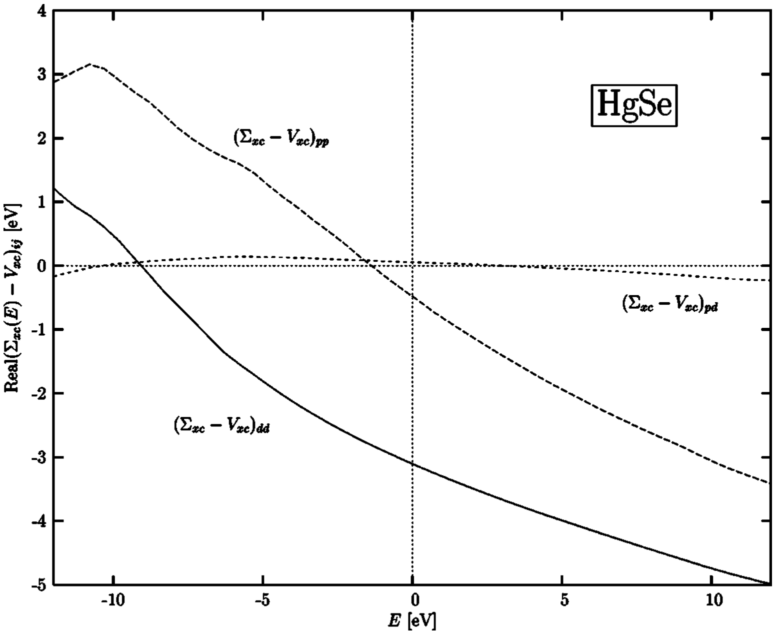

FIG. 1. Diagonal and off-diagonal matrix elements of $(\Sigma(E)-V_{xc})_{ij}$ for Γ_{15} symmetry at the semicore *d* and the valence-band maximum in the *GW*-RPA in HgSe.

IV. BEYOND THE PERTURBATIVE *GW*-RPA THEORY

In this section possible extensions of the *GW* theory or its technical ansatz will be shortly discussed. As suggested in previous sections, at the core of the successful theory of the electronic structure of II^B-VI compounds stays the correct description of the *sp*-*d* interaction and the semicore *d* states. However, in the *GW*-RPA theory, applied perturbatively on top of the zeroth-order, LDA Kohn-Sham Hamiltonian, the quasiparticle shifts of semicore *d* states are moderate and are not sufficient to bring a satisfactory agreement with experiment. This observation is consistent with all previous *GW* results for materials containing semicore electrons and it has been debated on the way out of this difficulty.[10,13,17]

It is clear that in a perturbative application of the *GW* method, as is the case of this and almost all other *GW* calculations, the unphysically large LDA hybridization of cation-semicore *d* and anion *p* states cannot be removed. Therefore, it seems that some decoupling of the *GW* and LDA methods is necessary, which would result in a partial *p*-*d* dehybridyzation. This decoupling could be realized in several ways. One possibility would be to use as the starting point for the *GW* calculation, not the LDA band structure, but another one, in which cation *d* and anion *p* states do not mix so much. Although there are some schemes, in particular, the self-interaction correction (SIC) scheme,[30,31] which seem to describe rather well the semicore states, a marriage of two approaches might face formal difficulties and has not been realized so far. Other possibilities of decoupling *GW* from the LDA offer, e.g., (i) calculation of off-diagonal elements of the self-energy, (ii) going towards the self-consistency of the *GW* method, or (iii) inclusion of vertex corrections. We will briefly discuss in the following these three possibilities.

A. Off-diagonal self-energy

The results presented in Tables I–III have been obtained solving the Dyson equation within the diagonal approximation. In this approximation, the self-energy, Green's functions, and exchange-correlation Kohn-Sham potential V_{xc} are projected onto the LDA wave function of each state of interest [ϕ_{kn} in Eq. (2)]. The off-diagonal matrix elements are neglected. It is clear, however, that states of the same symmetry can have nonzero matrix elements. For example, off-diagonal matrix elements of the Γ_{15} symmetry, represented in both the VBM and semicore *d* states, might lead to the *p*-*d* dehybridization. In order to verify this hypothesis and check the validity of the diagonal approximation we have done the off-diagonal *GW* calculation for HgSe. Mercury chalcogenides are the best cases to study this question, because of the largest among all II^B-VI materials spatial extension of semicore orbitals.

We have calculated the off-diagonal elements of the *GW* self-energy of HgSe for the 20 lowest eigenstates at the Γ point. In the "off-diagonal" case, the quasiparticle wave functions are symmetry-allowed linear combinations of LDA wave functions in the basis,

$$\psi_{kn}^{QP} = \sum_{m} \alpha_m^n \psi_{km}^{LDA}, \tag{5}$$

and the quasiparticle energy E^{QP} is obtained solving the matrix equation (20×20 in our case)

$$\sum_{m} [(E^{QP} - E_{kn}^{LDA})\delta_{nm} + \langle \phi_{kn}^{LDA} | \Sigma(E^{QP}) - V_{xc}^{LDA} | \phi_{km}^{LDA} \rangle] \alpha_m^n = 0. \tag{6}$$

Figure 1 shows the energy dependence of the most important matrix elements of $\Sigma(E^{QP})-V_{xc}^{LDA}$ which might contribute to the *p*-*d* dehybridyzation. The energy zero is at the LDA value of the VBM level. The *pp*, *dd*, and *pd* matrix elements are diagonal and mixed matrix elements, respectively, of the Γ_{15} symmetry present both at the VBM and the Hg 5*d* levels. The quasiparticle shifts of the VBM and the Γ_{15} component of the Hg 5*d* shell are determined by the values of $\Sigma - V_{xc}^{LDA}$ at around $E=-0.4$ eV and $E=-8$ eV, respectively. In order to visualize the effect of the *p-d* coupling, the 20×20 $\Sigma - V_{xc}^{LDA}$ matrix can be reduced to a 2×2 matrix, where only the same partners of the Γ_{15} representation present at the VBM and the semicore Γ_{15}^{d} level are taken into account. In this case, the additional quasiparticle shift δ due to the off-diagonal elements $(\Sigma - V_{xc}^{LDA})_{pd}$ is given by

$$\delta = \frac{2|(\Sigma(E^{QP}) - V_{xc}^{LDA})_{pd}|^2}{E_p^{LDA} + (\Sigma(E^{QP}) - V_{xc}^{LDA})_{pp} - E_d^{LDA} - (\Sigma(E^{QP}) - V_{xc}^{LDA})_{dd}}. \tag{7}$$

Because the denominator in Eq. (7) is of the order of 7–8 eV and $(\Sigma(E^{QP}) - V_{xc}^{LDA})_{pd}$ is smaller than 0.1 eV, δ is of the order of 1 meV. An exact diagonalization of the 20×20 matrix [Eq. (6)] for all states at Γ results in quasiparticle energies that differ from the ones obtained within the diagonal approximation no more than a few meV. This is much less than the overall accuracy of the present implementation of the *GW* method. We conclude, therefore, that the diagonal approximation works extremely well and no *p-d* dehybridazation is obtained by going beyond it.

B. Towards self-consistency

The first step towards self-consistency could be updating the eigenvalues when the *GW* self-energy is calculated. This is a tedious approach mainly because of the recalculation of the dynamical response. We have performed a numerical shortcut at this point and have fitted the energy dependence of quasiparticle shifts calculated at the Γ, *X*, and *L* points to analytical functions, which were used then in the dynamical-response and self-energy calculations. The column denoted $G'W'$ in Tables IV–VI presents the results obtained within one iteration step of updating eigenvalues in *G* and *W*. The formula for self-energy is still the RPA one.

As can be seen, updating eigenvalues has a visible effect on both the absolute energy gap and the position of semicore *d* states. Both quantities agree now with experiment better. This is true in particular for the energy gap. The shift of semicore states, although as about twice as large as in the standard RPA-*GW* calculation, is still not sufficient to bring a satisfactory agreement with experiment.

It should be noted, however, that this kind of updating eigenvalues cannot replace the true self-consistency. On the one hand, it results in an unphysical screening, which violates the sum rules. On the other hand, it ignores the dynamical effects contained in the shape of the quasiparticle spectrum and the response. It is known, however, that these dynamical effects play essential role. An exploratory calculation employing the renormalized quasiparticle spectrum in the construction of the input Green's function in Eq. (1) was presented by Rohlfing *et al.*[13] Although this approach turned out to be successful for the semicore states, it was less so for the valence states, giving too big energy gaps. Moreover, one could expect that a renormalization of the screened Coulomb interaction *W* in Eq. (1), not done in Ref. 13, would then deteriorate the agreement with experiment. The basic problem here seems to be caused by the RPA-type, renormalized screening. Without including vertex corrections, such a renormalized screening turns out to be unphysical. The very large widening of the valence band, resulting from the self-consistency of the GW approach, was demonstrated for the homogeneous electron gas,[33] potasium,[34] silicon,[34,18] and germanium.[18]

We close these considerations recalling the often-stressed statement of Mahan: that the self-energy diagrams and vertex functions go together.[35]

C. TDLDA vertex corrections

A systematic evaluation of the vertex corrections is an extremely difficult problem. Moreover, there are possible various ways to include higher-order terms. In one approach, for example, the starting point is given by the Hartree approximation. Successive iterations of the—so called—Hedin's equations[4] give in the first iteration step the *GW* formula for the self-energy and the lowest-order diagrams beyond the *GW* formula in the next iterations. In calculations for real materials such an approach is less practical, because the electronic structure within the Hartree approximations is by far not satisfactory. Therefore, a common approach is to evaluate the *GW* formula for the self-energy with such *G* and *W* which are easily available and approximate the electronic structure in possibly the "best" way. This leads in practice to the non-self-consistent *GW* approach based on the LDA *G* and RPA screening calculated from the LDA *G*'s. The vertex corrections are defined as higher-order vertex diagrams in the screened interaction *W*.

As noticed by Streitenberger,[36] Hybertsen and Louie[37] and Del Sole, Reining, and Godby,[38] one can start the iteration of Hedin's equations from the LDA Hamiltonian, taking as the zeroth-order self-energy the exchange-correlation LDA potential V_{xc}^{LDA}. After one iteration cycle the following expression for the self-energy is obtained:

$$\Sigma = iGW\Gamma = iG\widetilde{W}, \tag{8}$$

where ϵ^{-1} in *W* is not the RPA inverse dielectric function, but one with exchange-correlation corrections included

$$\epsilon^{-1} = 1 + v_c\chi_0(1 - v_c\chi_0 - f_{xc}\chi_0)^{-1}. \tag{9}$$

Here v_c is the Coulomb interaction, $\chi_0 = -iGG$ is the independent-particle polarizability, and $f_{xc} = \delta V_{xc}/\delta n$ is the time-dependent LDA (TDLDA) exchange-correlation kernel. With the vertex function Γ given by

$$\Gamma = (1 - f_{xc}\chi_0)^{-1}, \tag{10}$$

the product $W\Gamma$ can be expressed as $\widetilde{W} = \widetilde{\epsilon}^{-1} v_c$, with

$$\widetilde{\epsilon} = 1 - v_c\chi_0 - f_{xc}\chi_0. \tag{11}$$

This result has a straightforward physical interpretation: The created extra particle in the system is screened taking account of the exchange-correlation effects, which are included within the TDLDA theory. In the RPA theory these effects in screening are neglected.

As in Ref. 38 we call this approach the *GW*Γ method. The results for Zn, Cd, and Hg chalcogenides are presented in

Table IV–VI, respectively (column denoted $GW\Gamma$). A comparison with the standard GW-RPA calculations (column GW in Tables IV–VI shows that the effect of the TDLDA vertex corrections on the energy gap ranges between 0.1 and 0.2 eV for sulphur compounds and almost zero for tellurium compounds. Thus, it is rather moderate, although it contributes to the increase of the energy gap. The fact that sulphur compounds show the largest effect can be understood in terms of the localization properties of the valence bands. In the series of anions S-Se-Te sulphur leads to the most localized states, tellurium to the less. Because as is commonly accepted the exchange-correlation effects in screening are particularly enhanced for localized states, we could expect that for the binding energies of semicore d states the effect of the $GW\Gamma$ approach is quite pronounced. This is indeed the case: These states undergo an extra quasiparticle shift of the order of 0.4–0.6 eV.

In Tables IV–VI there are shown also results of the TDLDA-vertex corrected self-energy calculations with the updated G and W (column denoted $G'W'\Gamma$). Because the TDLDA f_{xc} kernel that defines the Γ [Eq. (10)] is not a functional of the updated G (it is strictly connected to the LDA-G), the self-consistency of the $GW\Gamma$ approach could be easily questioned. Nevertheless, it is interesting to see how in the case of II^B–VI compounds the self-consistency and vertex corrections "go together," even if both effects are only approximatively included and not compatible with each other. The results are encouraging. Both the energy gaps and binding energies of the semicore states are now in still better agreement with the experiment than with all previous approaches.

Summarizing, we have examined in this section possible extensions to the standard, non-self-consistent GW-RPA approach. The neccessity of such extensions for II^B–VI compounds comes from the fact that the GW-RPA method (i) gives systematically about 0.3–0.6 eV too small energy gaps and (ii) underbinds the semicore d states by about 0.8–2 eV. It was shown that including off-diagonal elements of the self-energy has only a negligible effect. A partial self-consistency, based on updating quasiparticle energies in G and W gives a pronounced effect on both the energy gaps and the position of semicore states. The vertex corrections based on the TDLDA approach contribute to similar downshifts of the semicore states. The best results are obtained within the combined approach, when the self-consistency and vertex corrections are both included. It is important to note, however, that in all examined schemes the unphysically strong hybridization of semicore d and valence p states has not been removed. A measure of this hybridization is the value of the spin-orbit splitting at the VBM. As can be seen in Table VI for HgSe and HgTe, the Δ_o values remain practically unchanged in all schemes and are about 0.2 eV smaller than in the experiment. This is a direct consequence of using in all cases the diagonal approximation for the self-energy, which has been shown to work perfectly for the perturbative GW-RPA case. One could expect, however, that the true self-consistent GW theory should lead to the pd dehybridization.[39]

TABLE VII. LDA and GW absolute energy gaps at Γ for zinc-blende Zn, Cd, and Hg chalcogenides obtained with the cation 20+ or 2+ pseudopotentials. Two results for the case of 2+ pseudopotentials correspond to two different schemes of treating the core charge. The column (GW-I-2+) corresponds to Eq. (14) and the column (GW-II-2+) to Eq. (17). All values in eV. Spin-orbit splitting not included.

	LDA-20+	GW-20+	LDA-2+	GW-I-2+	GW-II-2+
ZnS	1.84	3.41	2.18	4.27	3.36
ZnSe	1.02	2.37	1.19	3.17	2.17
ZnTe	1.04	2.27	1.18	3.09	2.00
CdS	0.82	2.13	1.22	3.86	2.37
CdSe	0.29	1.38	0.56	3.10	1.53
CdTe	0.49	1.51	0.70	3.19	1.57
HgS	−0.65	0.03	−0.11	2.59	0.25
HgSe	−1.14	−0.51	−0.79	1.90	−0.54
HgTe	−0.90	−0.31	−0.62	2.12	−0.40

V. GW CALCULATIONS USING CATION 2+ PSEUDOPOTENTIALS: ROLE OF CORE-CHARGE CORRECTIONS

Ab initio pseudopotentials work most successfully for those atoms and their compounds, for which the valence and core electrons are spatially well separated. Moreover, the biggest computational advantage of the pseudopotential technique is achieved when only the strictly outermost electronic shell is dealt explicitly with and all other shells built the inert atomic core. These conditions are clearly not fulfilled for atoms of the group II^B. In the case of the Zn, Cd, and Hg atoms there is a pronounced spatial overlap of the valence-electron and the semicore d-electron densities. Since the LDA exchange-correlation functional is not linear in the density, one faces a fundamental difficulty in defining the Zn^{2+}, Cd^{2+}, or Hg^{2+} pseudopotentials. Problems are partially solved when the technique of Louie, Froyen, and Cohen of the partial core-charge correction is applied.[40] However, even when the core charge is taken into account in the construction of the pseudopotentials and the exchange-correlation functional, the resulting LDA band structures of II^B–VI compounds show systematic differences between the all-electron calculations and the calculations based on the Zn^{2+}, Cd^{2+}, and Hg^{2+} pseudopotentials. For example, the latter give 0.2–0.5 eV bigger absolute energy gaps (see Table VII). Apart from these fundamental problems use of Zn^{2+} or Cd^{2+} pseudopotentials is still very popular, especially when large supercells for surface or defect calculations must be constructed. An interesting question arises, how rilable are GW calculations when the strictly valence-shell pseudopotentials and core-charge corrections in the underlying LDA Hamiltonian are used? An example of such calculations are the calculations of Zakharov *et al.*,[16] in which the Zn 3d and Cd 4d states had been kept in the core. As noted already, these calculations produced quite satisfactory results for the energy gaps. On the other hand, however, as was shown in the Ref. 12, a GW calculation for CdS based on the Cd^{2+} pseudopotential gave an unusually large energy gap.

Our own experience supports the results of Rohlfing *et al.* and we obtain much too large energy gaps within the *GW*-RPA when using the cations' pseudopotentials of the valency 2+. This is independently of whether the pseudopotentials were constructed with or without the core-charge corrections. In the usual approach, starting with the LDA Hamiltonian

$$H^{LDA} = \frac{p^2}{2m} + V_{ext} + V_{har} + V_{xc}(\rho_v + \rho_c) \tag{12}$$

and the many-body Hamiltonian of valence states (*MB* states for *many-body*),

$$H^{MB} = \frac{p^2}{2m} + V_{ext} + V_{har} + \Sigma_{xc}, \tag{13}$$

one obtains the Dyson equation

$$G = G^{LDA} + G^{LDA}[\Sigma_{xc} - V_{xc}(\rho_v + \rho_c)]G. \tag{14}$$

G and G^{LDA} mean the many-body and LDA Green's functions of valence electrons. The external, Hartree, and exchange-correlations potentials are easily recognized. ρ_v and ρ_c denote the valence and core-charge (in practice, the partial or model core charge) densities, respectively. The important fact is that in the Dyson equation [Eq. (14)] there appears a difference between the self-energy and exchange-correlation potential *corrected by the effects of the core charge*. We call this usual approach the *GW*-I scheme.

However, working with pseudopotentials constructued with core-charge corrections in the exchange-correlation potential puts the problem of the transferability of core corrections into the *GW* calculations. In the starting LDA Hamiltonian [Eq. (12)] such corrections are present; it seems therefore reasonable to demand that they be present in the many-body Hamiltonian of valence electrons as well. Here we would like to propose a simple procedure of transfering these core corrections into the *GW* scheme. We suggest that in the simplest approach they could be included in the many-body Hamiltonian in the same way as in the LDA Hamiltonian. As it turns out, such procedure gives results very similar to the *GW* results obtained when core electrons are dealt with explicitly.

Let us rewrite the LDA Hamiltonian H^{LDA} [Eq. (12)] in the following way:

$$H^{LDA} = \frac{p^2}{2m} + V_{ext} + V_{har} + [V_{xc}(\rho_v + \rho_c) - V_{xc}(\rho_v)] + V_{xc}(\rho_v). \tag{15}$$

If the quantity $[V_{xc}(\rho_v+\rho_c)-V_{xc}(\rho_v)]$ is considered as the "exchange-correlation" potential of the partial-core density, it can be added to the many-body Hamiltonian of valence states similarly as it is added in the Kohn-Sham-LDA equations:

$$H^{MB} = \frac{p^2}{2m} + V_{ext} + V_{har} + [V_{xc}(\rho_v + \rho_c) - V_{xc}(\rho_v)] + \Sigma_{xc}. \tag{16}$$

In this simple though approximative way the many-body Hamiltonian of the system of valence electrons carries also a built-in influence of core electrons in the similar way as the LDA Hamiltonian. Now, it is clear that in the resulting Dyson equation a difference $\Sigma_{xc}-V_{xc}(\rho_v)$ appears instead of $\Sigma_{xc}-V_{xc}(\rho_v+\rho_c)$:

$$G = G^{LDA} + G^{LDA}[\Sigma_{xc} - V_{xc}(\rho_v)]G. \tag{17}$$

We call the approach based on Eqs. (15)–(17) the *GW*-II scheme.

In the Table VII the $\Gamma_{1c}-\Gamma_{15v}$ energy gaps are compared as obtained from the LDA and *GW*-RPA approaches using either 20+, or 2+ pseudopotentials of cations. The energy gaps obtained within the *GW*-I scheme are about 1–2 eV larger than experimental gaps and the ones obtained including core electrons explicitly. This also agrees with the observation of the Ref. 12 for CdS. On the other hand, when core corrections are included in the many-body Hamiltonian, as is done in the *GW*-II scheme, the *GW* energy gaps turn out to agree quite well with the calculations based on the cation's 20+ pseudopotentials. These results suggest that when strictly valence-electron pseudopotentials must be used (of the valency 2+ for the group II elements), one should use the *GW*-II scheme rather than the normal *GW*-I scheme. This conclusion should be general, not limited to the elements of the group II^B.

VI. CONCLUSIONS

The results of a systematic study of the electronic structure of II^B–VI zinc-blende compounds within the *GW* approximation are presented. Tables I–VI show that the *GW*-RPA applied perturbatively on top of the LDA Hamiltonian gives 0.3–0.6 eV too small energy gaps. This contrasts the usual good agreement of the *GW* results with experiment for standard semiconductors. The binding energy of the semicore *d* states is 0.8–2.0 eV too small. For both quantities, the Zn compounds show the biggest deviations from experiment in absolute units, the Hg compounds the smallest. This correlates well with the fact that in the series of Hg—Cd—Zn chalcogenides the localization of the semicore *d* shells grows and respectively grows the importance of the short-range correlations not included in the *GW* theory.

Several extensions beyond the perturbative, RPA, and non-self-consistent way of applying the *GW* method were examined. It was shown on the example of HgSe that the inclusion of the off-diagonal matrix elements of the self-energy (i.e., a nonperturbative, but still not self-consistent *GW* approach) gives basically the same results as the diagonal approximation. Bigger changes in the right direction—i.e., further opening of the energy gaps and increase of the binding of semicore *d* states—are obtained when the eigenvalues in the Green's function and response are iteratively updated. Such a procedure might be considered as a partial self-consistency, although the true self-consistency should include also dynamical effects in G and W which might give rise to different results. A $GW\Gamma$ approach based on the TDLDA corrections to screening results in a moderate increase of the gap and a quite pronounced increase of the binding energy of the semicore d states. Finally, a hybrid approach in which the TDLDA vertex corrections are included and eigenvalues are updated gives the results most close to experiment.

All calculations presented in this work have been done using the frequency-dependent screening, consistently calculated from the LDA bands. In order to verify the accuracy of the plasmon-pole approximation, which is most often applied together with the GW approach, we have parallelly presented in Tables I–III the results of one of the plasmon-pole models. It was shown that the application of the plasmon-pole model gives rise to systematic deviations: First, the absolute energy gaps and binding energies of semicore d states are ~ 0.1 eV bigger. Second, the valence-band widths show *opposite shifts than are obtained from the full, ω-dependent screening*. Instead of a contraction of valence bands, the plasmon-pole model produces an expansion.

In the last section the validity of the pseudopotential approach in which the semicore d states are frozen in the core was examined. It was shown that working with Zn^{2+}, Cd^{2+}, or Hg^{2+} pseudopotentials results in much too large energy gaps even if the core-charge corrections to the LDA exchange-correlation potential are included. However, a simplest ansatz of the LDA core corrections to the many-body Hamiltonian of valence-only electrons gives rather good results for the GW electronic structure (Table VII).

In the end it is worth noting that among some other methods of treating correlations better than LDA does, which have found certain popularity in connection with *ab initio* calculations,[41] the GW approach offers probably the best possibilities for systematic improvements. For this reason, we believe that further developement of the GW approach is important for an increasingly better description of the electronic structure of solids.

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