Quasiparticle energy of semicore *d* electrons in ZnS: Combined LDA+*U* and *GW* approach

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We present a first-principles study of quasiparticle energies in ZnS, with particular emphasis on the semicore *d* electrons that are located too shallow by ~2.8 eV compared to experiment in the local density approximation (LDA). Although the many-body correction in the *GW* approximation pulls down the *d* band, the correction (−0.7 eV) is too small to reproduce measured values. The LDA+*U* method also shifts the *d* band down compared to LDA. With a reasonable choice of *U*, *d*-state energy in agreement with experiment may be achieved. Subsequent quasiparticle calculation within the *GW* approximation performed to the LDA+*U* mean-field solution, however, pushes the *d* band back close to the *GW* result. These results show that the standard *GW* method is insensitive to the reference mean-field Hamiltonian for this class of materials and suggest that going beyond *GW* may be needed for an accurate description of the *d* electron level in this system.

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The II^B-VI compound semiconductors exhibit a variety of interesting and technologically important properties that are not observed in other semiconductors. Many group II chalcogenides are well-known for their potential in optoelectronics applications since they have wider band gaps and offer greater tunability than GaAs. Recently, zinc oxide and chalcogenide based dilute magnetic semiconductors (DMS) have also attracted considerable research interest.[1] Therefore detailed knowledge of the electronic properties of these materials is becoming increasingly important. Surprisingly, theoretical understanding of the electronic structure of these supposedly simple *sp* semiconductors turns out to be rather challenging. In particular, the quasiparticle energies of the semicore *d* states in these materials have been a subject of much research interest and debate.[2–13] For example, the calculated quasiparticle energy of the semicore *d*-states in ZnS within the *GW* approximation is about 2 eV higher than measured values.[14,15] Similar discrepancy for these semicore *d*-states between theory and experiment is found for most II^B-VI compounds. Although improvement is found by going beyond the traditional *GW*scheme,[8] the difference is still sizable (~1.5 eV for ZnS) and this problem remains a subject of intensive discussion.

In traditional quasiparticle calculations within the *GW* approximation (GWA),[16] the self-energy is given by

$$\Sigma^{GW}(\mathbf{r},\mathbf{r}';E) = \frac{i}{2\pi}\int dE' \exp(iE'\delta) \times G(\mathbf{r},\mathbf{r}';E+E')W(\mathbf{r},\mathbf{r}';E'), \quad (1)$$

where δ is a positive infinitesimal number, and *G* and *W* are the electron Green function and dynamically screened Coulomb interaction, respectively. The quasiparticle equation (the Dyson equation)

$$[T+V_{ext}(\mathbf{r})+V_H(\mathbf{r})]\Psi_i(\mathbf{r}) + \int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';E_i^{qp})\Psi_i(\mathbf{r}') = E_i^{qp}\Psi_i(\mathbf{r}) \quad (2)$$

can then be solved to obtain the quasiparticle energies E_i^{qp} and wave functions Ψ_i. In the above expression, *T* is the kinetic energy operator, and V_{ext} and V_H are the external potential and the Hartree potential, respectively. In practice, both the *G* and *W* operators are constructed within the quasiparticle approximation by using the noninteracting particle wave functions ψ_i and energies ϵ_i obtained from density functional theory (DFT) based calculations:

$$G(\mathbf{r},\mathbf{r}';E) = \lim_{\delta\to 0^+}\sum_i \frac{\psi_i(\mathbf{r})\psi_i^*(\mathbf{r}')}{E-[\epsilon_i+i\delta\,\mathrm{sgn}(E_f-\epsilon_i)]}, \quad (3)$$

$$W(\mathbf{r},\mathbf{r}';E) = \int d\mathbf{r}''\epsilon^{-1}(\mathbf{r},\mathbf{r}'';E)v(\mathbf{r}'',\mathbf{r}'), \quad (4)$$

where E_f is the Fermi energy and *v* is the bare Coulomb interaction. The static dielectric function $\epsilon(\mathbf{r},\mathbf{r}')$ is calculated within the random phase approximation (RPA), which is then extended to finite frequencies using the generalized plasmon-pole (GPP)[16] model. A recent work by Fleszar and Hanke[11] has shown that the plasmon-pole approximation works quite well for the group IIB-VI semiconductors. Compared to the full integration in frequency domain, energy difference is 0.1 to 0.2 eV for the *d*-state energy and even better for the band gap. The exchange-correlation potential in the DFT calculations is usually treated within the local density approximation (LDA) or the generalized gradient approximation (GGA). This scheme is sometimes referred to as the G^0W^0 approach and has now become the standard of

quasiparticle calculations. Subsequent updating of the quasiparticle energies and wave functions in the construction of the G and W operators (denoted as the G^1W^1 scheme) is possible but often found not necessary. In the standard approach, the basic concept is to view the many-electron Hamiltonian H in a form of $H=H_0+(H-H_0)$, where H_0 is some chosen mean-field Hamiltonian, and to perform the GW approximation to the term $(H-H_0)$ in evaluating the electron self-energy operator. A most common form of H_0 would be the DFT Kohn-Sham Hamiltonian within the LDA. In such calculations, the quasiparticle energy is given in terms of a self-energy correction to the Kohn-Sham eigenvalues: $\delta\Sigma(E)=\Sigma(E)-V_{xc}$. The quasiparticle energy to first order (i.e., neglecting the off-diagonal element effects), can then be evaluated:

$$E_i^{qp} = E_i^{\mathrm{LDA}} + \langle \psi_i | \delta\Sigma(E_i^{qp}) | \psi_i \rangle. \tag{5}$$

The calculated quasiparticle energies are usually within a couple of tenths of an eV compared to experimental values. However, standard applications of the GWA (by setting H_0 equal to the LDA or GGA Kohn-Sham Hamiltonian) to II^B-VI semiconductors encounter unexpected difficulties. The significant underestimate of the binding energy of the d states in the LDA or GGA calculations introduces spurious pd hybridization. This may have significant effects on the properties of the d states and the valence (p) bands. Although self-consistent GW calculations including off-diagonal element effects should in principle remove the spurious hybridization effects, such calculations are formidably expensive. Alternatively, one may seek for a better starting mean-field solution and then perform the GW calculation. It is generally believed that the underestimate of the binding energies of semicore d states comes largely from the incomplete cancellation of the self-interaction of d electrons in the LDA or GGA. Therefore computational schemes [e.g., LDA+U[17] or self-interaction corrected (SIC)[18]] in which the self-interaction is effectively removed may give a better mean-field description of the ground state properties. Subsequent quasiparticle calculations within the GWA may then be applied. In this paper, we report combined LDA+U and GW calculations for the prototypical II^B-VI semiconductor ZnS, with particular emphasis on the position of the semicore d levels.

In the LDA+U method[17] the density functional to the total energy consists of three contributions:

$$E^{\mathrm{LDA}+U}[\rho^\sigma(\mathbf{r}),\{\mathbf{n}^\sigma\}] = E^{\mathrm{LDA}}[\rho^\sigma(\mathbf{r})] + E^U[\{\mathbf{n}^\sigma\}] - E^{\mathrm{dc}}[\{\mathbf{n}^\sigma\}], \tag{6}$$

where E^{LDA} is the LDA functional for spin densities ρ^σ, E^U is a Hubbard or Hartree-Fock type of interaction arising from localized electrons (Zn d electrons in this case) with orbital occupation density matrices $\mathbf{n}^\sigma$, and E^{dc} is a "double-counting" term that accounts for the averaged electron-electron interaction already included in the LDA functional. Applying the variational principle to the above defined LDA+U functionals, we have, in addition to the usual one-electron LDA Hamiltonian, an orbital-dependent correction term

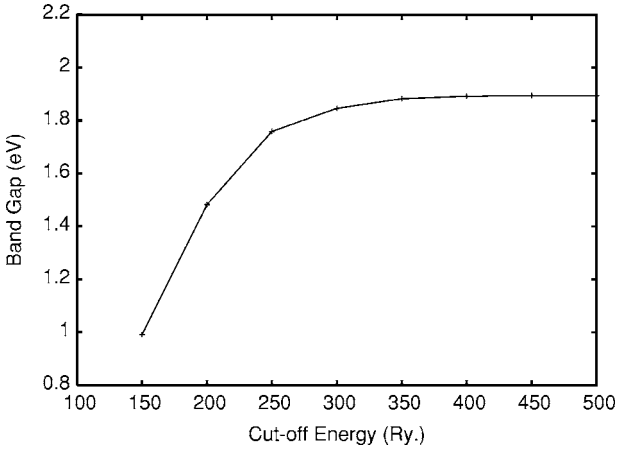

FIG. 1. LDA band gap as a function of energy cutoff.

$$\delta\mathbf{V} = \sum_{m_1,m_2} |m_1\rangle \delta V_{m_1,m_2} \langle m_2|, \tag{7}$$

where $|m\rangle$ denotes localized orbitals. The matrix elements $\delta V_{m_1,m_2}$ are constructed with two input parameters, the screened on-site Coulomb interaction U (8 eV), and the exchange J (1 eV). These parameters are calculated using the screened Coulomb interaction $W(\mathbf{r},\mathbf{r}')$ defined in Eq. (4) and the maximally localized Wannier functions[19] of the d states:

$$U = \frac{1}{(2l+1)^2} \sum_{m_1,m_3} \langle m_1,m_3|W(\mathbf{r},\mathbf{r}')|m_1,m_3\rangle \tag{8}$$

and

$$J = U - \frac{1}{2l(2l+1)} \sum_{m_1,m_3} [\langle m_1,m_3|W(\mathbf{r},\mathbf{r}')|m_1,m_3\rangle - \langle m_1,m_3|W(\mathbf{r},\mathbf{r}')|m_3,m_1\rangle]. \tag{9}$$

We first calculate the electronic structures of ZnS in the LDA and the LDA+U method implemented[20] within the pseudopotential plane-wave formalism. All three semicore sub-shells of Zn, namely, 3s, 3p, and 3d, are treated as valence electrons. Since these orbitals are strongly localized, a very high energy cutoff (E_{cut}) in the plane-wave expansion of the wave functions is needed. Figure 1 shows the calculated energy gap E_g as a function of E_{cut}. The calculated band gap is underestimated significantly if the cutoff energy is set below 300 Ry. Therefore an E_{cut} of 350 Ry is used in all calculations.

Figure 2 shows the calculated energy position of d-states at Γ as a function of the screened Coulomb interaction U within the LDA+U method. The d-state energy decreases linearly with increasingly U as expected. The LDA+U+GW results, however, are fairly insensitive to the value of U as will be discussed in more detail later. Figure 3 compares the band structures of ZnS calculated within the LDA and the LDA+U method using the calculated Coulomb and exchange parameters (U=8 eV and J=1 eV). The effective removal of the self-interaction in the LDA+U calculation separates the semicore d from the valence p states. This separation has several interesting consequences. First, the av-

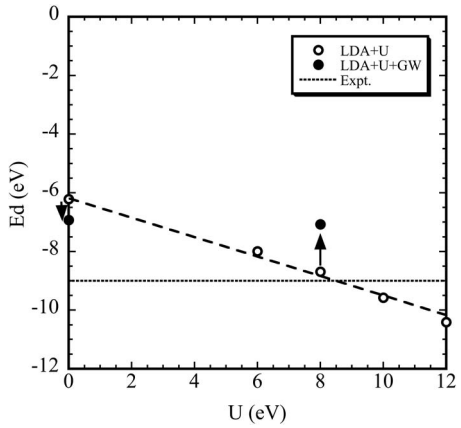

FIG. 2. The position of d-states (at Γ) as a function of the U parameter. The LDA+U results (open circles) and the LDA+U +GW results (closed circles). The dashed line is a guide for the eye.

eraged energy position (E_d) of the d states (−8.78 eV at the Γ point) relative to the top of the valence band now compares favorably with the measured values −8.97−−9.03 eV.[14,15] This is in contrast to the LDA result (−6.22 eV at Γ), as shown in Table I. In addition, the bandwidths of both the valence p states and the d states are reduced noticeably due to the reduced pd hybridization in the LDA+U calculations. This reduction of the valence bandwidth is also reflected by an increase in the calculated band gaps: 2.16 eV within the LDA+U vs 1.88 eV within the LDA. The calculated static dielectric constant (Table I) is also slightly improved within the LDA+U method when compared to the experiment.

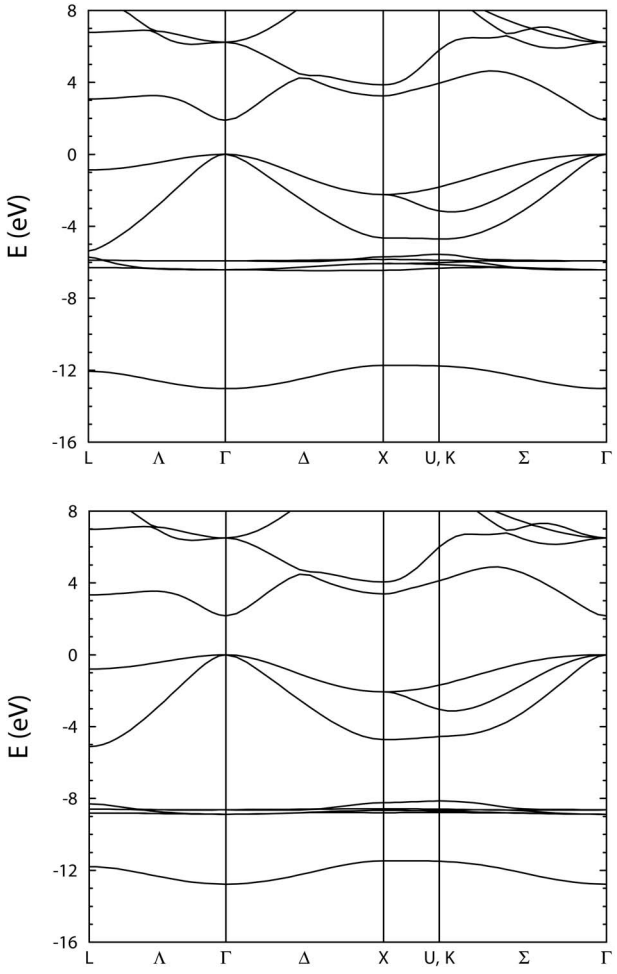

FIG. 3. Band structure obtained by (left) LDA and (right) LDA+U.

TABLE I. Comparison of the calculated electronic properties of ZnS within LDA and LDA+U.

	Band gap (eV)	$E_d(\Gamma)$	ϵ_∞
LDA	1.88	−6.22	6.01
LDA+U	2.16	−8.78	5.82
Expt.	3.80	−8.97[a], −9.03[b]	5.1

[a]Reference 14.
[b]Reference 15.

Therefore it appears that the LDA+U calculations improve the agreement between theory and experiment, especially for the energy of the d states. However, the LDA+U method is within the DFT framework. There is no *a priori* justification which warrants a direct comparison between the calculated band structure and the measured quasiparticle energies. On the other hand, since the self-interaction of the Zn $3d$ electrons is effectively removed in the LDA+U method, one expects the calculated single particle wave functions and energies may serve as a better mean-field solution for subsequent perturbative treatment within the GWA. We hereby denote the scheme in which GW calculations are done on top of the LDA+U single particle solution as LDA+U+GW whereas the traditional GW calculation is denoted as LDA+GW. In the LDA+U+GW calculation, the quasiparticle equation is slightly modified to reflect the additional exchange-correlation potential $\delta\mathbf{V}$ introduced in Eq. (7):

$$[T + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) + \delta\mathbf{V}]\Psi_i(\mathbf{r}) + \int d\mathbf{r}'\Delta\Sigma(\mathbf{r},\mathbf{r}';E_i^{qp})\Psi(\mathbf{r}')_i = E_i^{qp}\Psi_i(\mathbf{r}), \quad (10)$$

where $\Delta\Sigma$ is the many-body correction to LDA+U. It is defined using the GW self-energy Σ, the LDA exchange-correlation potential V_{xc}, and the orbital dependent correction term $\delta\mathbf{V}$ as

$$\delta\Sigma = \Sigma - V_{xc} - \delta\mathbf{V}. \quad (11)$$

The calculated quasiparticle energies at the Γ point within various schemes are shown in Figs. 2 and 4. The LDA+GW calculation in the G^0W^0 approximation increases the band gap to 3.54 eV from 1.88 eV within the LDA. This compares well with the experimental value of 3.8 eV. The d state energy, however, deviates significantly from the widely quoted experimental value.[14,15] The calculated d-state energy at the Γ point within the G^0W^0 scheme is about −6.95 eV (averaged and measured from the valence band maximum), which is about 2 eV higher than experiment but agrees well

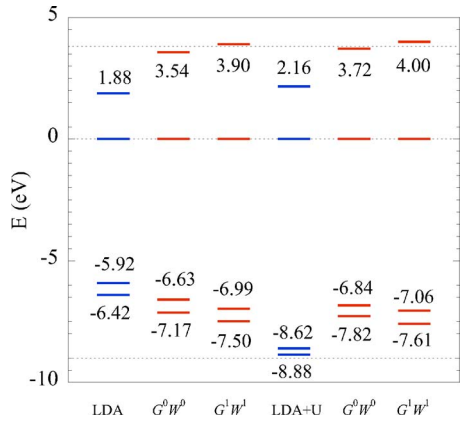

FIG. 4. (Color online) Energy levels at Γ. The upper (lower) *d* levels are doubly (triply) degenerate. The dotted lines indicate measured values for the band gap and *d*-state energy, respectively. The energy is measured from the top of the valence band (also indicated by a dotted line.)

with previous calculations.[8] We then apply the LDA+U+GW scheme described above to this problem. Interestingly, although the LDA+U calculation gives the *d* level position (−8.78 eV) that agrees very well with experiment, the self-energy correction within the G^0W^0 (more precisely, diagonal G^0W^0) approximation pushes the *d* level back up to −7.10 eV. Therefore the improvement over the conventional LDA+GW calculations is not significant. This is not an unexpected result since the final quasiparticle energy should be independent of H_0, provided that $\Delta H=H-H_0$ is small enough for perturbation theory. We have also partly addressed the self-consistent issue in the quasiparticle calculations by updating the quasiparticle energies in the construction of the *G* and *W* operators, denoted as the G^1W^1 scheme. This scheme gives minor improvement in the calculated *d* state energy as shown in Fig. 4. This once again suggests that the fundamental physics involved in this problem has yet to be understood.

There are several related issues that have been discussed intensively in the literature. Unfortunately, no consensus is reached so far. It was shown[13] that treating the exchange energy within the exact-exchange scheme greatly improves the description of the *d* states, probably owing to the near elimination of self-interaction within the exact-exchange method. For example, the calculated E_d for ZnS is about −7.05 eV measured from the valence band maximum, which is similar to our LDA+GW result. However, subsequent *GW* calculations show negligible improvement, with E_d changing from −7.05 eV to −7.08 eV.[13] This result further confirms our conclusion that the *GW* results ought to be insensitive to the starting mean-field solution if it is appropriately applied. This conclusion apparently contradicts Ref. 13 claiming that LDA gives a poor starting mean-field solution. The discrepancy is ascribed to the difference in the LDA+*GW* results. In Ref. 13, the GW correction pushes the *d* band up compared to the LDA value, which is contrary to the results of all other groups[4,6,9,11] including ours. In a very recent paper[12] it was shown that an all-electron exact exchange treatment gives almost perfect agreement between theory and experiment as far as E_d is concerned. However, the same calculations give a band gap that is more than 1.2 eV larger than experiment for ZnS and about 2.2 eV too small for BN. It was also argued[12] that removing the core-valence exchange energy gives a much better agreement between the calculated and measured band gaps of several semiconductors. However, the same argument does not apply to many insulators. Moreover, as discussed above, there is no rigorous justification for using the Kohn-Sham eigenvalues as quasiparticle energies even if one knows the exact exchange-correlation energy functional.

In summary, we have investigated the *d*-state energy of ZnS within the *GW* approximation. We found that the starting Hamiltonian plays a minor role in the final *GW* quasiparticle energies. While LDA+U (U=8 eV and J=1 eV) calculations give a much deeper *d* level compared to LDA by 2.6 eV which agrees well with the experiment, the LDA+U+GW value is only 0.15 eV lower than that calculated within the LDA+GW scheme. The discrepancy between the calculated *d*-state energy and measured values is still as large as 2 eV. The G^1W^1 correction to G^0W^0 is not significant (−0.3 eV). Thus further investigation is necessary to settle this issue.

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