Quasiparticle band structure of ZnS and ZnSe

Weidong Luo,* Sohrab Ismail-Beigi, Marvin L. Cohen, and Steven G. Louie
Department of Physics, University of California at Berkeley, Berkeley, California 94720
and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720
(Received 16 July 2002; published 27 November 2002)

We calculate the quasiparticle band structure of ZnS and ZnSe using the plane-wave pseudopotential method and the *GW* approximation for the self-energy. The Zn semicore $3d$ states are treated as valence states. A systematic study of the role of various approximations is presented, including the local density approximation (LDA) and generalized gradient approximation (GGA) for the ground-state properties, the role of self-consistency both in the dielectric function and the self-energy Σ, the effect of off-diagonal matrix elements of $(\Sigma - V_{xc})$ in the Kohn-Sham orbital basis, and the plasmon-pole approximation. This study demonstrates that the LDA and GGA give similar results, and that self-consistency in updating the quasiparticle energies improves the accuracy of the band gap as well as the energies of the semicore $3d$ states. The calculated quasiparticle band gaps of ZnS and ZnSe agree well with experimental values when the *GW* approximation is used. There is some discrepancy for the calculated quasiparticle energies of the semicore states and some possible reasons are discussed.

DOI: 10.1103/PhysRevB.66.195215 PACS number(s): 71.20.Nr, 71.15.Mb

I. INTRODUCTION

In the last 15 years, the *GW* approximation[1,2] to the self-energy has become a well-established *ab initio* method for calculating the quasiparticle band structure of semiconductors. The approach[2] uses the eigenvalues and wave functions from density-functional theory[3] as a starting point and then constructs the Green function and the screened Coulomb interaction for the electron self-energy operator. In practice, one often uses the pseudopotential method[4] and the local density approximation[5] (LDA) or generalized gradient approximation[6] (GGA) for the density-functional part of the calculation. This approach gives accurate band gaps for various group IV and group III-V semiconductor bulk materials[2] and also produces good results for the valence-band offsets in semiconductor heterojunctions.[7]

This study examines applications of the *GW* method to study II-VI compounds, where the semicore *d* states have a strong influence on the valence and low-energy conduction states. In fact, in zinc compounds such as ZnS and ZnSe, the Zn $3d$ semicore states have a higher energy than the $4s$ valence states. Thus, treating the Zn $3d$ semicore states as part of the frozen core of the pseudopotential can lead to large errors in the electronic structure. Previous work on this subject has shown that semicore *d* states have a strong influence on the band structure of compounds such as GaN, ZnS, and CdS.[8,9]

Previously, it has been found that the $3d$ semicore states in Zn compounds are under-bound by 2–3 eV in LDA calculations.[10] An interesting question is whether the *GW* approximation gives the correct quasiparticle energy for these states. This issue was studied previously,[9,11] but the conclusions did not lead to a consistent picture. Since the semicore states are highly localized, the choice of the density-functional approximations (LDA or GGA) may be important in determining the quality of the Kohn-Sham orbitals and their accuracy in approximating the true quasiparticle wave functions. This question is also explored below.

II. METHODS

The quasiparticle energy spectrum is calculated using the standard *GW* approach.[2] The quasiparticle energies and wave functions of the quasiparticle excited states can be obtained by solving the Dyson equation[2]

$$[T+V_{ext}(\mathbf{r})+V_H(\mathbf{r})]\psi(\mathbf{r})+\int d\mathbf{r}'\Sigma(\mathbf{r},\mathbf{r}';E^{qp})\psi(\mathbf{r}') = E^{qp}\psi(\mathbf{r}), \quad (1)$$

where T is the kinetic energy operator, V_{ext} and V_H are the external potential due to the ions and the electrostatic Hartree

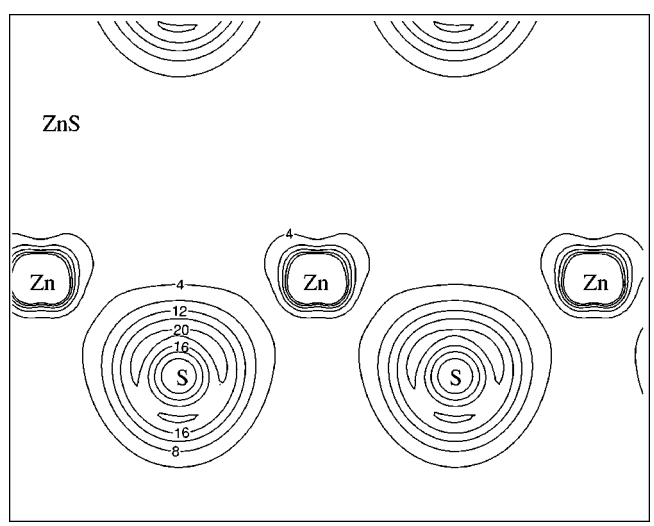

FIG. 1. Total valence charge density of ZnS (electrons/cell).

 ©2002 The American Physical Society

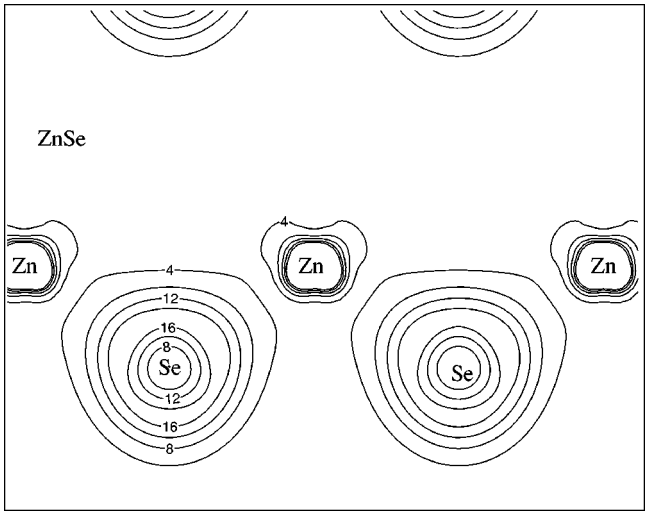

FIG. 2. Total valence charge density of ZnSe (electrons/cell).

potential, and Σ is the electron self-energy operator. The *GW* approximation takes the self-energy operator[2] Σ to be

$$\Sigma(\mathbf{r},\mathbf{r}';E)\cong\frac{i}{2\pi}\int d\omega e^{-i0^{+}\omega}G(\mathbf{r},\mathbf{r}';E-\omega)W(\mathbf{r},\mathbf{r}';\omega), \tag{2}$$

where G is the Green function and W is the screened Coulomb interaction, $W=\epsilon^{-1}V_c$ (ϵ is the dielectric function and V_c is the bare Coulomb interaction). The eigenvalues and eigenfunctions (Kohn-Sham orbitals) from density-functional theory (DFT) calculations are used to calculate initial static dielectric matrices. Using a generalized plasmon-pole model, frequency-dependent dielectric matrices are then calculated and used to construct the screened Coulomb interaction W. The Kohn-Sham orbitals and eigenvalues from the DFT calculations are also used to construct the Green function G in the quasiparticle approximation.

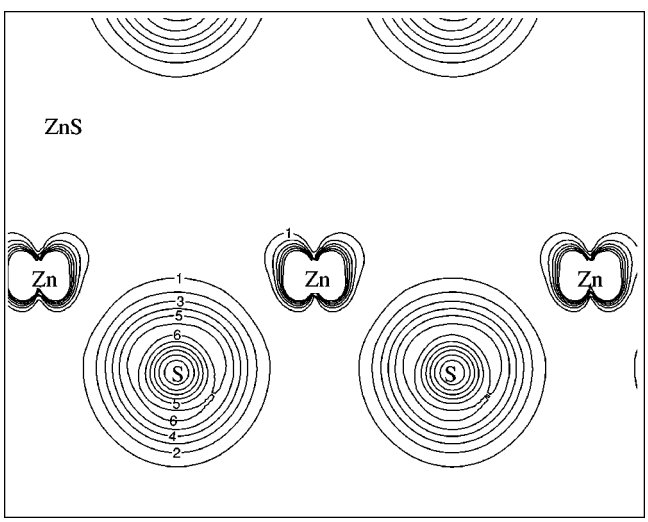

FIG. 3. The charge density of the highest valence-band wave function of ZnS at Γ (electrons/cell).

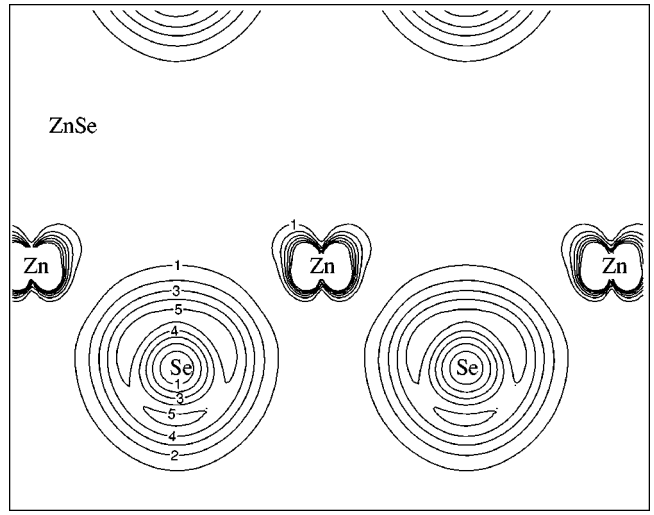

FIG. 4. The charge density of the highest valence-band wave function of ZnSe at Γ (electrons/cell)

We use the plane-wave pseudopotential density-functional method to obtain wave functions and eigenvalues as input for the quasiparticle calculations. This is done by solving the Kohn-Sham equation

$$\left[T+V_{ext}(\mathbf{r})+V_H(\mathbf{r})+\frac{\delta E_{xc}}{\delta n(\mathbf{r})}\right]\psi_i=E_i\psi_i\,, \tag{3}$$

where $[\delta E_{xc}/\delta n(\mathbf{r})]=\mu[n;\mathbf{r}]$ is the exchange-correlation potential and $n(\mathbf{r})=\Sigma_{occ}|\psi_i(\mathbf{r})|^2$ is the total electron density. Both the LDA and GGA are used as approximations to the exchange-correlation potential. Because of the existence of semicore d states in Zn, we need to pay careful attention to the treatment of semicore states in the pseudopotential, the choice of basis set, and convergence questions.

In order to include the effect of semicore d states, we treat the $3d$ states in Zn as valence states when constructing the pseudopotential. As shown by Rohlfing *et al.*,[12] treating the $3d$ states, as valence states, while keeping the $3s$ and $3p$

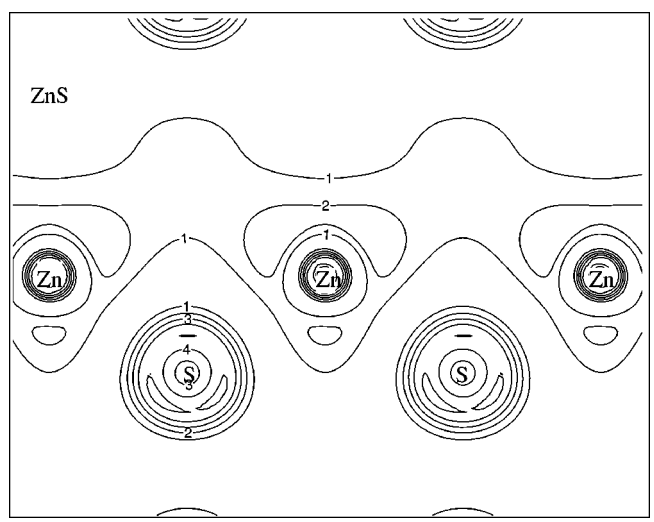

FIG. 5. The charge density of the lowest conduction-band wave function of ZnS at Γ (electrons/cell).

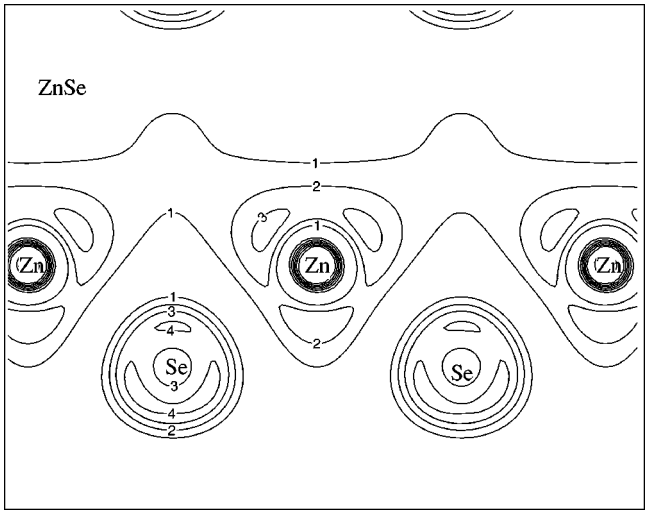

FIG. 6. The charge density of the lowest conduction-band wave function of ZnSe at Γ (electrons/cell).

states in the core can result in large errors in the quasiparticle energy eigenvalues. Our own test calculations for ZnS and ZnSe reproduce this finding. The correct way to describe the semicore states in Zn is to include the entire $3s$, $3p$, and $3d$ shell as valence states, which leads to a Zn^{20+} pseudopotential. Very similar to what is described in Ref. 9, we first construct the pseudopotential for the Zn^{2+} ion, which has the electronic configuration (Ne)$3s^2 3p^6 3d^{10}$ and then test the energies of the $3s$, $3p$, $3d$, and $4s$ states of the pseudopotential in the neutral atom configuration. The cutoff radius of the pseudopotential configuration is then varied until good agreement with all-electron results is achieved.

Since the semicore states are highly localized, the calculations can be difficult to converge. In a previous work, Rohlfing *et al.*[9] used a Gaussian-orbital basis set which, while computationally less expensive, is more difficult to monitor or control systematically for convergence and basis set bias. In this work, we use a plane-wave basis set, which, while computationally demanding, is bias-free and straightforward to converge. In the initial DFT calculation, a plane-wave cutoff energy of 200 Ry and ten k points in the irreducible Brillouin zone are used, which converge the energy eigenvalues of the semicore $3d$ states to within 0.1 eV and the eigenvalues of s,p valence states to within 0.05 eV. We choose a cutoff energy of 49 Ry for the correlation parts of the self-energy and a cutoff energy of 180 Ry for the (Hartree-Fock) exchange energy,[2] choices that converge the eigenvalues of the $3d$ semicore states to 0.5 eV and the s,p valence states to 0.1 eV for both ZnS and ZnSe.

III. RESULTS AND DISCUSSIONS

The DFT stage of our calculations produces Kohn-Sham eigenvalues, wave functions and total electron densities for ZnS and ZnSe. Figures 1 and 2 show the total valence electron density. Figs. 3 and 4 show the amplitude of the wave functions at the top of the valence band at Γ for ZnS and ZnSe, respectively, while Figs. 5 and 6 show the amplitude of the lowest conduction-band wave functions at Γ.

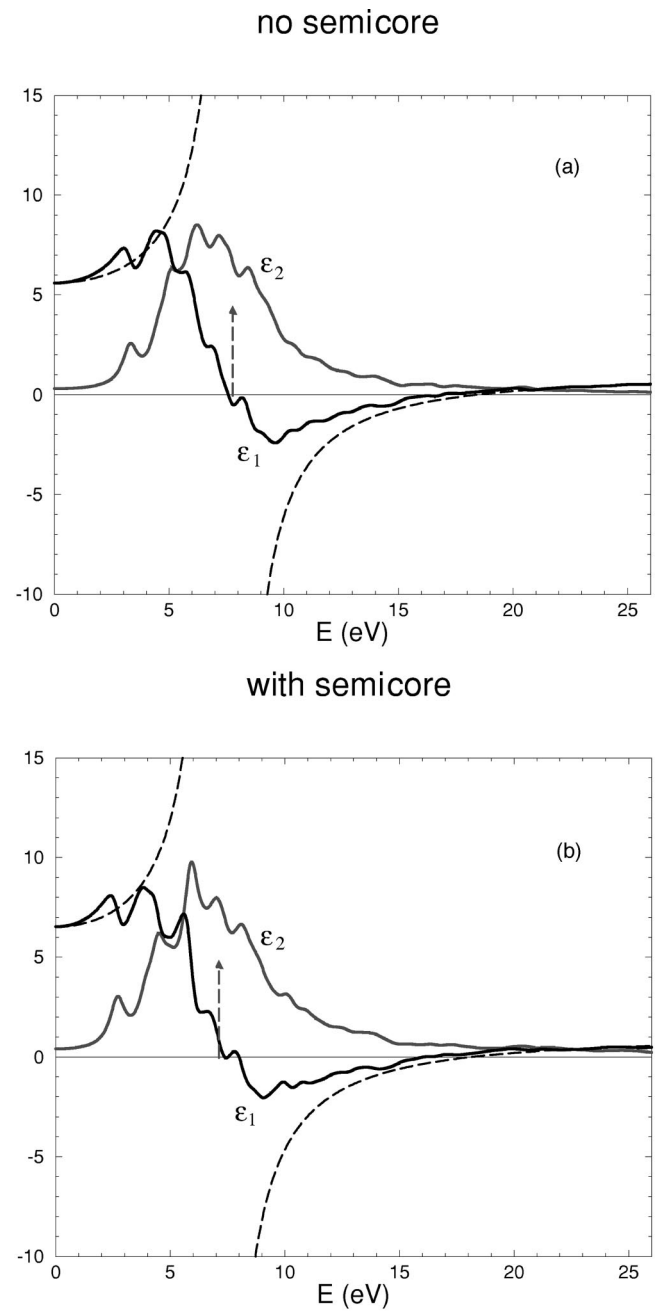

FIG. 7. The real part $[\epsilon_1(\omega)]$ and imaginary part $[\epsilon_2(\omega)]$ of the dielectric function $\epsilon_{00}(\mathbf{q}=0,\omega)$ for ZnS with and without semicore states ($E=\hbar\omega$). The GPP model result is also plotted in dashed line, the arrow indicates the imaginary part (δ function).

Using the DFT results, we calculate the *ab initio* static random-phase approximation (RPA) dielectric matrices $\epsilon_{GG'}(\mathbf{q},\omega=0)$ and extend them to finite frequencies with a generalized plasmon-pole (GPP) model.[2] While the GPP model is known to work well for delocalized valence states, its applicability to localized semicore states may seem questionable. We test the GPP for ZnS with localized semicore states by calculating the true frequency-dependent RPA dielectric function $\epsilon_{00}(\mathbf{q}=0,\omega)$ both with and without the semicore states, and we found that the two cases are very similar to each other and both agree with the GPP model, as

TABLE I. The band-gap energy (E_g), semicore d state binding energy (E_d) with respect to the valence-band maximum, and static dielectric constant (ϵ_∞) of ZnS using the LDA+GW approach. The LDA results, "first shot" GW results, GW results using updated dielectric matrices, GW results using Gaussian-orbital basis set from Ref. 9, and experimental results are listed (the larger value 7.9 eV of E_d in Ref. 9 is an interpolation of self-consistency and renormalization effect). See text for details.

	LDA	GW (first shot)	GW (updated ϵ)	GW (other)[a]	Expt.
ϵ_∞		5.96	4.79		5.1
E_g (eV)	1.65	3.19	3.64	3.50	3.80
E_d (eV)	6.1	6.9	7.4	6.4, 7.9	8.97(6),[b] 9.03(15)[c]

[a]Reference 9.
[b]Reference 13.
[c]Reference 14.

shown in Fig. 7. Therefore, we use the GPP model in the work reported below.

The Kohn-Sham eigenvalues and wave functions from DFT calculations are initially used to calculate the dielectric matrices and the Green function. Later, we also use the updated quasiparticle energies to recalculate both the dielectric matrices and update the Green function for a "self-consistent" recalculation of the self-energy. Our results show that self-consistency in constructing the Green function has a small effect of about 0.1 eV on the band-gap energy, whereas self-consistency in constructing the dielectric matrices has a much larger effect as discussed below.

Aside from the issue of the self-consistency of the energy eigenvalues used for construction of the dielectric matrices and Green function, the LDA and GGA Kohn-Sham orbitals are usually assumed to be identical to the true quasiparticle wave functions.[2] We test this assumption by expanding the quasiparticle wave function in the Kohn-Sham orbitals and treating the term ($\Sigma - V_{xc}$) as a perturbation. We find that the mixing coefficients α_{ij} of Kohn-Sham states i and j (for symmetry allowed orbitals), given by the pertubation expression

$$\alpha_{ij} = \frac{\langle \psi_i^{DFT} | \Sigma - V_{xc} | \psi_j^{DFT} \rangle}{E_i - E_j}, \tag{4}$$

TABLE II. The band-gap energy (E_g), semicore d state binding energy (E_d), and static dielectric constant (ϵ_∞) of ZnS using the GGA+GW approach. The GGA results, "first shot" GW results and experimental results are listed.

	GGA	GW (first shot)	Expt.
ϵ_∞		5.42	5.1
E_g (eV)	2.03	3.27	3.80
E_d (eV)	6.0	6.8	8.97(6),[a] 9.03(15)[b]

[a]Reference 13.
[b]Reference 14.

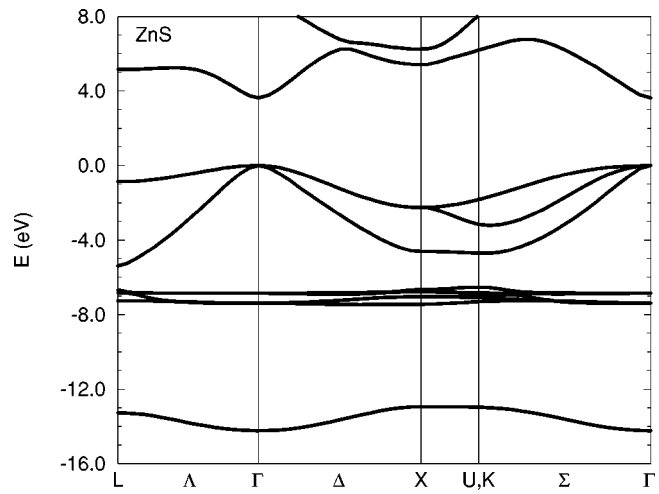

FIG. 8. ZnS GW band structure.

are very small. Our test results for ZnS using the LDA show that $|\langle \psi_{3d}^{LDA} | \Sigma - V_{xc} | \psi_{con}^{LDA} \rangle| < 0.10$ eV, while $|E_{3d}^{LDA} - E_{con}^{LDA}| \sim 10$ eV, and that $|\langle \psi_{3d}^{LDA} | \Sigma - V_{xc} | \psi_{val-3p}^{LDA} \rangle| < 0.02$ eV, while $|E_{3d}^{LDA} - E_{val-3p}^{LDA}| \sim 7$ eV (at Γ). This is clear evidence that our DFT wave functions agree very well with the quasiparticle wave functions and that the mixing between the semicore $3d$ and higher states is negligible for our purpose. Therefore, we ignore such mixing and take the Kohn-Sham orbitals to be identical for the quasiparticle wave functions.

Results for the band gap (E_g), semicore d state binding energy (E_d) relative to the top of the valence band, and dielectric constant (ϵ_∞) of ZnS using LDA+GW are presented in Table I. Clearly, the LDA alone underestimates E_g and E_d. Taking the LDA wave functions and eigenvalues as input, we calculate the dielectric matrices and Green function, and use these to calculate the "first shot" GW quasiparticle energies. While the band gap becomes much closer to the experimental value, the semicore state binding energy, though improved, is still sizably different from the experimental value. The corresponding "first shot" GW results using the GGA are shown in Table II: there is little difference between the LDA+GW results and GGA+GW results, strong evidence of idea that the GW approximation successfully corrects for the deficiencies of DFT regardless of the approximation employed (LDA or GGA): it does not

TABLE III. The band-gap energy (E_g), semicore d state binding energy (E_d), and static dielectric constant (ϵ_∞) of ZnSe using the LDA+GW approach. The LDA results, "first shot" GW results, GW results using updated dielectric matrices and experimental results are listed.

	LDA	GW (first shot)	GW (updated ϵ)	Expt.
ϵ_∞		8.05	6.42	5.4
E_g (eV)	0.89	2.32	2.41	2.96
E_d (eV)	6.3	7.0	7.2	9.37(7),[a] 9.20(15)[b]

[a]Reference 13.
[b]Reference 14.

TABLE IV. The band-gap energy (E_g), semicore d state binding energy (E_d), and static dielectric constant (ϵ_∞) of ZnSe using the GGA+GW approach.

	GGA	GW (first shot)	GW (updated ϵ)	Expt.
ϵ_∞		6.81	5.76	5.4
E_g (eV)	1.32	2.51	2.69	2.96
E_d (eV)	6.5	7.3	7.5	9.37(7),[a] 9.20(15)[b]

[a]Reference 13.
[b]Reference 14.

strongly depend on the initial guess. The GW results calculated by Rohlfing *et al.*[9] using a Gaussian basis set are also listed in Table I and the agreement between the two basis sets is gratifying.

Using the quasiparticle energies from the "first shot" GW calculation, we calculate RPA dielectric matrices, Green functions, and then GW quasiparticle energies which are listed in Table I as "GW (updated ϵ)."[2] As expected, the dielectric constant (ϵ_∞) decreases because of the increased band gap and the resulting refined quasiparticle band-gap energy is increased slightly. The semicore d binding energy is also increased to 7.4 eV. Overall, we see that the GW approximation improves the band gap and semicore binding energies. The agreement between the band gap and the experimental value is excellent, while there is still a sizable difference remaining for the semicore state binding energy. We show the quasiparticle band structure along high-symmetry directions in Fig. 8.

Similar results for ZnSe are displayed in Tables III and IV. Similar to ZnS, the GW approximation improves both the band-gap energy (E_g) and semicore state binding energy (E_d). There is good agreement for E_g between theory and experiment, while a sizable difference remains for the semicore state binding energy. The corresponding band structure is shown in Fig. 9.

In summary, for both the ZnS and ZnSe systems, the LDA+GW or GGA+GW approaches give similar agreement for the calculated band-gap energies with the experimental values, whereas semicore state binding energies have larger discrepancies. Rohlfing *et al.*[8] have provided a possible explanation. They used a simple model to include some renormalization and satellite effects in the self-consistent Green function and this inclusion provides an energy shift of 1.5 eV for the ZnS semicore states, resulting in a binding energy of 7.9 eV (see Table I), but there are still unclarified problems in such an approach.[8] However, the key point is that for these localized d states, neglected and complex many-body effects can shift energies by amounts on the order of remaining discrepancies between the GW and experimental results. Therefore, a full *ab initio* prediction of the d level energies must await further theoretical advances.

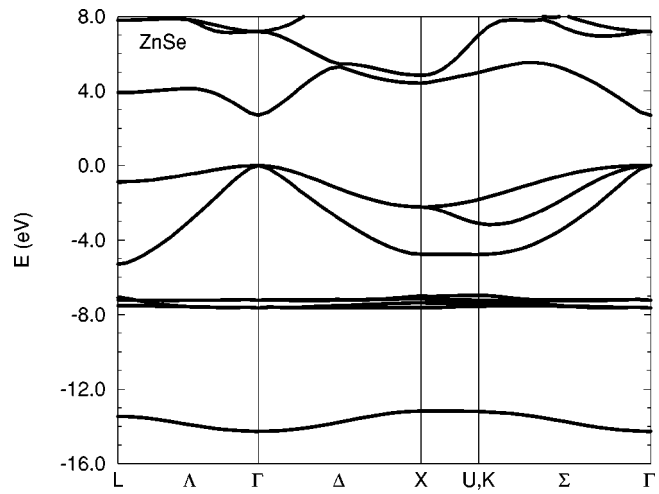

FIG. 9. ZnSe GW band structure.

IV. CONCLUSIONS

We have investigated the quasiparticle properties of ZnS and ZnSe within the DFT+GW approach and have focused on the role of the 3d Zn semicore states. We find that the choice of LDA or GGA approximation as a starting point makes little difference for the band-gap and semicore state binding energies, and that the LDA and GGA wave functions are both in excellent agreement with the true quasiparticle wave functions. The self-consistency of quasiparticle energies in constructing the Green function has a small effect on the band-gap and semicore state energies, whereas the role of self-consistency in constructing the dielectric matrices has a much larger and quantitatively important effect. The final band-gap energies agree well with the experimental values. However, there are still sizable differences between the calculated semicore state binding energies and their experimental values. There is evidence that the existence of satellites in the spectrum of the semicore state may explain part of the discrepancy but further investigation is clearly necessary.

ACKNOWLEDGMENTS

This work was supported by National Science Foundation Grant No. DMR00-87088 and by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, U.S. Department of Energy under Contract No. DE-AC03-76SF00098. Computational resources have been provided by NSF at the National Center for Supercomputing Applications. We also thank Michael Rohlfing for discussions and helpful criticism.

*Electronic address: wdluo@civet.berkeley.edu

[1]L. Hedin, Phys. Rev. **139**, A796 (1965).
[2]M.S. Hybertsen and S.G. Louie, Phys. Rev. B **34**, 5390 (1986).
[3]W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).
[4]M.L. Cohen, Phys. Scr. **T1**, 5 (1982).
[5]D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[6]J. Perdew, *Electronic Structure in Solids '91* (Akademie Verlag, Berlin, 1991).

[7] S.B. Zhang, D. Tomanek, S.G. Louie, M.L. Cohen, and M.S. Hybertsen, Solid State Commun. **66**, 585 (1988).
[8] M. Rohlfing, P. Krüger, and J. Pollmann, Phys. Rev. B **56**, R7065 (1997).
[9] M. Rohlfing, P. Krüger, and J. Pollmann, Phys. Rev. B **57**, 6485 (1998).
[10] S.B. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. B **52**, 13 975 (1995).
[11] F. Aryasetiawan and O. Gunnarsson, Phys. Rev. B **54**, 17 564 (1996).
[12] M. Rohlfing, P. Krüger, and J. Pollmann, Phys. Rev. Lett. **75**, 3489 (1995).
[13] R. Weidemann, H.-E. Gumlich, M. Kupsch, H.-U. Middelmann, and U. Becker, Phys. Rev. B **45**, 1172 (1992).
[14] L. Ley, R.A. Pollak, F.R. McFeely, S.P. Kowalczyk, and D.A. Shirley, Phys. Rev. B **9**, 600 (1974).