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Band gaps and quasiparticle energy calculations on ZnO, ZnS, and ZnSe in the zinc-blende structure by the *GW* approximation

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We have calculated the quasiparticle band gaps of ZnO, ZnS, and ZnSe in zinc-blende structure within the *GW* approximation using a full random-phase approximation dielectric matrix. The linear muffin-tin orbital basis was used for this calculation and the $3d$ orbitals of the Zn atom were treated as valence band in every case. The calculated band gaps are 3.59, 3.97, and 3.10 eV for ZnO, ZnS, and ZnSe, respectively. The gaps of ZnS and ZnSe are in good agreement with the experimental values and so is the gap of ZnO if we compare it with the experimental optical gap of wurtzite ZnO. [S0163-1829(99)01139-X]

I. INTRODUCTION

The wide-gap semiconductor materials are very important for applications in the fields of optical device technology. For example, the visual display, high-density optical memory, transparent conductors, solid-state laser devices, solar cell, and so on are considered to be derived from these materials. In these optical device technology, the first-principle device design technology is now highly desired since it relieves us from the huge trial-and-error work and assists us in creating attractive devices with less cost and uncertainty. Up to now, most works on *ab initio* device design have been based on the density-functional theory[1,2] (DFT) within the local-density approximation (LDA).[2] They are intended to describe the material structure rather than the optical properties since the DFT scheme cannot describe the optical excitations in principle. Optical excitations can be described however within the time-dependent DFT.[3]

The LDA is appealing since the local nature of the exchange and correlation potential Vxc results to produce a set of single-particle equations that are much simpler to solve numerically than the integrodifferential equations in the Hartree-Fock approximation. Owing to this simplicity, LDA method has been applied to a wide class of systems and it is the fact that many surprisingly good results have been obtained even if the systems are relatively localized and show almost no image of the homogeneous electron gas. These good results may be attributed to the subtle cancellations between the effects of the strong energy dependence and of the nonlocality.

However, there are some serious problems with the LDA. One of them is the discrepancy in the quasiparticle band-gap values from the experimental ones. It often occurs that the LDA calculation yields too smaller band gap than the experiments. When gradient corrections are taken into account within the generalized gradient approximation,[4] the band gap is not significantly improved.[5] In fact, there is no reason that the band gap should be given correctly even with the exact DFT. Therefore, improving the exchange-correlation functional is unlikely to solve the band-gap problem. This failure should be considered to originate from the lack of nonlocality and energy dependence in the exchange-correlation potential. A more realistic but relatively simple approximation to the selfenergy, which takes account of both nonlocality and dynamic correlations, was developed in the early 1960s by Hedin, known as the *GW* approximation (GWA).[6] This approximation was originally derived from a many-body perturbation theory.

In spite of the theoretical simplicity of GWA, its applications to real systems have been hampered by the large size of the computations. The first self-energy calculations for semiconductors within the GWA was done in 1986, which was based on the pseudopotential method with plane waves.[7] The $3d$ orbitals are usually regarded as core states since the size of the computations to get the selfenergy with plane-wave basis was huge. However, it is well known that since the $3d$ orbital and the $2p$ orbital have strong interactions and they affect the valence band crucially[8] in some material as discussed later, it is very important to consider them as valence states to reproduce the actual electronic properties.

In this paper, we used the recently developed *GW* scheme based on the linear muffin-tin orbital[9,10] (LMTO) product basis[11] to calculate the quasiparticle energies of some prototype wide-gap materials, treating the $3d$ orbitals as valence states. The method reduces the size of the dielectric matrix considerably compared with methods based on plane-wave basis and allows us to treat localized states in the same footing as extended states. The materials of ZnO, ZnS, ZnSe in zinc-blende structure would be typical materials where the role of the $3d$ orbitals is important. Therefore it is timely to study these materials from first principles. This work should be regarded as a starting point for the applications of LMTO-GWA for the wide class of wide-gap semiconductor materials in which the $3d$ orbitals should be taken into account directly.

This paper is organized as follows; Sec. II briefly describes the theoretical method. In Sec. III, the calculated quasiparticle energy are presented with some experimental data. A summary is given in Sec. IV.

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II. THEORY

In this paper, the standard LMTO method,[9,10] which can be applied to systems with *d* and *f* electrons, is used to obtain the LDA band structures and LDA wave functions, which are employed as input for the *GW* calculations. The 3*d* orbitals are included into the valence complex as nonlocal state without much difficulty into our *GW* calculation. The quasiparticle energy calculations are done using the full random-phase approximation (RPA).[11] 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

$$[E_k(\omega)-H_0(r;\omega)]\varphi_k(r,\omega)-\int dr'\sum(r,r';\omega)\varphi_k(r';\omega)=0, \tag{1}$$

where the H_0 includes the kinetic-energy operator, potential due to the ions and the Hartree potential of the electrons. In the GWA, the selfenergy Σ is given by the expression

$$\sum(r,r';\omega)=i\int\frac{d\omega'}{2\pi}G(r,r';\omega+\omega')W(r,r';\omega')e^{i\delta\omega'}, \tag{2}$$

where $G(r,r';\omega+\omega')$ is the full Green's function and $\delta=0^+$. $W(r,r';\omega')$ is the dynamically screened Coulomb interaction given by

$$W(r,r';\omega)=\int d^3r''\varepsilon^{-1}(r,r'';\omega)v(|r''-r'|), \tag{3}$$

where $\varepsilon^{-1}(r,r'';\omega)$ is an inverse dielectric matrix and $v(|r''-r'|)$ is a bare Coulomb potential. It is useful to regard the GWA as a Hartree-Fock approximation with a dynamically screened interaction rather than as a perturbation theory. The calculation of ε^{-1} within the RPA was described in detail in a previous publication.[11,12] To screen the Coulomb interaction, we have performed the full RPA dielectric functions for each material instead of making the plasmon-pole approximation[7,13,14] or other similar approximations.[15]

The zeroth-order Green's function G^0 is constructed using the LDA eigenfunctions and eigenvalues $E^{\mathrm{LDA}}_{n,k}$, which are calculated by using LMTO method. Here, we make advantage of the fact that the quasiparticle wave functions are well approximated by the LDA wave functions.[7,16] Once the self-energy operator is constructed, the quasiparticle energies are calculated as

$$E^{qp}_{n,k}=E^{\mathrm{LDA}}_{n,k}+\left\langle n,k\left|\sum-V^{\mathrm{LDA}}_{xc}\right|n,k\right\rangle, \tag{4}$$

where V^{LDA}_{xc} is the LDA exchange-correlation potential.

The LMTO basis within the atomic sphere approximation[9,10] (LMTO-ASA) has the following form:

$$\chi_{RL\nu}=\phi_{RL\nu}+\sum_{R'L'\nu'}\phi_{R'L'\nu'}h_{R'L'\nu',RL\nu}, \tag{5}$$

where the *RL* denotes the site and angular momentum (*l*,*m*), respectively, ϕ is the solution to the Schrödinger equation inside the muffin-tin sphere, $\dot{\phi}$ is its energy derivative taken at some fixed energy ε_ν and $h_{R'L'\nu',RL\nu}$ is a coefficient. The response function, which is needed to make ε^{-1} within the RPA, consists of Bloch states, so that the Hilbert space spanned by the response function is composed of products such as $\phi\phi$, $\phi\dot{\phi}$ and $\dot{\phi}\dot{\phi}$.[11] A large fraction of these products is linearly dependent and we construct an optimized basis for ε^{-1} by forming linear combinations of these product functions. The number of basis functions per atom is typically ~100.[11,17]

TABLE I. Experimental lattice constants (in Å) on ZnO, ZnS, and ZnSe in zinc-blende structures.

Compound	Lattice constant
ZnO	4.62[a]
ZnS	5.4109[b]
ZnSe	5.667[c]

[a] Reference 18.
[b] Reference 19.
[c] Reference 20.

In our calculation, the existence of the spin was ignored. 22 irreducible *k* points have been chosen to perform the self-energy calculations for each material. It was sufficient to obtain convergence in the self-energy.[17] $(\mathrm{O}_{1s},\mathrm{Zn}_{3p})$, $(\mathrm{S}_{2p},\mathrm{Zn}_{3p})$, and $(\mathrm{Se}_{3d},\mathrm{Zn}_{3p})$ were taken into account for the calculation of the correlated part of the self-energy as well as all valence electrons for ZnO, ZnS, and ZnSe, respectively. All core and valence electrons were included into the calculation of the exchange part of the self-energy. 3*d* electrons of Zn were treated directly as valence electrons.

III. RESULTS

The experimental values of the lattice parameters[18–20] have been chosen for our calculations as shown in Table I. Although the ZnO usually has the wurtzite structure,[21] it is known that the zinc-blende structure exists as a meta stable state.[18,22] Table II shows the result of quasiparticle band gaps of ZnO, ZnS, and ZnSe in zinc-blende structures as well as the experimental optical band gaps[23] of ZnS and ZnSe in zinc-blende structures and those[23] of ZnO, ZnS, and ZnSe in wurtzite structures. The calculated band gaps of ZnO, ZnS, and ZnSe are 3.59, 3.97, and 3.10 eV, respectively. We can see from Table II that the band gaps of ZnS and ZnSe in our calculations agree well with the experimental values. Before we compare the calculational results with the experimental optical gaps, we should pay some attentions to the following points. (1) There exists some difference of the meaning between the quasiparticle band gaps and the optical one. (2) Real systems have spin-orbit interactions, however, this effect of spin-orbit coupling is not included and only the scalar relativistic contribution is taken into account in our calculations. (3) We have used the atomic-sphere approximation in our LMTO band-structure calculations.

The experimental gaps are obtained from optical measurements. It is possible that there are excitons with binding energies smaller than the one-particle gap measured in photoemission experiments. In this case, the optical gap is smaller than the photoemission gap. To take account of excitonic effects, we need the two-particle Green function, which de-

TABLE II. Quasiparticle band gaps (in eV) of ZnO, ZnS, and ZnSe in zinc-blende structures by GWA calculations of this work and other previous ones. Experimental band gaps in zinc-blende (ZB) and in wurtzite (WZ) structure (see Ref. 23) are also appended. Parentheses beside the experimental gap value presents the absolute temperature where the gap was observed.

Compound	GWA(ZB)		Experimental gap (ZB)	Experimental gap (WZ)
ZnO	3.59			3.4376-3.4790(1.6 K)
ZnS	3.97	3.50[a], 3.98[b]	3.78(19 K)	3.8643-3.9808(77 K)
ZnSe	3.10	2.84[b]	2.82(10 K)	2.874(4.2K)

[a] Reference 14.

[b] Reference 13.

scribes the interaction between particles and holes. Our calculated gaps are obtained from the one-particle Green functions, which contain no information about excitonic excitations. Strictly speaking, the gaps should therefore be compared with the photoemission gaps. We notice that the calculated gaps are a bit larger than the experimental optical gaps in all the three materials considered, consistent with the possibility of having excitons.

The optical data for ZnO in zinc-blende structure does not yet exist as far as we know. However, it is reasonable to compare our result with the experimental data corresponding to the wurtzite structure because we expect that the difference between the optical gap of zinc-blende structure and that of wurtzite structure would not be large. The optical band gap in gamma point is generally affected dominantly by the distance between the anion sublattice and the cation sublattice. In the case of the wurtzite and the zinc-blende structure, the difference in the distance is small. Moreover, both have tetrahedral bonds and only differ in the second-nearest neighbors. The smallest distance between Zn and O is 2.0005 Å in this zinc-blende structure. We have checked the gap-value dependencies on a lattice structure in LDA level by making wurtzite lattice where the smallest distance between Zn and O is 2.0005 Å. This wurtzite lattice has $a=3.2668$, $c=5.3347$, and $u=0.375$ as its lattice constants and is almost the same as the actual one. The difference of the LDA gap between the actual zinc-blende and this semivirtual wurtzite lattice is only 30 meV. Then the effect of second-nearest neighbors is almost completely negligible. Moreover, the experimental optical gaps of ZnS and ZnSe in wurtzite and zinc-blende structures are almost same. It is, therefore, reasonable to assume that the experimental optical gap of ZnO is very close to the one corresponding to the zinc-blende structure, namely 3.5 eV. Our predicted gap of 3.59 eV is in very good agreement with this value but it remains to be confirmed by experiment.

The calculated gap values correspond to the energy differences between the lowest conduction band and the center of gravity of the two split upper valence bands of real system due to the spin-orbit interactions. Since the spin-orbit splitting for the ZnS is small (less than 0.07 eV) (Ref. 13) and that for ZnO would be smaller than that for ZnS, these are almost negligible in our paper. However, that for the ZnSe is reported as large as ~0.4 eV.[13,23] The energy difference between the conduction-band bottom and the lower level of the two split upper valence bands of ZnSe is obtained as 3.24 eV experimentally.[13] This means that the energy difference between the lowest conduction band and the center of gravity of the two split upper valence bands is 2.96 eV. This value shows better correspondence with our calculational result of 3.10 eV than the case of comparing simply with the experimental value in Table II.

There is also a question concerning the use of the atomic-sphere approximation in the band-structure calculations. The error from the atomic-sphere approximation derives from the overlapping atomic spheres. To check the magnitude of the error, we have performed calculations with several different sets of atomic radii. The difference in the gap values was found to be small and it was almost within 0.1 eV in LDA level.

GW calculation for ZnS in Ref. 14 included the $3d$ semicore state whereas the work in Ref. 13 for ZnS and ZnSe did not include the $3d$ semicore state. Both works however employed the plasmon-pole approximation, whereas the present work uses the full RPA response function. The previous results are compared with present work in Table II. As can be seen, they are generally in good agreement.

Table III shows the quasiparticle energies at gamma point

TABLE III. Quasiparticle energies (in eV) of ZnO, ZnS, and ZnSe in zinc-blende structures by full RPA GWA calculations.

Level	ZnO		ZnS		ZnSe	
	LDA	GWA	LDA	GWA	LDA	GWA
Γ_1	−17.44	−17.93	−13.11	−13.08	−13.42	−13.27
Γ_{15}	−5.72	−6.69	−6.80	−8.41	−7.02	−8.82
Γ_{12}	−4.61	−6.38	−6.41	−8.28	−6.72	−8.75
Γ_{15}	0.00	0.00	0.00	0.00	0.00	0.00
Γ_1	1.10	3.59	1.94	3.97	1.07	3.10
Γ_{15}	13.65	17.14	6.41	8.69	5.85	7.95

compared with the LDA eigenvalues. We note that the energy of the top of the valence states has been aligned with the LDA one. The result for ZnO in zinc-blende structure is new as far as we know. In particular, the semicore states Γ_{15} derived from the $3d$ orbitals of Zn are significantly lowered from the LDA values by the *GW* self-energy corrections. This is in agreement with experiment. The semicore state in ZnSe in zinc-blende structure has been considered in a previous publication.[17] The semicore state in ZnO in wurtzite structure has also been calculated using a model *GW* approach,[15] which is expected to work well for corelike state. The model takes no account of energy dependence but in the extreme limit of no overlap between the core and the valence states, the self-energy may be shown to depend only on the static value of the screened interaction W.[24] Our full *GW* calculation gives a somewhat better result than that using the model *GW* approach.

The calculated $3d$ semicore binding energies of the materials considered here and in previous works[14,15,17] are systematically lower than the experimental values. One possible reason for this is that the strong hybridization between the semicore states and the valence states may result in large nondiagonal matrix elements of the selfenergy, which are not taken into account in our calculations.[25] Another possible reason is the tendency of the RPA to overscreen, leading to lower binding energy. It would be interesting to figure out the origin of this systematic discrepancy in future studies. Interesting to observe is the energies of occupied Γ_1 states, which, despite their high-binding energies, are not significantly altered by the GWA. On the other hand, the high-lying states Γ_{15} are significantly pushed up by the self-energy corrections. These results, however, should be taken with some caution due to the rather large energies of the states. The screened interaction entering in the self-energy is not expected to be as accurate at high energies as at low energies.

IV. CONCLUSION

The quasiparticle energies of ZnO, ZnS, and ZnSe in zinc-blende structures have been obtained using the GW approximation. We have treated $3d$ electrons of Zn as valence electrons and performed full RPA calculations for these materials. Our results show good agreements with the experimental values and demonstrate the applicability of the GWA to the quasiparticle band-structure calculations for a wide class of wide-gap compounds. We may interpret this result as a strong indication that the GWA could describe the screening effect also in the presence of $3d$ semicore orbitals correctly. Our machine IBM SP-2 can achieve the GWA calculation for each material within two days in 1 CPU. This would mean that the parallel or the vector calculation technique as well as the further development of the machine might make the LMTO-GWA method a rather practical tool for optical devise design by the first principle.

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