Quasiparticle calculations of semicore states in Si, Ge, and CdS

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We investigate binding energies of semicore states in prototype semiconductors by quasiparticle calculations. Band-structure calculations within the local-density approximation and standard GW quasiparticle calculations underestimate these energies systematically. Employing an extended GW approach we obtain very good agreement of calculated quasiparticle energies of semicore states in Si, Ge, and cubic CdS with experimental data. This is achieved by renormalizing the quasiparticle peaks in the spectrum and including plasmon-induced satellite structure in the Green's function. [S0163-1829(97)50936-2]

Quasiparticle band-structure calculations based on the GW approximation (GWA) of the self-energy operator as suggested by Hedin and Lundqvist[1,2] have become the ''state of the art'' in electronic structure calculations for semiconductors. The most simple variant of this approach has been applied very successfully[3–7] to calculate valence and conduction bands of elemental and III-V semiconductors with an accuracy of about 0.1 eV, as compared to experiment. The same accuracy has recently been obtained for valence and conduction bands of the II-VI compound CdS which was studied including the Cd $4d$ semicore states.[8] The binding energy of the latter, however, was found to be about 1 eV too small. This deviation between the standard GW results for semicore states and experiment is thus an order of magnitude larger than that for extended valence- and conduction-band states. Within standard GWA we find a systematic underbinding of, e.g., Ge $3d$ and Si $2p$ semicore levels, as well (see below). Motivated by these unusual deviations we have addressed the question of whether a self-consistent evaluation of the self-energy can help to overcome these shortcomings and can lead to semicore binding energies with the same accuracy as is now routinely achieved in standard GW calculations for valence and conduction bands. So far, little work has been done in this field due to the large numerical effort involved for strongly localized states. Bechstedt has calculated self-energies of semicore states within a simplified GW scheme.[9] More recently, Aryasetiawan and Gunnarsson have developed an approach for applying GWA to all-electron calculations for bulk crystals, yielding binding energies of semicore states which are considerably closer to experiment than respective local-density approximation (LDA) results.[10] Yet, the calculated semicore d energies still deviate from experiment by about 1 eV. Self-consistent self-energy calculations have recently been performed by de Groot and co-workers[11] and by Ummels *et al.*[12] for valence and conduction bands in semiconducting systems, as well as by von Barth and Holm[13] and by Shirley[14] for the homogeneous electron gas.

In this paper, we report on improved GW calculations for semicore states, i.e., for electronic states of the highest completely occupied electronic shell. In particular, we investigate the importance of self-consistency in the evaluation of the self-energy and the influence of the energetic structure of the Green's function. It turns out that the binding energies of the studied semicore states result in very good agreement with experimental data when more realistic Green's functions are employed instead of the most simple one resulting from LDA input data, alone.

In our calculations we employ basis sets of localized Gaussian orbitals both within LDA and GWA for the representation of the wave functions and all two-point functions. This allows for a very efficient description of localized states, as discussed in detail in Ref. 15. The inner-core states are eliminated by using norm-conserving *ab initio* pseudopotentials that are constructed according to the prescription of Hamann.[16] The localized semicore states that we are interested in are explicitly included in the valence shell. It is important to note that the other semicore states of the same shell are treated as valence states, as well, to correctly describe their exchange-correlation interaction with the considered semicore states.[8]

In the GW approximation[1,2] the self-energy operator is given by

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

But it is an open question which G and which W should be employed. In principle, the space and energy dependence of all operators, e.g., of the Green's function or the polarizability, entering the self-energy, have to be calculated fully self-consistently within GWA. This very demanding procedure, however, is usually not carried out. Instead, it is now the common procedure to construct the self-energy operator non-self-consistently by employing the results of a preceding LDA calculation and to determine *quasiparticle corrections* to the LDA energies resulting in the quasiparticle (QP) band structure. We characterize this approach by the self-energy $\Sigma^0 \equiv iG^{\mathrm{LDA}} W^{\mathrm{LDA}}$. One of the motivations for this approach is the excellent band-structure results it yields.[3–8] In the case of semicore levels it turns out, however, that this non-self-consistent evaluation of Σ is not sufficient. A fully self-consistent evaluation of the self-energy would be very desirable, therefore, when semicore QP binding energies are to be calculated. Since such calculations are far beyond current days computational possibilities we have, instead, investigated well-defined first steps towards a more appropriate evaluation of the self-energy.

TABLE I. Calculated QP binding energies (in eV) of the semicore states Cd $4d$ in cubic CdS, Ge $3d$ in Ge, and Si $2p$ in Si (see text). The zero of the energy scale is given by the respective valence-band maximum. The experimental data are weighted averages of spin-orbit split levels.

	LDA	GWA			Exp.
		G^{LDA}	G^{QP}	G^{QPS}	
Cd $4d$	-7.2	-8.1	-8.2	-9.1	-9.2,[a] -9.5[b]
Ge $3d$	-24.6	-27.7	-28.2	-30.0	-29.5,[c] -29.7[d]
Si $2p$	-89.4	-94.8	-97.9	-100.4	-99.0,[c] -100.0[d]

[a]Ref. 17.
[b]Refs. 18 and 19.
[c]Ref. 20.
[d]Ref. 21.

We begin our discussion by addressing the underlying LDA results. We have calculated the binding energies of Cd $4d$, Ge $3d$, and Si $2p$ states in cubic bulk CdS, in Ge, and in Si, respectively. These states are characterized by increasing binding energies and the mean value of their radii are 1.29, 0.74, and 0.54 a.u., respectively. They thus cover a sufficiently large range of localization allowing for a systematic discussion of localization-induced trends. For the three states we obtain LDA binding energies which deviate by as much as about 2, 5, and 10 eV from experiment (see first column of Table I). To some extent, this systematic underestimation of binding energies within LDA is related to unphysical self-interactions inherent in that approximation.[22,23]

Application of the standard GWA, i.e., employing Σ^0, yields considerably improved binding energies but they still deviate from experiment by about 1, 2, and 5 eV for Cd, Ge, and Si, respectively (see second column of Table I). From our results we conclude that this systematic underestimation of semicore binding energies is partly caused by employing LDA results, in particular, for constructing the first factor G^{LDA} of the self-energy operator. Since the QP amplitudes and energies as obtained from GWA may differ from the original LDA results, this single-iteration scheme for Σ^0 is not self-consistent. For delocalized valence and conduction states, however, this approximation appears well justified. Their QP shifts are relatively modest and the first iteration for $\Sigma(E)$ turns out to be already in very good agreement with the final self-consistent operator.[3] QP shifts of localized semicore states, on the contrary, turn out to be considerably larger than those of delocalized states. This is due to the fact that the coupling of individual states of a semicore shell by plasmons, which is the basic correlation effect, is much stronger than the plasmon-induced coupling of a particular valence or conduction state to all other valence or conduction states. It cannot be expected, therefore, that a non-self-consistent $\Sigma^0(E)$ can be used with good accuracy for the calculation of semicore states. Instead, the resulting QP energies must be used to self-consistently evaluate the Green's function when constructing the self-energy operator. We label the respective Green's function by G^{QP}. For the second factor of Σ, i.e., for the screened Coulomb interaction W, we restrict ourselves throughout this paper to employing the random-phase approximation (RPA) expression W^{LDA} based on LDA results without taking the modified Green's function G^{QP} into account in the evaluation of the dielectric matrix.

Investigations of the screening properties in Si by Tenelsen and Bechstedt[24] indicate that this is in very good agreement with a self-consistently calculated W including vertex corrections. Furthermore, we assume throughout this paper that the wave functions $|n\rangle$ are given by the LDA wave functions. We characterize this type of self-consistent approach by $\Sigma = iG^{\text{QP}}W^{\text{LDA}}$. The QP binding energies resulting from this approximation are compiled in the third column of Table I. Updating of the QP spectra in the construction of the self-energy operator results in an increase of all calculated binding energies being largest for the most localized Si $2p$ and smallest for the least localized Cd $4d$ state. The resulting binding energies are, however, still about 1, 1.5, and 2 eV smaller than the experimental values for Cd, Ge, and Si, respectively.

For the first three approaches discussed so far (LDA, GWA using G^{LDA}, GWA using G^{QP}), the deviations from experiment and the energy *corrections* from one approach to the next are smallest for the Cd $4d$ and largest for the Si $2p$ state, respectively. This behavior is closely related to the increasing localization and binding energy of these states.

Finally, we investigate the influence of the energetic structure of the Green's function on the self-energy. The Green's functions employed so far were formed by simple poles related to effectively independent particles. Their spectral function consists of sharp, normalized single-particle peaks. For an interacting electronic system, however, this simple pole structure is no longer valid. The QP poles become renormalized and additional satellite features arise at energies below and above the QP energy of each particular state.[2,9,25,26] This modification of the Green's function affects the self-energy operator and the QP energies for semicore states, in particular. We investigate this influence by the following procedure. First we calculate the complete energy dependence of $\Sigma_n(E)=\langle n|\Sigma(E)|n\rangle$ for all states n by employing the conventional single-pole Green's function G^{QP}. From this self-energy, we calculate the spectral function and construct a new Green's function G^{QPS} explicitly including the renormalized QP poles and the satellites. For each state n, it is given by[27]

$$G_n^{\text{QPS}}(E)\equiv\langle n|G^{\text{QPS}}(E)|n\rangle=\frac{1}{E-E_n^{\text{QP}}-\langle n|\Sigma(E)|n\rangle}. \quad (2)$$
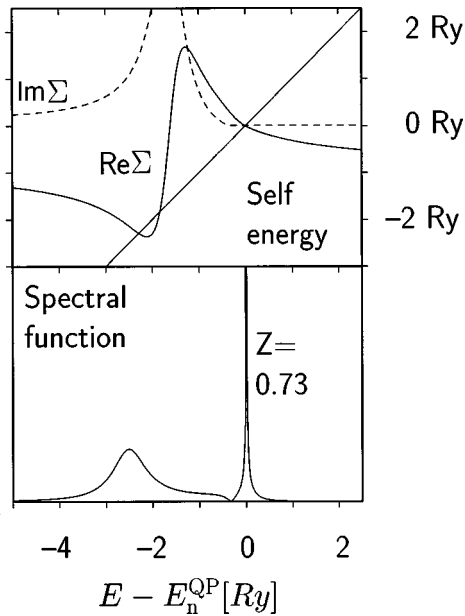
FIG. 1. Self-energy and spectral function of the Ge $3d$ state along the real-energy axis, as resulting from the model (3).

Employing the new Green's function G^{QPS}, we once again calculate the self-energy operator and evaluate the resulting self-energy for the QP semicore states. For the iteration we need the energy dependence of $\Sigma(E)$ for all states n. This might, in principle, be obtained by evaluating $\Sigma(E)$ for all energies along the real energy axis. Such a procedure is, however, very demanding due to the multiple-pole structure of Σ along the real axis. Therefore, we employ instead a model of the self-energy of a given state n as suggested by Rojas et al.:[25]

$$\langle n|\Sigma(E)|n\rangle = a_n + \sum_{j=1}^{p} \frac{b_n^j}{E - E_n^j}. \qquad (3)$$

Here we take only two poles, i.e., $p=2$, into account. For the determination of the respective $2p+1$ parameters, the self-energy of state n must be calculated explicitly for $2p+1$ energies E. We choose these in the complex energy plane starting from the real QP energy E_n^{QP} and increasing the imaginary part of $E = E_n^{QP} + li\Delta E$, $l = 0,1,\dots,2p$, in $2p$ steps with $\Delta E = 0.8$ Ry.

As a typical example, we show in Fig. 1 the resulting self-energy of the Ge $3d$ state for energies along the real axis. Near the QP energy, $\Sigma(E)$ is characterized by a decreasing real part. This results in a renormalization of the QP peak in the spectral function by the renormalization factor $Z_n = 1/[1 - \partial\langle n|\Sigma(E)|n\rangle/\partial E]$. The imaginary part of the self-energy is almost zero in this region leading to a very small broadening of the QP peak. At energies far below the

QP energy, Σ shows a pole and an additional satellite structure is found in the spectral function of the state, which is induced by plasmons that are mainly responsible for the correlation among the electrons, as briefly mentioned above. Within the simple model (3), satellites in the spectrum of the Ge $3d$ state are only present below but not above the respective QP energy.[28]

To simplify the following GW calculations, we map the Green's function $G_n^{QPS}(E)$ of each state n onto an analytical pole form with one QP pole and a small number of satellites,

$$G_n^{QPS}(E) = Z_n^{QP} \frac{1}{E - E_n^{QP}} + \sum_i Z_n^{sat,i} \frac{1}{E - E_n^{sat,i}}, \qquad (4)$$

where $Z_n^{sat,i}$ and $E_n^{sat,i}$ may be complex. For most of the states n, consideration of one satellite pole in Eq. (4) turns out to be sufficient. Due to particle conservation, the complete weight, i.e., the sum of all renormalization factors Z_n in Eq. (4), adds up to one. The most important effect of the new Green's function G_n^{QPS} is that some weight is shifted from the QP pole to the satellites which occur at lower energies in the case of semicore states. With this new Green's function we calculate a new Σ. The rearrangement of spectral weight in G_n^{QPS} leads to a reduction of the correlation part of Σ by about 20%. Since the correlation energy of a semicore state is positive, its QP band-structure energy is thus lowered, i.e., its binding energy increases. In our calculations we observe a respective increase in the binding energies by 0.9 eV for the Cd $4d$, 1.8 eV for the Ge $3d$, and 2.5 eV for the Si $2p$ state. The QP binding energies resulting with G_n^{QPS} are in very good agreement with experiment (see Table I). The remaining deviations are of the order of 1% in all three cases. This suggests that the quantitative accuracy of GWA calculations for semicore states can strongly be improved by updating the QP spectrum and by including satellites in the Green's function. Our approach, certainly, is far from being a fully self-consistent evaluation of the self-energy; but it constitutes an important and well-defined first step towards a better treatment of semicore states.[31]

In this paper we have presented investigations of QP semicore binding energies using different GW self-energy operators of increasing complexity with an increasing degree of self-consistency. For localized semicore states it has turned out that the QP energies need to be included in the construction of Σ thus requiring a self-consistent scheme. Furthermore, the energy dependence of $\Sigma_n(E)$ of each state leads to a renormalization of the QP weight and to the occurrence of additional satellite structures in the spectral function. We have found that these important structural features of the Green's function can be taken into account by a fairly simple model yielding a significant increase of the quasiparticle binding energies of semicore states leading to gratifying agreement with experimental data.

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[27] At the QP energy, the self-energy has been scaled to zero for convenience: $\langle n|\Sigma(E_n^{\mathrm{QP}})|n\rangle = 0$.

[28] Within GWA the largest contribution to the correlation energy results from coupling between electrons and plasmons, in particular, when a plasmon-pole model is employed. Therefore, the electronic spectrum of each state consists of a sharp QP peak and plasmon-induced satellites. When particle-hole excitation processes are included in the self-energy operator, the shape of the QP peak changes to an asymmetric form as was discussed by Nozières and De Dominicis (Ref. 29) and by Almbladh and Hedin (Ref. 30). These features and their influence on the self-energy are neglected in our approach.

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[31] Including renormalization and satellites in the self-consistent Green's function also influences the energies of valence and conduction bands, leading to increased gap energies (Refs. 11 and 12). In our present QP calculations employing G^{QPS} we obtain gap energies of 3.21 eV for CdS, 0.93 eV for Ge, and 1.49 eV for Si, respectively. In this context, Ummels *et al.* (Ref. 12) have also investigated the effect of vertex corrections on the valence and conduction band structure beyond the GWA. It turns out that these vertex corrections and the self-consistency effects cancel each other to a large extent. Taking both corrections into account, the authors eventually find gap energies very close to those resulting from the standard, non-self-consistent GW approach (Ref. 12). In the case of localized semicore states, on the other hand, we have arrived at systematically improved QP binding energies by only including self-consistency effects. This could indicate that vertex corrections are less important for localized semicore states.