$3d$ semicore-states in ZnSe, GaAs and Ge

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We present the self-energy corrections for the semicore states in ZnSe, GaAs and Ge within the GW approximation. Good agreement with experiment is found. To study the error trend in the local density eigenvalues which increases from ZnSe to Ge, we have also performed Slater transition state calculations. This increasing error can be understood in terms of the change of the occupation numbers of the orbitals and the Coulomb energies. We derived a simple formula to describe this increasing error.

I. INTRODUCTION

It is well-known that the eigenvalues in the local density approximation (LDA)[1] for localized states are often in large error compared to the experimental values. The LDA eigenvalues are usually too high. For example, in ZnSe, the position of the Zn $3d$ states is about 2.5 eV too high, in GaAs the position of the Ga $3d$ is 4 eV too high, and in Ge the error is even larger. The trend that the more localized states have larger error is clearly exhibited here.

One purpose of this paper is to perform self-energy calculations for the semicore states in ZnSe, GaAs, and Ge within the GW approximation[2,3]. While it has been found that the GW approximation (GWA) gives accurate results for delocalized states as well as very localized core states[4,5], it is not a priori clear that it can describe localized semicore states which, unlike deep core states, can contribute significantly to the polarization. In a model GW calculation for ZnO it was found that the position of the $3d$ band relative to the the valence-band edge was lowered from the LDA result -5.4 eV to -6.4 eV compared with the experimental results -8.6 and -7.5 eV,[6] i.e., a substantial fraction of the LDA error remained. Conventional full GW calculations based on plane waves have not been performed due to the large number of plane waves required to represent localized states. However, the recently developed GW method to deal with localized states[7] has enabled us to perform the present calculations. It is found that the GWA gives a good description of the semicore states.

A second purpose of the present paper is to find a simple physical explanation and formula for the increasing error observed in the series ZnSe, GaAs, and Ge and to compare this with the errors in a free atom. Although the width of the d-band is very small in these systems (e.g. 0.5 eV in ZnSe and even smaller in GaAs and Ge), the error in the eigenvalues is nevertheless much smaller than for the corresponding atom. For instance, the $3d$ eigenvalue is about 6.5 eV too high in a free Zn atom. It is then interesting to ask why the atomic limit has not been reached for such a small band width.

A major part of the error in the LDA eigenvalues is attributed to the self-interaction. This error accounts for the a large part of error when the LDA is applied to atoms.[8] The self-energy error in the LDA total energy is rather small due to the fact that the sum rule for the exchange-correlation hole is satisfied by the LDA. On the other hand, the self-energy error in the LDA eigenvalues can be large since the sum rule arguments do not necessarily imply a good exchange-correlation potential. It is therefore interesting to apply the Slater transition state method[9] which is a simplification of the so called ΔSCF method.[5] This method focuses on the eigenvalues, but since it is derived from total energy calculations, it avoids to a great extent the problems with self-interaction, exchange-correlation potential as well as the neglect of relaxation contained in the normal LDA calculations. For the solid, the transition state calculation is accompanied by a substantial transfer of screening charge to the atom with a core hole, which is essential for the results.[10,11] Zhang *et al* have recently performed transition state calculations for various Zn compounds.[12] Here we in particular focus on the changes as the $3d$ state becomes increasingly localized in the series Zn, Ga and Ge.

The paper is organized as follows: in section II we describe the theory and method of calculations, in section III we present and discuss our results and in section IV we draw our conclusions.

II. THEORY AND METHODS OF CALCULATIONS

A. Slater transition state method

The Slater transition state method is an approximate way of performing a self-consistent field (SCF) calculation[5]. The measured quasiparticle energy in photoemission experiments is given by $\epsilon = E_0(N) - E(N-1, i)$ where $E_0(N)$ is the groundstate of N-particle system and $E(N-1, i)$ is in general some excited state of the $N-1$ particle system which corresponds to the presence of a hole left behind. The quasiparticle energy of a d-hole, ϵ_d, may then be obtained as follows:

$$
\begin{aligned}
\epsilon_d &= \int_0^1 dn_d \frac{dE}{dn_d} \\
&\approx \left.\frac{dE}{dn_d}\right|_{n_d=1/2} \\
&= \epsilon_d(n_d)|_{n_d=1/2}
\end{aligned} \tag{1}
$$

which is the Slater transition state rule. The last expression is given by the eigenvalue of the particular state we are interested in with the presence of half a hole in the corresponding orbital. In the case of a solid, this half a hole has to be compensated to maintain charge neutrality by allowing the other electrons to screen it. In practice, we perform a supercell calculation and create half a hole in the appropriate orbital in one of the atoms. In our case, it is the $3d$ orbital in Zn, Ga or Ge. The calculation is performed self-consistently in order to allow for the screening by the surrounding electrons and for the orbital to then relax but maintaining the presence of half a hole in the orbital. A "bound state" is formed which is derived from the $3d$ orbital and the energy of this bound state is identified as the quasiparticle energy of the $3d$ state measured in a photoemission experiment.

In practice, the computational steps are as follows: We first perform a normal supercell calculation with a cube as a unit cell (four times the primitive unit cell). We create half a hole in the $3d$ orbital in one of the Zn (Ga, Ge) atoms by reducing the $3d$ charge by one half. This extra positive charge pulls down the $3d$ states of the atom where the hole is located creating a very localized "bound state" with almost no dispersion. In the subsequent iterations, the presence of half a hole is maintained by reducing the weight of the bound state by one half in the Brillouin zone integration for the charge density. This extra charge must be compensated to maintain charge neutrality in the system. This is done by letting the Fermi level adjust itself to give the correct number of electrons, i.e. the lowest conduction states which were previously empty are now partly occupied. This procedure is repeated in each iteration until self-consistency is achieved.

B. GW approximation

In the GW approximation (GWA) the self-energy is given by

$$
\Sigma(\mathbf{r},\mathbf{r}';\omega) = \frac{i}{2\pi}\int d\omega G(\mathbf{r},\mathbf{r}';\omega+\omega')W(\mathbf{r},\mathbf{r}';\omega') \tag{2}
$$

The screened potential W is given by

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

where ϵ^{-1} is an inverse dielectric matrix and v is a bare Coulomb potential.

The calculation of ϵ^{-1} within the random phase approximation (RPA)[13] is described in detail in a previous publication[7]. This is done without making the plasmon-pole or other similar approximations. The bandstructure is calculated using the linear muffin-tin orbital (LMTO)[14] method which can be applied to systems with d and f electrons. The LMTO basis within the atomic sphere approximation[14] has the following form:

$$
\chi_{\mathbf{R}L} = \phi_{\mathbf{R}L} + \sum_{\mathbf{R}'L'} \dot{\phi}_{\mathbf{R}'L'} h_{\mathbf{R}'L',\mathbf{R}L} \tag{4}
$$

where $\mathbf{R}L$ denote the site and angular momentum (l, m) respectively, ϕ is the solution to the Schrödinger equation inside the muffin-tin sphere and $\dot{\phi}$ is its energy derivative taken at some fixed energy ϵ_ν. The response function within the RPA consists of products of Bloch states so that the Hilbert space spanned by the response function is composed of products of the type $\phi\phi$, $\phi\dot{\phi}$, and $\dot{\phi}\dot{\phi}$. 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 50-100.[7]

We have performed self-energy calculations for ZnSe, GaAs and Ge within the GWA. The zeroth order Green function is constructed from the LDA wavefunctions and eigenvalues which are calculated by using the LMTO method.

III. RESULTS AND DISCUSSIONS

The results for the $3d$ binding energies are shown in Table 1. The GWA reproduces the experimental results quite well. This shows that the GWA is also able to describe rather localized states.

The LDA eigenvalues are compared with experiment in Table 1. As expected, the eigenvalues are much too high, and the errors increase along the series Zn, Ga and Ge. A large part of these errors are corrected in the transition state calculations, which, however, give results somewhat below the experimental energies. This is probably due to the fact that the LDA overestimates the exchange-correlation energy between a 3d electron and the 3s-3p core.[15] This overestimate is about 1 eV in the series K-Cu.[16] For ZnSe similar results were obtained by Zhang *et al.*.[12] We note the slight difference in our results and their results which we believe is due to the different exchange-correlation potentials and the different methods as also discussed in Ref. 27 of Zhang *et al.*.[12].

Let us analyze these results. The LDA Hamiltonian is given by

$$
H = H_0 + \int d^3r' v(\mathbf{r}-\mathbf{r}')\rho(\mathbf{r}') + v_{xc}(\rho\mathbf{r}) \tag{5}
$$

where H_0 describes the kinetic energy and the nuclear potential and v is the Coulomb potential. The change in the Hamiltonian in the presence of half a hole is given by

$$\delta H = \int d^3r' v(\mathbf{r}-\mathbf{r}')[\rho'(\mathbf{r}') - \rho(\mathbf{r}')] + v_{xc}[\rho'(\mathbf{r})] - v_{xc}[\rho(\mathbf{r})] \quad (6)$$

where ρ' is the new density with half a hole. ¿From first order perturbation theory, the change in the $3d$ eigenvalue is then

$$\begin{aligned}\Delta\epsilon_d &= \langle\psi_d|\delta H|\psi_d\rangle \\ &= \int d^3r d^3r' \rho_d(\mathbf{r}) v(\mathbf{r}-\mathbf{r}')[\rho'(\mathbf{r}') - \rho(\mathbf{r}')] \\ &+ \int d^3r \rho_d(\mathbf{r}) \delta v_{xc}(\mathbf{r}) \end{aligned} \quad (7)$$

where $\delta v_{xc} = v_{xc}(\rho') - v_{xc}(\rho)$. Writing

$$\rho = \sum_i n_i \rho_i, \quad \rho_i = |\psi_i|^2$$

where n_i is the occupation number of orbital ψ_i. We get

$$\begin{aligned}\Delta\epsilon_d &= \sum_i n_i \int d^3r d^3r' \rho_d(\mathbf{r}) v(\mathbf{r}-\mathbf{r}')[\rho_i'(\mathbf{r}') - \rho_i(\mathbf{r}')] \\ &+ \sum_i \delta n_i \int d^3r d^3r' \rho_d(\mathbf{r}) v(\mathbf{r}-\mathbf{r}') \rho_i'(\mathbf{r}') \\ &+ \int d^3r \rho_d(\mathbf{r}) \delta v_{xc}(\mathbf{r}) \\ &= \sum_i (\delta n_i U_{id}' + n_i \delta U_{id}) + \sum_i \delta n_i / R_i \\ &+ \int d^3r \rho_d(\mathbf{r}) \delta v_{xc}(\mathbf{r}) \end{aligned} \quad (8)$$

where $U_{id} = \langle\rho_i|v|\rho_d\rangle$, $U_{id}' = \langle\rho_i'|v|\rho_d\rangle$ and $\sum_i \delta n_i / R_i$ describes the interaction with other cells than the one where the hole is located.

In Table 2 we present the occupation numbers and the onsite Coulomb integrals with and without the half hole and in Table 3 we use these values to make estimates for the change in the binding energy of the $3d$ states using the above formula. The last term in Eq. (8) is found to be negligible for our purpose. As can be seen, the agreement between the estimation (8) the full calculation is quite good.

¿From Table 2 we can see that the screening charge mainly resides in the s and p orbitals. This is in agreement with what has been found earlier for adsorbates[10] and $3d$ states.[11] The onsite screening is not complete, an extra charge of about 0.1 still remains in the central atom where the half hole is created. The screening becomes more complete as we go from ZnSe to Ge. The first term in Eq. (8) (first line in Table 2) shows a strong variation along the series Zn, Ga and Ge, whereas the second term (second line in Table 2) is almost constant. This constant behaviour results from two opposing effects. The change in the $3d$ orbital due to relaxation gets smaller as we go from ZnSe to Ge since the orbital becomes more localized (inert). The change in the $d-d$ Coulomb integral therefore gets smaller when we go from ZnSe to Ge, as can be seen in Table 2. The number of s and p electrons, however, increases. These two effects compensate one another to produce a constant value. For the purpose of analyzing our results, we can assume this term to be almost constant. This term describes the relaxation of the electrons on the atom where the semicore hole is created. The term that contains physically relevant effects for the trend in the shift of the $3d$ eigenvalue is then the first term $\sum_i \delta n_i \; U_{id}'$, which describes the effects of the redistribution of charge between the atoms.

¿From Table 3 we can see that $U_{sd}' \approx U_{pd}'$. Treating the second term in Eq. (8) as a constant term and neglecting the last termi, which contains the exchange-correlation contribution, we get the $3d$ shift

$$\begin{aligned}\Delta\epsilon_d &= \sum_i \delta n_i \; U_{id}' + \sum_i \delta n_i / R_i + \;\; constant \\ &= \delta n_d U_{dd}' + \delta n_{sp} U_{sp,d}' + (\delta n_d - \delta n_{sp})/R \\ &+ \; constant \end{aligned} \quad (9)$$

where $U_{sp,d}'$ is the average of U_{sd}' and U_{pd}', $\delta n_{sp} = \delta n_s + \delta n_p$, and R is an average distance between the central Zn atom, where the half hole is located, and the surrounding atoms. The third term is the potential at the central Zn atom coming from the excess charge in the surrounding atoms. Since $\delta n_{sp} \approx \delta n_d$ and $U_{sp,d}$ is not very different from $1/R$, we make a further approximation

$$\Delta\bar{\epsilon}_d \approx \delta n_d (U_{dd}' - U_{sp,d}') + \;\; constant \quad (10)$$

In Table 2 we list the results obtained using this simple formula with $\delta n_d = 0.5$. If we put the constant equal to 4.5 eV, we find that we get reasonable agreement with the correct result.

The physical interpretation of the above formula is that the following. When we perform the transition state calculation, the eigenvalue is shifted due to the removal of half a $3d$ electron and the creation of a screening charge. The parts of this shift which change with the $3d$ hole localization are due to the $3d$ hole itself (U_{dd}' in Eq. (10)) and to the charge transfer into the sp-like levels ($U_{sp,d}'$ in Eq. (10)). These two terms partly cancel each other, but the cancellation becomes less complete as the $3d$ hole gets more localized. This explains the increasing error in the LDA eigenvalue. In the atom the term $U_{sp,d}'$ is missing, since there is no charge transfer from the surrounding when a hole is made. Since this term is not small, the atomic limit is not reached even if the $3d$ band width becomes very small.

Finally, we observe that this approach requires that the semicore state is sufficiently localized to form a localized state in the transition state calculation. In this case the calculation gives a single number for the $3d$ band position instead of the full $3d$ band structure as in the GW calculation. If a localized state would not form, the transition state calculation would be identical to the LDA band structure calculation. In contrast to the GW approach, the continous change from a broad $3d$ band to a semicore state is therefore not entirely satisfactorily described in the transition state calculation. The problem is illustrated for Cu metal, where the $3d$ band is about $0.5\ eV$ too high.[21] In this case it would not be meaningful to correct this error in a transition state calculation, even if a bound state would form, since the $3d$ band would then be described by just a single binding energy. On the other hand, a GW calculation lowers the position of the $3d$ band by $0.2-0.3\ eV$.[22]

IV. SUMMARY AND CONCLUSIONS

We have calculated the self-energy corrections for the semicore states in ZnSe, GaAs and Ge within the GW approximation and obtained good agreement with experiment. This demonstrates that the GWA is not only capable of giving a good description for extended states but also for the rather localized semicore states. We have also performed Slater transition state calculations in order to study the increasing error from ZnSe to Ge in the LDA eigenvalues. We derived a simple formula to describe this increasing error. In the free atom the transition state calculation gives a large correction to the LDA eigenvalue due to the attractive potential from the created half a $3d$ hole. In the solid the correction is much smaller, since the $3d$ hole is screened by the transfer of charge to the sp levels in the atom with the hole. As the $3d$ level becomes more localized, this compensation becomes less complete, and the transition state correction to the LDA eigenvalue becomes larger.

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TABLE I. Removal energies (- eigenvalues) of the semicore d-electrons in eV.

	ZnSe	GaAs	Ge	Zn atom
LDA	6.6, 6.8[a]	15.4	24.4	10.9
Transition state	9.7, 10.0[a]	20.3	30.1	18.5
GW	8.7	18.5	28.5	
Exp	9.0[b],9.38[c]	19.3[b]	29.6[b]	17.3[d]

[a]Ref. 12
[b]Ref. 18
[c]Ref. 19
[d]Ref. 20

TABLE II. s, p and d occupation numbers and their changes in the presence of the d-hole and the Coulomb integrals as explained in Eq. (8). All energies are in eV.

	ZnSe			GaAs			Ge		
	n'	n	δn	n'	n	δn	n'	n	δn
s	0.92	0.74	0.18	1.23	1.08	0.15	1.47	1.36	0.11
p	0.86	0.74	0.12	1.43	1.20	0.23	2.16	1.85	0.31
d	9.54	9.98	-0.44	9.54	10.03	-0.49	9.53	10.03	-0.50
	U'	U	δU	U'	U	δU	U'	U	δU
sd	15.24	14.93	0.31	16.09	15.78	0.31	16.97	16.64	0.33
pd	14.00	13.86	0.14	14.60	14.39	0.21	15.24	14.99	0.25
dd	29.27	28.84	0.43	32.26	31.87	0.39	34.84	34.48	0.36

TABLE III. The contributions from the different terms in Eq. (8) in eV. Here $\Delta\epsilon_d$ (Slater) is the result of the full transition state calcualtion and the results of the approximate formulas Eq. (8) and Eq. (10) are given by $\Delta\epsilon_d$ and $\Delta\bar{\epsilon}_d$ respectively.

	ZnSe	GaAs	Ge
$\sum_i \delta n_i\, U'_{id}$	-8.5	-10.0	-10.8
$\sum_i n_i\, \delta U_{id}$	4.6	4.5	4.5
$\sum_i \delta n_i / R_i$	0.6	0.6	0.6
$\Delta\epsilon_d$	-3.3	-4.9	-5.7
$\Delta\epsilon_d\ (Slater)$	-3.1	-4.4	-4.9
$\Delta\bar{\epsilon}_d$	-2.8	-4.0	-4.9

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