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Self-consistent-field–complete-neglect-of-differential-overlap cluster calculations of deep impurities in semiconductors

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A self-consistent-field method to calculate energy levels of deep transition-metal centers in semiconductors based on the complete-neglect-of-differential-overlap (CNDO) approximation is presented. The method can be used for a quantitative interpretation of optical transitions between strongly localized states at the impurity center, which are usually interpreted by crystal-field theory in terms of unknown parameters like the crystal-field splitting parameter $\Delta = 10Dq$. Special emphasis is laid on the formulation of correct boundary conditions for the cluster of 17 atoms in II-VI compounds. In case of Cu centers in cubic ZnS Δ is calculated to be 0.84 eV compared with the experimental value of 0.77 eV. The method does not use any parameter which is adjusted to properties of the center or the crystal, as has to be done using the extended Hückel approximation.

I. INTRODUCTION

The properties of deep energy level impurities in semiconductors have become a point of special interest in the last few years. This is due to the fact that these centers control the efficiency of optoelectronic devices such as solar cells as well as other semiconducting circuits (e.g., the carrier lifetimes). On the other hand, the optical and EPR properties of deep centers have been the subject of many investigations for a long time. For a great number of impurity centers, some properties as well as the observed spectra are at least qualitatively understood. Because of the great variety of such deep impurity centers the situation is much more complex than with the so-called shallow impurities which can be described with successive approximations in the framework of effective mass theory. Deep centers cannot be understood as starting from crystal properties but only from the local properties of the atoms surrounding the impurities.

Although the methods described here may be applied to many different deep impurity centers, we want to restrict ourselves to transition-metal impurity centers in II–VI and similar compounds. For many purposes, transitions from strongly localized electronic states into band states are of special interest. As far as the optical and EPR spectra of transition-metal impurities are concerned, however, transitions between strongly localized states are experimentally and theoretically intensively studied. Very detailed spectra can be observed and are interpreted in terms of group-theoretical methods in a qualitative way by crystal field theory.[1-9]

This method starts in the zeroth approximation with the free impurity ion. As a first step the interaction with the surrounding crystal is described by a crystal-field potential, thus neglecting overlap between impurity electrons and the electrons of the rest of the crystal. In a second step the effects of electron overlap are partly taken into account. It is a special feature of crystal-field theory that except for these assumptions, no other approximations are necessary. Crystal-field theory is mainly a group-theoretical method answering the question, what is the most general energy level scheme of a special center which is consistent with the symmetry of the surrounding crystal? The energy level scheme is then calculated in terms of certain unknown crystal-field parameters whose number is determined by symmetry arguments and whose values are found by fitting to the experimentally observed spectra.

For many centers such as transition-metal impurities in II–VI compounds the assumption of a crystal-field potential can in no way be used for a quantitative estimation of the observed spectra, which indicates that covalent bonding plays a dominant role. Nevertheless, all these spectra can be interpreted completely in terms of crystal-field parameters. Crystal-field theory is therefore a more general method than expected from the assumptions involved. It can be used for strongly localized states whose transitions are not dominated by lattice relaxation effects. Phonon coupling can also be included and a great number of centers have to be interpreted in terms of a Jahn-Teller effect. This effect mostly influences the fine structure and Zeeman effect of the spectra as well as the phonon satellites.

In spite of the fact that crystal-field theory is a well-established method, little has been done for a quantitative estimation of the crystal field parameters. We here present a calculation based on a linear-combination-of-atomic-orbitals–complete-neglect-of-differential-overlap–self-consistent-field (LCAO-CNDO-SCF) method. This method gives not only the crystal-field splitting, but also the wave functions from which all the fine-structure properties may be found by simple perturbation theory. We restrict ourselves to the calculation of the crystal-field splitting parameter $\Delta = 10Dq$.

II. CLUSTER MODEL FOR DEEP IMPURITIES

To calculate strongly localized states of isolated impurities, a cluster of atoms has to be used which contains the impurity at the center and which has the correct point symmetry of the crystal (cf. Messmer and Watkins,[10] Hemstreet,[11] and others). With one atom of the first, second, . . . neighbors, all others have to be included so that they can be transformed by the symmetry transformations. This has to be done to enable a comparison with crystal-field theory. The suggestion of a very large cluster containing the impurity but having the symmetry of the unit cell with periodic boundary conditions is not feasible with an SCF-CNDO method, but may be used to determine energy differences between strongly localized states and band edges.

In calculating the energy levels of a cluster of atoms, serious problems involving the boundary conditions arise. In II–VI compounds, covalent bonding and long-range ionic bonding are both important. Picking the cluster of atoms out of the crystal, one must be concerned with a number of dangling bonds at the surface. These dangling bonds imply a certain amount of electron charge which would move inside the cluster unless fixed there by additional states. The method adopted here involves an additional potential at the outermost atoms which is described in Sec. V. Figure 1 by M. Städele shows the number of dangling bonds at the surface of a cluster divided by the number of atoms in the cluster for various cluster sizes with tetrahedral symmetry. One can clearly see that the error from improper treatment of the dangling bonds will not become small by simply increasing the size of the cluster. For the description of transitions between strongly localized states only, the correct formulation of the boundary conditions is more important than increasing the size of the cluster. We therefore restrict ourselves to tetrahedral clusters consisting of only 17 atoms.

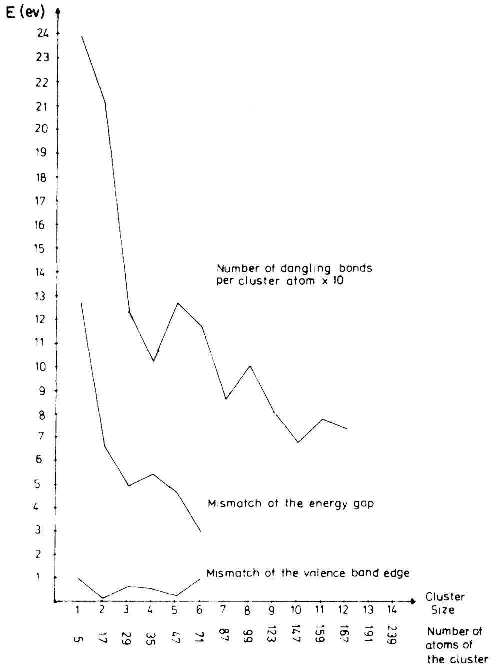

FIG. 1. Number of dangling bonds per cluster atom for various sizes of tetrahedral clusters.

The long-range ionic bonding forces are taken into account by calculating the electrostatic potential of all the effective point charges outside the cluster. The spherically symmetric part, which is constant inside the cluster, is described using Madelung's constant. The other terms of the potential with tetrahedral symmetry have a more rapid convergence. This Madelung potential can then be added to the Hamiltonian of the valence electrons of the cluster.

The Madelung potential is proportional to the effective charge of the ions which can be determined by the condition of self-consistency in connection with the condition of periodicity of the crystal. This is described in Sec. IV. The effective charge is not estimated here by a CNDO calculation of a unit cell with periodic boundary conditions because of the poor results of this method for energy-band calculations of II–VI compounds. The long-range ionic bonding also produces an effect which will not become small by increasing the size of the cluster.

As pointed out already by Kunz and Klein[13] such a potential causes only a small shift of energy level differences, though it produces a considerable shift of the energy level scheme as a whole. We therefore restrict ourselves to a rough approximation of the Madelung potential.

Proper treatment of both aspects of the boundary condition should result in a net charge of the cluster, which is not an integer multiplied by the electron charge. This may be demonstrated by a simple example: a copper center in ZnS. If the cluster contains five atoms, the number of valence electrons is 35, since Cu and S have electron configurations $(3d)^9\,(4s)^2$ and $(3s)^2\,(3p)^4$, respectively, and we have four sulfur atoms in the cluster. In the case of a completely ionic picture of the crystal we would have to take the divalent ions instead, in which case the cluster contains 41 electrons. The charge of the cluster is then zero or minus six. Since the LCAO formalism can be applied to an integer number of electrons only, the boundary condition must ensure that the charge of the cluster is any number between zero and minus six. In heteropolar crystals like II–VI compounds the situation is more complicated than in homopolar crystals like diamonds, in which case Messmer and Watkins[10] saturated the dangling bonds by simply adding extra electrons.

III. DETAILS OF THE CALCULATION

To calculate the energy levels of a cluster of atoms, various approximations of the LCAO formalism are possible. The extended Hückel theory contains as an unknown parameter, the Wolfsberg-Helmholtz constant. If this method is not used in a self-consistent way, two other parameters, the effective charge of the host ions and of the impurity ion, have to be introduced. Birman and Walter,[14] Biernacki,[15,16] and others fitted these parameters to crystal properties such as energy band gap and others. Introducing boundary conditions makes it possible for us to calculate a small cluster adopting a SCF–CNDO approximation.[17-19]

For our ground-state function we took a single Slater determinant with different orbitals for different spins. Since deep levels caused by transition elements have unfilled d shells, an open-shell procedure similar to Roothan's procedure[20] should be performed. For the t_2^5 configuration the ground-state function is then

$$\phi=[(N+N'+g)!]^{-1/2} \times \det\{\psi_1^c\cdots\psi_N^c\psi_1^c\cdots\psi_{N'}^c\psi_1^o\cdots\psi_g^o\}\,. \tag{1}$$

The superscripts c and o denote the closed and open shells, respectively. There are N closed orbitals with α spin and N' closed orbitals with β spin, while ψ^o is the g-fold degenerate orbital with a missing β electron. This method presents a combination of the procedure of different orbitals for different spins[21] by Pople and Nesbet and Roothan's procedure for open shells.[20] By analogy with Roothan's procedure the variation is carried out yielding three eigenvalue equations:

$$(h+J^{c\alpha}+\mathfrak{J}^{c\beta}+J^{\sigma\beta}-K^{c\alpha})\,|\psi_l^{c\alpha}\rangle=\sum_j\theta_{lj}\,|\psi_j^{\alpha}\rangle\,, \tag{2a}$$

$$(h+J^{c\alpha}+\mathfrak{J}^{c\beta}+\mathfrak{J}^{\sigma\beta}-K^{c\beta}-K^{\sigma\beta})\,|\psi_l^{c\beta}\rangle=\sum_j\theta_{lj}\,|\psi_j^{\beta}\rangle\,, \tag{2b}$$

$$(h+J^{c\alpha}+\mathfrak{J}^{c\beta}+a\mathfrak{J}^{\sigma\beta}-K^{c\beta}-bK^{\sigma\beta})\,|\psi_m^{\sigma\beta}\rangle=\sum_j\theta_{mj}\,|\psi_j^{\beta}\rangle\,. \tag{2c}$$

a, b, and f are Roothan's coefficients for the open-shell treatment. For a t_2^2 orbital $f=\frac{2}{3}$, $a=b=\frac{3}{4}$. The operators J^{α}, J^{β}, K^{α}, K^{β} for closed and open shells are defined as in Ref. 21. Neglecting the coupling between the open shell and the closed-shell core, Eqs. (2a)–(2c) can be diagonalized.

$$F^{c\alpha}\psi_k^{c\alpha}=\eta_k^{c\alpha}\psi_k^{c\alpha}\,, \tag{3a}$$

$$F^{c\beta}\psi_k^{c\beta}=\eta_k^{c\beta}\psi_k^{c\beta}\,, \tag{3b}$$

$$F^{o\beta}\psi_m^{\sigma\beta}=\eta_m^{\sigma\beta}\psi_m^{\sigma\beta}\,. \tag{3c}$$

It can be shown that for the case of a missing electron, the transition $E((e^{\beta})^1(t_2^{\beta})^3)-E((e^{\beta})^2(t_2^{\beta})^2)$ can be approximated by $\eta_{t_2}^{c\beta}-\eta_e^{c\beta}$ of (3b) using Koopmans theorem. The reason $E((e^{\beta})^1(t_2^{\beta})^3)-E((e^{\beta})^2(t_2^{\beta})^2)$ is not calculated directly is that the total energies have great values (about 5000 eV). Because of the several approximations made for the integrals, the difference of the two total energies has a great error. We also made calculations for a closed-shell model. In this case $N=N'$, $g=0$, and $f=0$ and Eqs. (2a)–(2c) become the single equation

$$(h+J^{c\alpha}+\mathfrak{J}^{c\beta}-K^{c\alpha}-K^{c\beta})\,|\psi_l^c\rangle=\sum_k\theta_{lk}\,|\psi_k^c\rangle\,, \tag{4a}$$

which can be diagonalized yielding

$$F\psi_k^c=\eta_k^c\psi_k^c\,. \tag{4b}$$

The occupied orbitals can be directly identified by $-\eta_k^c$. For our calculations of a 17 atom cluster we use 73 atomic orbitals: central copper, $3d, 4s, 4p$, 4 next-neighbor sulfur $3s$, $3p$, and 12 second-neighbor zinc $4s, 4p$. We report here on calculations of one-electron energy level schemes which may be used to interpret the optical spectra of one electron transition-metal ions such as Sc^{2+}, Ti^{3+}, Cu^{2+}, Ni^{+}, and also Y^{2+}, Ag^{2+}, La^{2+}, and Au^{2+}.

IV. CNDO EQUATIONS

The CNDO approximation of the LCAO formalism was introduced by Pople *et al.*[17] and extended to include d orbitals by Santry and Segal[18] and Clack *et al.*[19] In the case of d orbitals the one-center repulsion integrals are greatly different from those of $4s$ or $4p$ orbitals. A different repulsion integral was also used between s and d electrons. For orbitals at the central transition-metal ion the following diagonal elements of the F^c matrix were used:

$$F^{c\alpha}_{4s\,4s} = -I_{4s} + [P_{TT}(s) - 1 - P^{c\alpha}_{4s\,4s}]\gamma^{TT}_{4s\,4s} + [P_{TT}(d) - Z_T + 2]\gamma^{TT}_{3d\,4s} + \sum_{B\neq T} [P_{BB}(s) - Z_B]\gamma^{TB}_{4s\,ms} \tag{5a}$$

$$F^{c\alpha}_{3d\,3d} = -I_{3d} + [P_{TT}(d) - Z_T + 3 - P^{c\alpha}_{3d\,3d}]\gamma^{TT}_{3d\,3d} + [P_{TT}(s) - 2]\gamma^{TT}_{3d\,4s} + \sum_{B\neq T} [P_{BB}(s) - Z_B]\gamma^{TB}_{3d\,ms}, \tag{5b}$$

where T denotes the transition-metal ion and B the surrounding neighbors, sulfur ($m = 3$) and zinc ($m = 4$). For the noncentral S ($m = 3$) and Zn ($m = 4$) ions the following diagonal matrix elements were used:

$$F^{c\alpha}_{ms\,ms} = -I_{ms} + [P_{LL}(s) - Z_L + 1 - P^{c\alpha}_{ms\,ms}]\gamma^{LL}_{ms\,ms} + \sum_{B\neq L} [P_{BB}(s) - Z_B]\gamma^{LB}_{ms\,ns} + [P_{TT}(d) - Z_T]\gamma^{LT}_{ms\,3d}. \tag{5c}$$

The off-diagonal matrix elements are

$$F^{c\alpha AA}_{\mu\nu} = -P^{c\alpha}_{\mu\nu}\gamma^{AA}_{\mu\nu}, \tag{5d}$$

$$F^{c\alpha AB}_{\mu\nu} = -\beta_{AB}S_{\mu\nu} - P^{c\alpha}_{\mu\nu}\gamma^{AB}_{\mu\nu}. \tag{5e}$$

The Fock matrix for β spin is found by replacing $P^{c\alpha}_{\mu\nu}$ by $P^{c\beta}_{\mu\nu} + P^{o\beta}_{\mu\nu}$ in Eqs. (5a)–(5e).

In contrast to the CNDO/II version, we only used the valence state ionization energies I for the calculation of $(\mu_A|(-\frac{1}{2}\Delta - Z_A/r_A)|\mu_A)$ with orbital μ_A at atom A. Data for the electron affinities are not very reliable for transition elements. The I_μ were calculated from Moore's table.[22]

An exact calculation of the overlap integrals is needed for the description of the covalency in crystal-field splitting. Therefore the overlap integrals were calculated using polyexponential Slater-type orbitals taken from the tables of Watson,[23] Clementi and McLean,[24] and Synek.[25] The core integrals $(\mu_B|V_A|\mu_B)$ were approximated by γ^{AB} because it could be shown that the penetration integral was small for the large interatomic distance (4.422 a.u. for ZnS). The two-center integrals γ^{AB} were calculated by single-exponential Slater-type orbitals with Burn's exponents.[26]

The β parameters for S were taken from Pople's paper.[18] For β_{3d}(Cu) we used the data of Clack.[19] For Zn no data for the β parameter was available. Since only the β_{4s}(Zn) parameter for Zn is needed, we set $\beta_{4s}(\text{Zn}) = \beta_{4s}(\text{Cu})$ because the 4s orbitals of Cu and Zn are supposed to be very similar in our cluster.

V. BOUNDARY CONDITIONS

The long-range electrostatic potential of all the ions outside the cluster may be approximated by a Madelung potential arising from effective point charges. This is a good approximation for all ions except those very close to the cluster. Owing to the fact that crystal-field theory plays a dominant role in the interpretation of the energy level scheme, this effective point charge model is adopted for all ions outside the cluster. The spherically symmetric part may be described by Madelung's constant. The convergence of the other infinite sums, however, increases with increasing angular momentum. The justification of the method and a detailed discussion of the calculation will be published elsewhere. The potential arising from the atoms outside the cluster was taken to be equal to the Madelung potential at the site of a cluster atom A minus the electrostatic terms already calculated by the MO procedure

$$V_M(|R_A|) = \alpha\frac{Q_{\text{Zn}}}{R_0} - \sum_{i\neq A} \pm\frac{Q_{\text{Zn}}}{R_i}, \tag{6}$$

where the sum is over R_i, inside of the cluster. Thus to $F^{AA}_{\mu\mu}$ the term $e(\mu|V_M(R_A)|\mu)$ and to $F^{AB}_{\mu\mu}$ the additional term $e\frac{1}{2}S_{\mu\nu}[V_M(R_A) + V_M(R_B)]$ was added. This averaging procedure is justified because the electrostatic potential inside the cluster is sufficiently flat.

The boundary condition for proper treatment of the dangling bonds at the surface is of special importance for the strongly localized states of the cluster. The boundary condition has to be formulated in such a way as to produce the correct charge and bond order which is actually present in the vicinity of the impurity. For heteropolar crystals the total charge of the cluster will then not be an integer and therefore a method has to be used where the total charge of the cluster may differ from an integer value. Since the LCAO method is formulated with an integer number of electrons, a possible method is the introduction of a special (not integer) surface charge at the cluster. We introduced such a surface charge by adding an extra potential energy to the diagonal elements of the Fock-matrix of the outermost atoms of the cluster. This potential energy was determined from the condition of periodicity of the ideal crystal during the iteration steps to achieve self-consistency and turned out to be of the order of 3 eV. It was determined by a separate calculation of a cluster having a regular Zn atom instead of an impurity atom in the center.

To demonstrate the proper effect of our boundary

TABLE I. Effective charges of zinc and sulfur Q_{Zn}, Q_S, and energy gap E_g for three different boundary conditions.

	Boundary condition number 1	Boundary condition number 2	Boundary condition number 3
Q_{Zn}	$0.7e_0$	$-0.76e_0$	$0.42e_0$
Q_S	$-1.4e_0$	$2.8e_0$	$-0.42e_0$
E_g	6.3 eV	2.4 eV	4.9 eV

condition, we performed calculations with three different boundary conditions and compared the effective charges Q_{Zn}, Q_S, and energy gap in Table I. In a first calculation the cluster from the ideal crystal was considered as a molecule in a Madelung potential originating from the effective charges of the rest of the crystal, boundary condition number 1. The neglect of the dangling bonds at the surface produces effective charges Q_{Zn} and Q_S which are far from having equal absolute values they should have as a consequence of the condition of translational symmetry of the ideal crystal.

To avoid this deficiency there are two possibilities: First, the electronic charge can be redistributed after each iteration step so as to fulfill the condition $Q_{Zn} = -Q_S$. Another possibility is to add an additional potential to the second-neighbor zinc shell and to fit this potential after each iteration step so that $Q_{Zn} = -Q_S$ holds.

In boundary condition number 2 a potential is added to the diagonal elements of the Fock matrix $F_{4s\,4s}$ belonging to the outermost Zn so that they are equal to the $F_{4s\,4s}$ belonging to the central Zn atom. However, this periodicity of the matrix elements $F_{4s\,4s}$ of the central Zn and the outermost Zn does not lead to a periodic charge distribution. The effect of the dangling bonds causes a displacement of excess electronic charge from the surface of the cluster to the Zn atom inside, resulting in wrong signs of the effective charges. Therefore in boundary condition number 3 an extra potential is added to the second-neighbor Zn atoms. It is changed until the surface charges are fixed in such a way that the condition of the periodicity of the charges $Q_{Zn} = -Q_s$ inside the cluster is fulfilled.

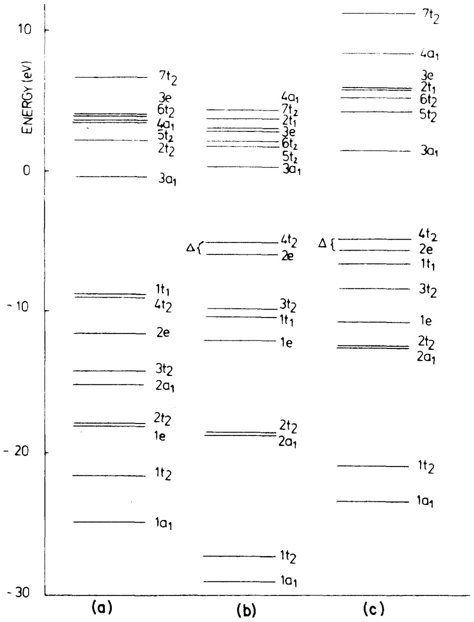

FIG. 2. Energy level schemes for different CNDO calculations: (a) ideal cluster calculation, (b) impurity cluster calculated by the open-shell formalism, (c) impurity cluster calculated by the closed-shell formalism.

VI. RESULTS

The calculation of the host cluster with boundary condition No. 3 is shown in Fig. 2(a). The second-neighbor $4p$ orbitals have been neglected, since calculations have shown that energy levels originating from these orbitals are very high in the conduction band. From Table I we see that due to the condition of periodic charges (boundary condition No. 3) the energy gap comes reasonably close to the experimental value of 3.9 eV. It has to be noted at this point that E_g is not equal to the difference $\eta(3a_1) - \eta(1t_2)$ [see Fig. 2(a)] but rather equal to

$$\eta(3a_1) - \eta(1t_2) - J_{1t_1\,3a_1} + K_{1t_1\,3a_1} \,. \tag{7}$$

This is due to the fact that for CNDO calculations the unoccupied levels cannot be identified by negative ionization energies. As pointed out by Ballhausen *et al.*[27] Coulomb and exchange terms

TABLE II. Crystal-field splitting $10Dq$ of impurity centers in II–VI compounds (eV).

	ZnS:Cu	ZnS:Ag	CdS:Cu	ZnO:Cu	ZnSe:Cu	ZnSe:Au
$10Dq$ theor.	0.84	0.60	0.81	0.95	1.05	2.6
$10Dq$ expt.	0.77 (Ref. 28)	0.88 (Ref. 14)	0.69 (Ref. 28)	0.70 (Ref. 30)		

TABLE III. Dependence of $\Delta = 10Dq$ on the β-value.

β_{3d} (eV)	-8	-20	-27.5	-30	-40	-50
$10Dq$ (eV)	0.25	0.59	0.77	0.84	1.09	1.32

have to be added. Formula (7) presents an average value between singlet and triplet states arising from lifting an electron from $1t_1$ to $3a_1$. Figure 2(b) shows the eigenvalues $\eta^{c\beta}$ for β spin. The diagrams 2(a) and 2(b) can be compared only roughly because the $\eta^{c\beta}$ cannot, in general, be identified with ionization energies, as can be done for the occupied values of the closed-shell calculation of $Zn\ S_4\ Zn_{12}$.

However, it can be seen that the designation of the valence-band levels remain almost the same except for the $1e$ and $2t_2$ levels of ZnS_4Zn_{12}, which are lifted into the energy gap in CuS_4Zn_{12} and become $2e$ and $4t_2$. In both cases these levels are mainly localized at the central d orbitals.

Following the discussion of Sec. III, we identify Δ with $\eta^{c\beta}(t_2) - \eta^{c\beta}(e)$ yielding a Δ value of 0.70 eV, comparing well with the experimental value 0.77 eV.[28] Figure 2(c) shows the eigenvalues of the closed-shell calculation of (4). In this case Δ has a value of 0.84 eV and is lying 1.62 eV above the $1t_1$ orbital. The band gap calculated by the difference between the $3a_1$ and $1t_1$ orbitals together with the correction for the virtual orbitals is 4.82 eV. A few other systems having a d^9 configuration have also been calculated and are compared with experimental data in Table II. The best results are those for ZnS : Cu and CdS : Cu with errors of 9% and 17%, respectively. ZnS : Ag is calculated with β_{3d} parameters $\beta_{3d}(\text{Ag}) = \beta_{3d}(\text{Cu})$ because no β_{3d} parameter for silver has thus far been given. Since the value of $10Dq$ depends on charges in the β_{3d} parameter (see Table III), reliable values for the $\beta_{3d}(\text{Ag})$ have still to be found either by direct calculation or by fitting β_{3d} to the results of a full SCF calculation. Impurities in which Zn is substituted by Cu are probably the best to calculate, since Cu is next to Zn in the periodic chart of the elements. Silver, on the other side, has quite a different ionic radius which may produce lattice deformations. Such effects are not included in our calculation. The values for ZnO : Cu and ZnSe : Au are calculations by the open-shell formalism and were already given by the authors.[29] The β_{3d} parameter of gold was also taken to be equal to $\beta_{3d}(\text{Cu})$.

VII. DISCUSSION

In spite of the strong approximations made by the CNDO method, the values for $10Dq$ agree quite well with experimentally found data. We believe this is so because of the proper handling of the boundary conditions. The most serious approximation is the calculation of the nondiagonal elements of F using the parameter β. In order to investigate how Δ depends upon changes of β_{3d}, we made a closed-shell calculation with several β_{3d} values. The result is shown in Table III. Δ increases with increasing β_{3d}. The correct value for Δ is found when $\beta_{3d} = -27.5$. This value lies between the two values of -20 and -30 given by Clack. Convergence of the SCF calculations is good for the closed-shell calculations (12–20 iteration steps until $|E^{n-1} - E^{n}| < 10^{-3}$ eV). In the open-shell case, however, convergence is very poor and depends strongly upon the Hückel matrix starting the calculation. The open-shell calculation of copper in ZnS converges until $|E^{n-1} - E^{n}| \approx 0.5$ eV and then oscillates about this value. The reason for this is the strong effect caused by the one-center Coulomb integrals of the central d functions. If one electron is taken out of the t_2 orbital localized at the central d orbital, very strong Coulomb interaction integrals between the d functions arise ($\gamma_{3d\,3d}$ is about 20 eV). Thus, the approximation of the $3d$ one-center integral by only one integral seems insufficient. On the other hand, we neglected the coupling terms of the open-shell procedure which may also be a cause of the poor convergence. Nevertheless, we believe that the open-shell calculation yields the correct result shown in Fig. 2(b), which may become a stable solution if some of the strong approximations are released.

VIII. CONCLUSION

Comparing our calculations with those done by Birman and Walter[14] and Biernacki[15, 16] for the same centers, the striking difference is the self-consistency of our calculations. Self-consistent-field wave functions are appropriate to calculate further features of the centers such as fine structure and correlation effects.

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