PHYSICAL REVIEW B VOLUME 34, NUMBER 8 15 OCTOBER 1986

New technique in the calculation of defects in solids by molecular methods: Pure and Cu-doped ZnS

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(Received 24 February 1986)

We present a modification in the molecular-cluster methods for the calculation of defects in solids. The modification introduces a common energy reference for the perfect-cluster and defect-cluster calculations. Thus it is possible to compare the eigenvalues coming from the two calculations. Once this possibility is open, we discuss the applicability of the Koopmans theorem or of the transition state in the interpretation of the calculated results. We use one or the other, depending on the bandwidth, the self-energy, and the cluster size. The whole procedure is applied to pure ZnS and ZnS:Cu with very satisfactory results.

I. INTRODUCTION

The calculation of the electronic structure of a defect in a semiconductor is frequently made by the many versions of the Green-function method.[1] One obtains precise determinations of the density of states, transition energies, charge state as a function of the Fermi energy, etc. A simpler method of calculation, also much used because of its greater speed and conceptual simplicity, consists of calculating the defect and its crystal environment as a big isolated molecule.[2-5] Though these molecular methods are arbitrary in the definition of the boundary conditions at the most external atoms of the cluster, one can minimize their bad effects with some art and increasing cluster size. Aside from these intrinsic errors, the molecular methods have also suffered from two shortcomings: a doubtful use of the Koopmans theorem giving the meaning of the molecular one-electron energy eigenvalues, and the lack of a common energy reference for the molecular pure crystal and defect calculations. Lacking this common energy reference, it is impossible in these calculations to choose among the many possible charge states of the defect. For instance, the substitutional Cu atom in ZnS might be Cu^+ or Cu^{2+}, and in the molecular calculations one would be unable to decide.

It is the purpose of this paper to present a modification of the molecular method which might overcome the latter two shortcomings. We start from the "crystalline cluster" method of Brescansin and Ferreira[6] (BF) used to calculate the energy bands of pure NaCl by molecular methods. A self-consistent calculation consists of the solution of the Schrödinger equation for the many eigenstates and the Poisson equation for the potential. In the Brescansin and Ferreira paper, while the Schrödinger equation is solved in the molecular cluster of atoms, the Poisson equation is solved in the infinite periodic crystal. In a molecule, atoms of the same species are not equivalent if they are differently placed with respect to the molecular center. Thus consider the case of ZnS and the cluster ZnS_4Zn_{12} of one central Zn, a tetrahedral shell of four S atoms and the 12 nearest Zn atoms of a face-centered-cubic lattice. If the Poisson equation were solved in the molecule, the potential of the central Zn atom would turn out to be very different from the potential of the external Zn atoms. Thus one would obtain two sets of Zn energy bands, complicating any possible interpretation. The BF scheme overcomes this difficulty.

Our calculations on the Cu substitutional in ZnS used the cellular method.[7] In an ionic crystal such as ZnS or NaCl, the use of the cellular method, instead of the multiple-scattering method, is expected to be of no consequence because the electronic charge stays mostly in the inscribed spheres, and muffin-tin errors are small. In what follows, we review the BF scheme, adapt it to defects, discuss the Koopmans theorem as applied to solids and defects, and present and discuss our calculated results.

II. THE BF SCHEME

The Brescansin and Ferreira scheme,[6] to calculate the pure crystal bands through a calculation in a molecule, consists of solving the Poisson equation in an infinite periodic crystal. One elects, in the molecule, representatives of the atoms of the infinite crystal. For instance, in the molecule ZnS_4Zn_{12} the central Zn is elected representative of the Zn atoms of the crystal, while one of the four S is elected representative of the S atoms. After solving the Schrödinger equation in the molecule, one finds the spherically averaged (denoted by subscript "av") number density

$$n(r)=\left[\sum_{\substack{i\\ \text{occup}}}\psi_i(\mathbf{r})^*\psi_i(\mathbf{r})\right]_{\text{av}}$$

inside the representative Zn and S atoms, and repeats these number densities in the whole infinite crystal. In the intersphere region of the crystal the number density is made constant, with a value that neutralizes the charge of the spheres. Then the Poisson equation is solved in the crystal, using standard Ewald methods. The crystal potential is then put in the muffin-tin format. After these procedures, one uses the crystal potential in the molecule, but shifts so that the intersphere potential becomes a constant of values 1—2 Ry. The potential in the outer region of the molecule, that is the region outside a sphere circumscribing the molecule, is made equal to

$$V(r)=C^{te}R_0/r \ , \tag{1}$$

where C^{te} is the intersphere potential and R_0 is the circumscribed sphere radius.

After completing the calculation for the pure crystal one begins the self-consistent calculation for the defect. At each iteration, the potential is calculated as

$$V(r)=V_{\mathrm{DM}}-V_{\mathrm{PM}}+V_{\mathrm{crystal}} \ , \tag{2}$$

where V_{crystal} is the self-consistent potential of the crystal calculation; V_{PM} (PM is pure molecule) is the potential one obtains solving the Poisson equation in the molecule, and not in the crystal; and V_{DM} (DM is defect molecule) is a molecular potential for the molecule containing the defect and its environment. To exemplify, V_{crystal} is the potential of the infinite ZnS crystal, but modified according to the BF scheme. V_{PM} is the potential of the molecule $\mathrm{ZnS_4Zn_{12}}$. V_{DM} is the potential of the molecule $\mathrm{CuS_4Zn_{12}}$.

Equation (2) is easy to interpret as expressing the perturbation of the defect by a difference of molecular potentials, defect minus pure, being applied to the crystal potential. V_{crystal} is taken as the muffin-tin. During the self-consistent calculation of the defect, the potential

$$\phi_{\mathrm{ext}}(\mathbf{r})=V_{\mathrm{crystal}}-V_{\mathrm{PM}} \tag{3}$$

is maintained fixed as an added external potential, while V_{DM} varies from one iteration to the following.

The advantage of the present procedure is obvious. One maintains in V_{crystal} the reference for the energy eigenvalues of the defect calculation. Thus the eigenvalues of the defect and the "perfect" crystal can be directly compared.

III. KOOPMANS THEOREM VERSUS TRANSITION STATE

For a bound state α, the energy eigenvalue ε_α is interpreted by means of the equation[8]

$$\frac{dE}{df_\alpha}=\varepsilon_\alpha \tag{4}$$

relating the derivative of the total energy E with respect to the occupation number f_α. From first-order perturbation theory, it is a simple matter to prove that

$$\frac{d\varepsilon_\alpha}{df_\alpha}=2S_\alpha \ , \tag{5}$$

where

$$S_\alpha=\int d^3r\int d^3r'\frac{n_\alpha(\mathbf{r})n_\alpha(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}+\varepsilon_{\mathrm{xc}} \tag{6}$$

may be named as the self-energy of electron α, due to the special form of its first term. The second term in Eq. (6) comes from the exchange-correlation functional E_{xc} and has the expression

$$\varepsilon_{\mathrm{xc}}=\tfrac{1}{2}\int d^3r\int d^3r'\,n_\alpha(\mathbf{r}')\frac{\delta^2E_{\mathrm{xc}}}{\delta n(\mathbf{r})\delta n(\mathbf{r}')}n_\alpha(\mathbf{r}) \ . \tag{7}$$

It has been a long-established fact by all workers in atomic[9] and molecular calculations that the eigenvalue ε_α is a very linear function of the occupation f_α. Thus the self-energy S_α does not depend much on f_α and we are permitted to write

$$E(f_\alpha)=E(0)+\varepsilon_\alpha(0)f_\alpha+S_\alpha f_\alpha^2 \tag{8}$$

and

$$E(1)-E(0)=\varepsilon_\alpha(0)+S_\alpha \tag{9a}$$

$$=\varepsilon_\alpha(\tfrac{1}{2}) \tag{9b}$$

$$=\tfrac{1}{2}[\varepsilon_\alpha(0)+\varepsilon_\alpha(1)] \ . \tag{9c}$$

Equations (9b) and (9c) are to be used in the comparison of the calculated energy eigenvalues with the results of optical absorption or emission experiments when the occupation of some states change by one unit.

The first important case to be considered is that of a Bloch state that spreads through the whole volume. Then the number density tends to zero, the self-energy is null, and, according to Eq. (9a), the eigenvalue coincides with the total energy difference. In this case we are in the full Koopmans regime, which is expected whenever we deal with Bloch states of broad bands such as the conduction band and highest valence bands. On the other hand, when we are dealing with localized defect eigenstates or deep and narrow valence bands, the electron that is added or removed does not spread in the whole bulk but remains confined to a few atoms. In this case, comparison with experiment has to be made by means of Eq. (9b) or (9c).

The distinction between the two cases (Koopmans vs transition state) is not straightforward. First consider a pure crystal, where we prepare a hole with a localized wave function, by combination of Bloch states of a single band. If the hole self-energy is large and the bandwidth small, the energy of the hole excitation will be outside the energy band. Thus this hole will not be scattered into the band continuum, and it is a truly measurable excitation of the crystal, provided its energy has been minimized.[10] On the other hand, if the self-energy is small and the bandwidth large, the localized excitation is meaningless because its energy falls within the band continuum, where it is scattered. Thus the use of the Koopmans theorem (no self-energy) or the transition state in interpreting the calculated results depends on the relative values of the self-energy and the bandwidth. To complicate matters further, we add that, from a cluster calculation, one cannot know the bandwidths, unless one uses very large clusters. Barring these enormous clusters, one must decide on the use of Koopmans or of the transition state, by recurring to the complementary information of an infinite crystal band-structure calculation. Thus the infinite crystal and the cluster calculations are complementary, in that from the former we determine the bandwidths and in the latter we define the localized excitations.

Consider now the case of an impurity creating a localized state in the band gap. Though localized, it is possible that the impurity wave function extends through many atoms[1] well beyond the cluster size. Due to its large extent, one knows that the self-energy is small [see Eqs. (6) and (7)]. In a small cluster calculation, it is possible that this self-energy turns out to be large, because one is artificially concentrating the wave function in the small space. Thus one must recognize that small clusters are inadequate to calculate small self-energies, therefore to calculate the stability limits of the many charge states of such impurity. In this circumstance, the best we can do with a small cluster is to interpret the impurity eigenvalue as the center of gravity of the energies for the addition and the removal of one electron,

$$E(1)+E(-1)-2E(0)\simeq 2\varepsilon_a(0)\,, \qquad (10)$$

in accordance with Eq. (8).

IV. RESULTS AND DISCUSSION

The band structure of ZnS is represented in Fig. 1. The conduction band is mainly a Zn 4*s* band, while the valence bands are S 3*s*, Zn 3*d*, and S 3*p* bands. The relative position of the Zn bands with respect to the S bands is controlled by a feedback mechanism. If the Zn 3*d* bands are raised, the mixing with the S 3*p* states increases and the Zn atoms lose electronic charge. This makes the potential in the Zn spheres more negative, which brings the Zn 3*d* bands down.

We made calculations on molecular clusters of 17 atoms, ZnS_4Zn_{12} and CuS_4Zn_{12}, and on clusters of five atoms, SZn_4. The five-atom cluster SZn_4 has eight valence electrons in S and ten *d* electrons at each Zn, a total of 48 valence electrons. The 17-atom cluster ZnS_4Zn_{12} has eight valence electrons at each S and ten at each Zn, totaling 162 valence electrons. In the small five-atom cluster SZn_4, each Zn has just one S neighbor. In this case the hybridization mechanism of controlling the position of the Zn bands is inefficient. Thus we had to populate the Zn 3*d* states with only 9.4 electrons, instead of 10, to maintain these bands between S 3*s* and S 3*p*. Thus the position of the Zn 3*d* bands in this case is quite arbitrary and non-self-consistent. The geometric parameters of the cellular calculation are in Table I.

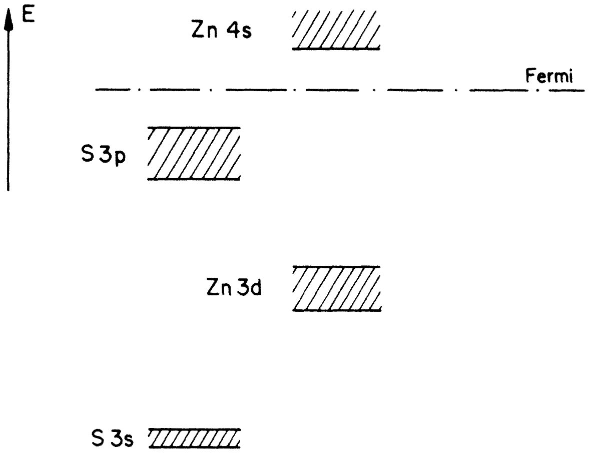

FIG. 1. Schematic representation of ZnS band structure. Hybridization of the Zn 3*d* and S 3*p* states controls the relative position of the S and Zn bands.

The clusters that were calculated are described in Table II. Clusters 1 and 4 are representations of pure ZnS. Cluster 2 is a modification of cluster 1 by removing a half electron from the central Zn 3*d* state. As said before, this removal has to be treated as a defect of the crystal and Eq. (2) used accordingly. Cluster 3 refers to a Cu acceptor. Cluster 5 is similar to the "pure" cluster 4 but has a half electron removed from the S 3*s* bands.

Our results for the many possible optical transitions (OT) are in Table III. The first OT is the band gap, which corresponds to a configuration change where the highest valence state loses one electron and the lowest conduction state gains one. According to the band-structure calculations,[18] these bands have large bandwidths, and we *must* use the Koopmans theorem. This OT is then calculated as the difference

$$E^{\mathrm{OT1}}((v^0,c^0)\rightarrow(v^{-1},c^1))=\varepsilon_c(1)-\varepsilon_v(1) \qquad (11)$$

between the eigenvalues for the conduction state ($3a_1$) and the highest valence state ($3t_2$) in cluster 1. The calculated result 4.46 eV is somewhat larger than experiment (3.91 eV). It had to be so because the conduction band is broad, and its cluster sampling by a single energy must be above the band minimum.

OT2 refers to the position of the Zn 3*d* band with

TABLE I. Cell parameters of the calculations. Point $\mathbf{r}$ belongs to cell i, centered at $\mathbf{a}_i$, if $\gamma_i(\mathbf{r}-\mathbf{a}_i)^2-\gamma_i R_i^2=$minimum. Cubic lattice parameter = 10.216 44 a.u. Exchange-correlation of Gunnarsson and Lundqvist (Ref. 11) without spin polarization.

	SZn_4			ZnS_4Zn_{12} and CuS_4Zn_{12}			
	S	Zn	Outer	Zn or Cu	S	Zn ext	Outer
R_i (a.u.)	1.9878	2.43604	6.85988	2.43604	1.9878	2.43604	9.6602
γ_i	1.	1.	−0.5	1.	1.	1.	−0.75

TABLE II. Clusters that were calculated and their configuration.

		Configuration			
Cluster	Formula	S 3s Valence Band	3d Valence Band	S 3p Valence Band	Zn4s Conduction Band
1	ZnS_4Zn_{12}	$1a_1^2 1t_2^6$	$d_{\rm int}^{10} d_{\rm ext}^{120}$	$2a_1^2 t_1^6 2t_2^6 e^4 3t_2^6$	$3a_1^0$
2	ZnS_4Zn_{12}	$1a_1^2 1t_2^6$	$d_{\rm int}^{9.5} d_{\rm ext}^{120}$	$2a_1^2 t_1^6 2t_2^6 e^4 3t_2^6$	
3	CuS_4Zn_{12}	$1a_1^2 1t_2^6$	$d_{\rm Zn}^{120} d_{\rm Cu}^{10}$	$2a_1^2 t_1^6 2t_2^6 e^4 3t_2^5$	
4	SZn_4	$1a_1^2$	$d^{37.6}$	t_2^6	$2a_1^0$
5	SZn_4	$1a_1^{1.5}$	$d^{37.6}$	t_2^6	

respect to the highest valence state. In this case, the calculated bandwidth of the d bands,[18] less than 1.0 eV, is smaller than the self-energy, which is equal to the eigenvalue difference between cluster 1 and 2,

$$\varepsilon_{d_{\rm int}}(1)-\varepsilon_{d_{\rm int}}(2)=1.90 \text{ eV} . \qquad (12)$$

Thus we must use the transition state for the d band, and calculate this OT as

$$E^{\rm OT2}((d_{\rm int}^{10},v^{-1})\rightarrow(d_{\rm int}^{9},v^{0}))=\varepsilon_v(1)-\varepsilon_{d_{\rm int}}(2) . \qquad (13)$$

OT3 refers to the substitutional Cu. In order to compare calculated results with experiment, one must decide whether to use Koopmans or the transition state for the impurity states. As said in the preceding section, a decision in favor of the transition state can only be made if the impurity wave function can be wholly contained in our 17 atoms cluster. Since we have no information on the spread of these wave functions, we decided to try the transition state. Thus we also made calculations on clusters like 3, but with plus and minus 0.5 electrons in the state $3t_2$. From these calculations we obtained self-energies that were much too large to permit the Cu impurity having different stable charge states. Thus we concluded that our 17-atom cluster was too small to contain the impurity wave functions, and had to be satisfied with tabulating just the Koopmans result as the center of gravity of the stability limits.

OT4 is the excitation of the Cu impurity by promoting an electron from e to $3t_2$,

$$E^{\rm OT4}((e^4,3t_2^5)\rightarrow(e^3,3t_2^6))=\varepsilon_{3t_2}(3)-\varepsilon_e(3) . \qquad (14)$$

Our interpretation of the 0.77 eV line coincides with that of Refs. 4 and 19, in that these states are mostly reconstructions of the top S 3p valence states, instead of the much lower Cu 3d states. The latter interpretation follows from the calculation of Gemma,[5] which presents a poorer fit to experiment.

OT5 is the creation of a hole in the S 3s band. Band-structure calculations give a S 3s bandwidth of about 1.2 eV, much smaller than our calculated self-energy

$$\varepsilon_{1a_1}(4)-\varepsilon_{1a_1}(5)=3.1 \text{ eV} . \qquad (15)$$

Thus we must calculate the energy of this OT using the transition state for the lower band, as explained in Table III. We may note in passing that, though the transition-state energy can be calculated in the central-S cluster 4, it cannot be calculated in the central-Zn cluster 1. On the

TABLE III. Calculated results for the energies of optical transitions.

Optical Transition (OT)	Change in Configuration	Energy	Calculated (eV)	Experiment (eV)
1. Band gap	$(v^0,c^0)\rightarrow(v^{-1},c^1)$	$\varepsilon_c(1)-\varepsilon_v(1)$	4.46	3.91[a]
2. Position of Zn d band	$(d_{\rm int}^{10},v^{-1})\rightarrow(d_{\rm int}^{9},v^0)$	$\varepsilon_v(1)-\varepsilon_{\rm din}(2)$	7.55	9.5[b]
3. Occupation or depletion of Cu acceptor	$(3t_2^5,v^0)\rightarrow(3t_2^6,v^{-1})$	$\varepsilon_{3t_2}(3)-\varepsilon_v(1)$	2.28	1.25[c]−1.44[d]
4. Excitation of Cu acceptor	$(e^4,3t_2^5)\rightarrow(e^3,3t_2^6)$	$\varepsilon_{3t_2}(3)-\varepsilon_e(3)$	center of gravity 0.71	threshold 0.77[e]
5. Position of S 3s band	$(1a_1^2,v^{-1})\rightarrow(1a_1^1,v^0)$	$\varepsilon_v(4)-\varepsilon_{1a_1}(5)$	14.06	13.5[f]

[a] Reference 12.
[b] Reference 13.
[c] Reference 14.
[d] Reference 15.
[e] Reference 16.
[f] Reference 17.

other hand, the Koopmans eigenvalue differences of the two clusters can be compared

$$\varepsilon_{t_2}(4)-\varepsilon_{1a_1}(4)=11.00\ \text{eV}=\varepsilon_{3t_2}(1)-\varepsilon_{1a_1}(1)$$

and do not differ by more than 0.01 eV. Thus, despite the fact that cluster 4 is very small, it seems to give reliable results for the S bands.

V. SUMMARY

Despite the fact that the Green-function methods for the calculation of impurity states in solids are more precise, the molecular methods are very attractive because of superior computational speed and conceptual simplicity. The molecular methods suffer from a built-in error coming from the arbitrariness of the boundary conditions at the cluster surface. Aside from this handicap, which can be minimized by art and larger clusters, these methods have suffered from the lack of a common energy reference for the perfect crystal and defect cluster calculations. Lacking this energy reference, the defect cluster eigenvalues, and their location with respect to the crystal bands, become largely a matter of free interpretation. In particular, one is never sure on what to use, the Koopmans theorem or the transition state, in the interpretation of the calculated energies.

In this paper we present an improvement of the molecular method by introducing a single energy reference to the pure and defect cluster calculations. This is attained by solving the Poisson equation in the perfect infinite crystal (not in the cluster), and by dealing with the defect as a perturbation on the crystal potential. The procedure requires a muffin-tin definition of the infinitely extended crystal potential, which is an extra source of error, but is small when one deals with ionic crystals. Having a common energy reference, one is now able to discuss the applicability of the Koopmans theorem or of the transition state. We show that one should use one or the other depending on the bandwidth, the self-energy, and the cluster size. In some cases, a decision on the Koopmans theorem or the transition state, may depend on the information obtained from an infinite crystal band-structure calculation.

The procedure was applied to ZnS and ZnS:Cu, using small clusters of five and 17 atoms. The calculated results present a very good consistency with known experimental facts, but we were unable to determine the stability limits of the many charge states of Cu, probably due to an insufficient cluster size.

ACKNOWLEDGMENTS

The work was supported by the Fundacão de Amparo à Pesquisa do Estado de São Paulo (FAPESP), Brazil.

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