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Evaluation of semiempirical quantum-chemical methods in solid-state applications. I. Molecular-cluster calculations of defects in silicon

Peter Deák* and Lawrence C. Snyder
Department of Chemistry, State University of New York, 1400 Washington Avenue, Albany, New York 12222

Raj K. Singh and James W. Corbett
Department of Physics, State University of New York, 1400 Washington Avenue, Albany, New York 12222

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Three typical semiempirical molecular-orbital methods developed by chemists; the spectroscopic version of the complete neglect of differential overlap (CNDO/S), the modified intermediate neglect of differential overlap (MINDO/3), and the modified neglect of diatomic overlap (MNDO), are evaluated in molecular-cluster model applications. The ionization energies, wave-function localizations, and equilibrium geometries of the clusters $X\mathrm{Si}_4\mathrm{H}_{12}$, where X is a silicon, sulfur, or oxygen atom or a vacancy, are compared with results obtained from *ab initio* Hartree-Fock calculations using an extended Gaussian-orbital basis set with third-order Moeller-Plesset perturbation theory. The importance of using an absolute ionization-energy scale in locating levels relative to the crystalline band gap is discussed. It is concluded that the MINDO/3 is superior among the three methods in representing defect properties using a molecular-cluster model of defects in silicon.

I. INTRODUCTION

The molecular-cluster model[1] (MCM) utilizing the semiempirical molecular-orbital methods of quantum chemistry was introduced fifteen years ago to address the problem of deep-level point defects in semiconductors. Although in the meantime more sophisticated techniques have emerged,[2–6] the MCM is still the fastest and cheapest tool by which microscopic models of various defect centers can be judged *en gros* in terms of the calculated one-electron energies and wave functions.[7–12] With the appearance of methods like the modified intermediate neglect of differential overlap[13] (MINDO/3) and the modified neglect of diatomic overlap (MNDO),[14] the calculation of the equilibrium geometry of large molecular clusters also became possible. The basis for the identification of a given microscopic model with an experimentally known defect center usually consists of a description of the defect wave functions, related spin-density distributions, the position of the corresponding levels relative to the gap, and the symmetry of the defect, as well as of vibrational and electronic excitation energies obtained from the MCM calculation.

Recent calculations with the MCM favor self-consistent methods in order to take into account charge rearrangement around the defect. The most frequently applied methods are based on one of the three successive stages of the zero differential overlap approximation to the Hartree-Fock-Roothaan (HFR) molecular-orbital theory introduced by Pople.[15] These are the complete neglect of differential overlap (CNDO), the intermediate neglect of differential overlap (INDO), and the neglect of diatomic differential overlap (NDDO). Originally these methods have been fitted to *ab initio* HFR results on diatomic molecules (CNDO/2). In comparison with experimental data, the neglect of correlation results in an underestimation of binding energies and overestimation of force constants and ionization energies (calculated by the Koopmans theorem). A new generation of methods based on these approximations, such as CNDO/S,[16] MINDO/3, and MNDO introduced new adjustable parameters to fit data experimentally observed on a set of small molecules. In a way these parameters simulate the effects of electron correlation for the experiments chosen.

Naturally, the reliability (transferability) of these parameter sets depends on the sample of molecules used to determine them. For example, CNDO/S was devised to reproduce ionization energies and electronic transitions of benzene derivatives, but it breaks down when applied to saturated hydrocarbons.[17] MINDO/3 and MNDO were parametrized using a larger sample of molecules. Both are being applied widely and quite successfully to organic molecules. This success in molecular organic chemistry induced the solid-state physics community adapt these methods for cluster-type calculations on defects in silicon. The methods were largely used in a "black box" mode, in the belief that they are well established and thoroughly tested by chemists. This is only partly true for silicon, and not at all true in a solid-state context.

The merits of the *basic approximations* are in fact well established in the case of relatively small molecules of low symmetry. Those molecules are very small compared to the clusters used to simulate the silicon lattice. It should be taken as a warning, however, that the heat of formation of neopentane for both the MINDO/3 and MNDO, and of cubane for the latter, are much less well reproduced than for smaller and less "crowded" molecules.[18] Neopentane is the carbon analogy of the $\mathrm{Si}_5\mathrm{H}_{12}$

cluster widely used in defect calculations.

The success of the semiempirical approximations largely depends on the parameter sets chosen. Not much can be stated about the particular *parameters of silicon.* The MNDO parameters generally used in solid-state applications have been published by the authors of the method[19] but no actual calculations were reported by them. One of the very few reports of a calculation on molecules containing Si—Si bonds[20] using these parameters, pointed out that MNDO is inferior to MINDO/3 in this respect although generally the MNDO is regarded as a better approximation. Dewar *et al.* published a new set of MNDO parameters for silicon and reported extended calculations as well.[21] These parameters, however, result in unphysical charge distributions between silicon and hydrogen, and a much too short Si—Si bond length in disilane. Recently, a third set of parameters is being published[22] along with a change in the core-core repulsion function in the Austin model (AM1). The MINDO/3 method has been applied[23] to a wider variety of molecules containing Si—Si bonds including large saturated silicon hydrids. However, very few experimental data are available for such molecules to test the results.

In summary, despite their common use in the solid-state physics community, not much is known about the performance of these methods in systems typical of solid-state applications for silicon. The choice of the semiempirical approximation used in MCM applications should not be decided on the basis of experience with organic molecules. The aim of this paper is to explore the merits of the CNDO/S, MINDO/3, and MNDO methods in silicon cluster applications. The use of experimental solid-state data to evaluate the results of such calculations is largely hampered by the approximations involved in the MCM itself. Our goal here is to provide a comparative test using *ab initio* methods to supply a reference.

We applied these semiempirical methods to the molecular clusters $X\mathrm{Si}_4\mathrm{H}_{12}$, where $X=\mathrm{Si}$, S, O, or a vacancy (V). We regard these clusters as hypothetical molecules and *do not try to compare* the computed results directly *to* experimental data of the corresponding impurities in *the solid.* Since no experimental reference data for such molecules exists, we have performed good quality *ab initio* calculations *including correlation corrections* and used the results as a reference. We will compare equilibrium geometries, ionization energies and wave-function localizations of the above mentioned defects.

II. CALCULATIONAL DETAILS

Our comparative calculations have been carried out on $X\mathrm{Si}_4\mathrm{H}_{12}$ clusters with $X=\mathrm{Si}$, S, O, or a vacancy (V). First the energy of the perfect cluster $\mathrm{Si}_5\mathrm{H}_{12}$ has been minimized with respect to the Si—H and Si—Si bond lengths. In all the other calculations ($X\neq\mathrm{Si}$) the terminator hydrogen atoms have been fixed, while all other atoms were allowed to relax freely. The resulting geometries can be described by the structural parameters given in Fig. 1.

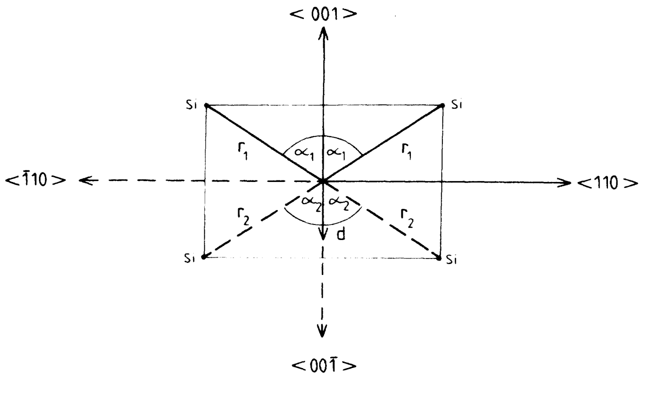

FIG. 1. Structural parameters of the $X\mathrm{Si}_4\mathrm{H}_{12}$ cluster with fixed hydrogen terminators.

Ab initio calculations using an extended Gaussian orbital basis have been performed for reference. This basis expands core atomic orbitals as a linear combination of three Gaussian functions. Each atomic valence orbital is represented by an inner and outer basis function, the inner expanded in two Gaussisans and the outer as a single Gaussian. This basis, named the 3-21G by Pietro *et al.*,[24] allows the valence shells of atoms to expand or contract with charge transfer. The equilibrium geometry for the ground state was calculated at the HF level. The vertical ionization energies have been computed as the difference between the total energies of the ground and ionized states calculated by third-order Moeller-Plesset perturbation theory[11,25] (MP3) at this geometry.

The CNDO/S method has been devised to give ionization energies and electronic excitation energies of benzene derivatives at experimental geometries.[16] It has been extended to saturated molecules with the inclusion of parameters for Si with an *spd'* basis by Deak.[17] Since it is not suited for geometry optimization, calculations with this method have been performed at the geometries provided by the *ab initio* calculation.[11]

The original parametrization of MINDO/3 did not include parameters of Si—O and Si—S bonds.[13] For calculations with $X=\mathrm{O}$ we have applied the parameters published by Edwards and Fowler,[26] which we find to be close to optimum. We have determined β and α parameters for the Si—S bond using the experimental bond length and the heat of formation of the SiS molecule. The parameters $\beta=0.281$ and $\alpha=1.082$ yield the results shown in Table I.

MNDO is generally applied in solid-state applications with the "old" parameter set for silicon.[19] This suffers from the constraint of equal resonance parameters for s and p orbitals. The "new" parameter set[21] has different values of resonance parameters and orbital exponents for s and p orbitals. Unfortunately however, the p orbital exponent is larger than the s exponent. The problems of parametrizing silicon and other third-row elements in MNDO is discussed in another forthcoming publication.[27] The new parameters yield unrealistic charge transfers from silicon to hydrogen, too short Si—Si

TABLE I. MINDO/3 results for molecules with Si—S bonds.

Molecule	$d_{\text{Si-S}}$ (Å)	ΔH_f (kcal/mole)	μ (D)	Ionization potential (eV)
SiS				
Calc.	1.925	16.7	1.373	8.47
Expt.	1.929[a]	16.9[b]		
SiH_3-S-SiH_3				
Calc.	2.183	-21.4	2.257	9.08
Expt.	2.136[a]			9.59[c]

[a] See Ref. 38.
[b] See Ref. 39.
[c] See Ref. 40.

bond length in molecules, as well as a poor description of the valence band of crystalline silicon.[28] We choose to use the better-known old parameters. The rotational invariance problem in the definition of MNDO two-electron integrals[29] has been corrected as described in Ref. 27.

III. RESULTS AND DISCUSSION

The equilibrium geometries obtained by the *ab initio*, MNDO, and MINDO/3 calculations are given in Table II. Except for the case of the vacancy where long bonds are involved, the *ab initio* calculation can be regarded almost as good as experimental data. The Si—Si bond-length in the "perfect" cluster ($X = \text{Si}$) obtained with MINDO/3 is close to the *ab initio* result. The bond length obtained by using MNDO is significantly shorter. The symmetry for $X = \text{S}$ and $X = V$ has been predicted to be T_d and D_{2d}, respectively, by all three methods. In both cases the predicted inward relaxation of the first-neighbor silicon atoms is larger with MNDO and smaller with MINDO/3 than the one obtained from the *ab initio* calculation.

The most important difference among the three methods is revealed by the calculation with $X = 0$. The *ab initio* calculation predicts a C_{2v} symmetry with the oxygen atom off center by 1.04 Å in the $\langle 100 \rangle$ direction. The relative position of the silicon pair closer to the oxygen is clearly different from that of the other pair. The MNDO calculation gives also a C_{2v} symmetry but with the oxygen close to the center, and the positions of the silicons are only slightly distorted from T_d. The MINDO/3 method on the other hand predicts a clear T_d symmetry with the oxygen on center. The "quenching" of oxygen off-center behavior by relaxing first-neighbor silicons using the MNDO approach has been known from the calculations of DeLeo *et al.*,[9] but it was attributed to the approximations involved in the MCM. The presented comparison suggests that the reason may lie just as much in the approximations of the semiempirical method applied.

The negatives of the semiempirical ionization energies of the defect clusters calculated by using Koopmans' theorem are compared with the negatives of the MP3 ionization energies in Fig. 2. Results are given for each method at a fixed geometry which is the equilibrium geometry of the *ab initio* Hartree-Fock calculation. Results are also shown for MNDO and MINDO/3 at their optimized geometries.

The CNDO/S and MINDO/3 give computed ionization potentials in the same order as the MP3 calculation. No parameters exist for sulphur in the revised CNDO/S method. The MINDO/3 ionization energies are quite close to the MP3 results for oxygen and for the vacancy. The optimized MINDO/3 geometry is close to the refer-

TABLE II. Equilibrium cluster geometries.

Molecule	*Ab initio*	MNDO	MINDO/3
Si_5H_{12} (T_d)			
$r_1 = r_2 = r$	2.383	2.267	2.372
$\alpha_1 = \alpha_2 = \alpha$	54.734	54.734	54.734
SSi_4H_{12} (T_d)			
Δr (%)	-2.1	-3.6	-0.3
V:Si_4H_{12} (D_{2d})			
Δr (%)	-2.6	-4.7	-1.5
$\Delta\alpha$	-2.7	-1.4	-1.1
O:Si_4H_{12} (C_{2v}/T_d)			
d (Å)	1.04	0.08	0.00
Δr_1 (%)	-2.7	-8.92	-11.66
Δr_2 (%)	-10.1	-8.75	-11.66
$\Delta\alpha_1$ (%)	-1.9	0.13	0.00
$\Delta\alpha_2$	-4.7	-0.18	0.00

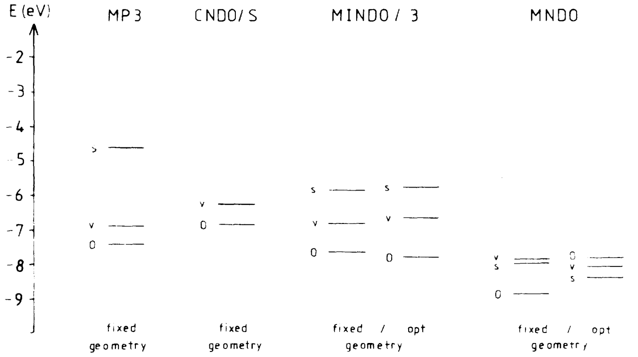

FIG. 2. Comparison of the ionization energies of defect clusters obtained from MP3 and from the semiempirical methods.

ence geometry for $X=S$ and $X=V$. The MINDO/3 ionization energy for $X=O$ hardly changes with moving the oxygen off center by 1.04 Å indicating a small energy difference between the two geometries. The MINDO/3 ionization energy for $X=S$ appears to be relatively high considering the better agreement with MP3 for $X=O$ and V. Together with the small inward relaxation of the Si atom this suggests that our tentative bonding parameter β between Si and S is too low in absolute value. The MNDO method gives ionization energies quite different from the previous methods both in relative order and in absolute position. The values are generally too high. The ionization energy of the cluster with $X=S$ is higher than that with the vacancy. This is very unlikely to be true. The ionization energy of the cluster with $X=0$ depends strongly on the geometry. We note that in the MNDO case at the near-T_d oxygen geometry, the ordering of the highest S and O levels is reversed relative to the one expected on simple electronegativity arguments.[30] We believe that this is also an artifact of the MNDO parametrization, for the MP3 calculation at the unrelaxed geometry still yields a higher ionization energy for $X=O$ than for $X=S$ by 0.7 eV. The predicted reversal in the real crystal based on local density-functional calculations[6] may have been an effect of the crystalline environment not provided by such a small cluster.

The localization of the highest occupied molecular orbitals (HOMO's) to the central atom and the first-neighbor shell for the three defect clusters is shown in Table III. All four methods predict the a_1 state of the S substituent to be the most localized with a relatively high coefficient on the sulphur atom itself. All three semiempirical methods seriously underestimate the localization of the a_1 level of the off-center oxygen (A center). This is most prominent with MNDO. Similarly MNDO underestimates the localization of the b_2 state of the vacancy. In general, the *ab initio* calculation predicts very high localizations which are well matched by MINDO/3 except for oxygen. The CNDO/S values are acceptably close to the *ab initio* values, while the MNDO localization values are considerably smaller. The very high localizations indicated by the *ab initio* calculation are certainly characteristic of the small cluster size. Nevertheless, they set the standard for the molecular case we are considering.

IV. LOCATING LEVELS RELATIVE TO THE GAP IN MCM CALCULATIONS

The following question can be raised: Of what use are defect ionization energies on an absolute scale? We will demonstrate that the widespread use of a "perfect cluster valence-band edge" as reference point for the defect energy levels is inappropriate. Rather the ionization energy of the defect should be compared to the ionization energy of the perfect solid as obtained from a band-structure calculation by the same method. The basic idea behind the MCM is the assumption that for a defect in which the defect wave function is well localized, the first few shells of neighbors of the host do at least qualitatively represent the real crystalline environment. On the other hand, those few shells perturbed by the defect certainly do not represent the bulk of the solid. Therefore it is generally assumed[31] that the reference "valence-band edge" is supplied by the energy of the HOMO of the defectless "perfect" cluster. Most often this HOMO energy is taken to be the zero point of the energy scale.

If one accepts this interpretation, the MCM seems to fail even in the simple, well-understood case of the unrelaxed vacancy in silicon. From various (non-MCM) calculations[2,4] it is known that the ideal vacancy yields a t_2 state in the gap and an a_1 resonance about 1 eV below the valence-band edge. Figure 3 shows the MNDO energy levels of the clusters Si_5H_{12} and Si_4H_{12} at the same geometry, the central silicon having been removed in the latter. The chosen geometry minimizes the total energy of the defectless cluster. The T_d symmetry of the eigenstates for Si_4H_{12} has been enforced by distributing the two electrons available for the topmost degenerate t_2 states evenly among them. If one takes the HOMO of the perfect cluster as the reference valence-band edge, the calculation predicts the a_1 state to be well in the gap. We note that qualitatively the same is computed to be true if the two electrons of t_2 are allowed to occupy just one of the three states.

The failure to properly locate the a_1 state can probably be attributed to the small cluster size. One can ask whether the a_1 state is being predicted too high, or the perfect cluster valence band edge too low. To answer this question we have performed similar calculations for the clusters XSi_4H_{12}, $XSi_{16}H_{36}$, $XSi_{28}H_{36}$, and $XSi_{34}H_{36}$ with fixed geometries of T_d symmetry. The Si—Si and Si—H bond lengths are the same as in Fig. 4. These clusters correspond to inclusion of first-, second-, third-, and fourth-silicon-neighbor shells to the central atom (X) respectively, which is either Si or a vacancy. The results are shown in Fig. 2. Solid lines connect the energies of the two topmost occupied and the two lowest unoccupied orbitals of the perfect clusters. The energies of the a_1 and t_2 defect states obtained from the vacancy calculations are connected by dashed lines. The numbers in the figure are the localization percentages of the defect wave functions to the first-neighbor shell. The

TABLE III. HOMO localizations in the first-neighbor shell (%).

Cluster (HOMO symmetry)	*Ab initio*	CNDO/S	MINDO/3	MNDO
S:Si_4H_{12} (a_1)	98.1		87.9	71.8
O:Si_4H_{12} (a_1)	92.3	78.8	78.8	68.0
V:Si_4H_{12} (b_2)	85.6	78.1	85.4	65.9

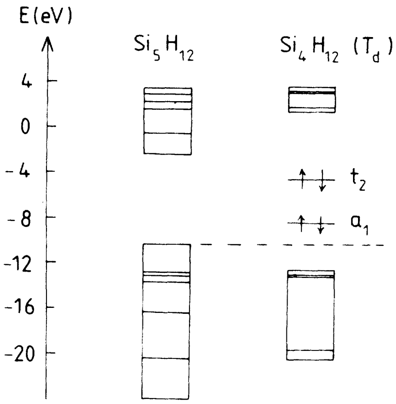

FIG. 3. MNDO-MCM electronic structure for the ideal vacancy in Si.

columns on the right-hand side of the figure represent the bands of silicon obtained from an approximate MNDO band-structure calculation at the same Si—Si distance. Details of that calculation will be given in the following paper.[28]

As one increases the cluster size and improves the representation of the host, the a_1 level is shifted toward the cluster valence-band edge. We must, however, take into consideration the presence of terminating hydrogen atoms which give a dipole layer at the surface and shift the ionization energies. The effect of the surface dipole layer in a finite cluster is of course different for orbitals with different localizations. The t_1 orbital has zero coefficients on the central atom due to its symmetry and in these relatively small clusters it is less affected than the t_2 state which has a larger part "surrounded" by the dipole layer. This explains the usually ignored fact that MCM calculations often give a valence-band edge which differs in symmetry from that of the solid. Since the a_1 defect state is more or less localized inside the dipole layer, its ionization energy can approximately be corrected by a simple Madelung potential calculated for the defectless cluster. Ionization energies corrected this way are connected by the dotted line in Fig. 4. Taking this correction into account, the change in the position of the a_1 level with increasing cluster size is small. It is clear that the qualitatively wrong prediction of the location of the a_1 state in the small cluster case is a consequence of the cluster valence-band edge lying too low. If one takes the above corrections for the surface dipole layer into account, the a_1 level ends up about 1 eV below the crystalline valence-band edge calculated by the same method. From the quantum-chemist's point of view this is not surprising at all. Semiempirical methods like MNDO have been devised to reproduce experimental ionization energies of molecules as the negative of the HOMO energies. Therefore if none of the common "tricks" are applied, for example manipulating the Si—H distance,[9] the parameters[32] of the hydrogen atoms, or omitting surface dangling bonds,[33,34] the HOMO energy of the cluster will fit the ionization energy of the corresponding hypothetical molecule. For example, the carbon analogy of our smallest cluster exists: It is the neopentane molecule with an ionization energy of 11.0 eV.[35] For comparison, the ionization energy of diamond is about 8 eV.[36]

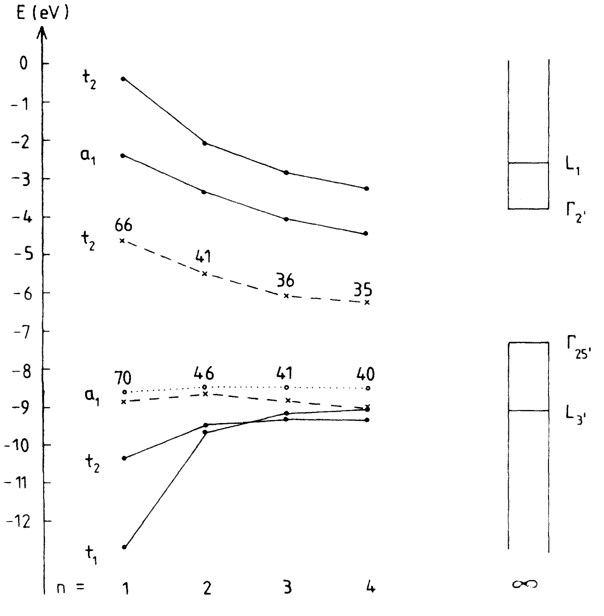

FIG. 4. MNDO-MCM calculations with increasing number (n) of Si shells around the central atom as compared to an approximate MNDO band structure. For explanation see text.

It is clear that in using cluster calculations with hydrogen atoms as terminators one should be very careful in locating the occupied a_1 state related to the on-center oxygen substitutional with respect to the band edges of the solid. This orbital is not sufficiently localized to use the previous Madelung-potential correction. Instead, we modified the one-center one-electron MNDO parameter, $U_{\mu\mu}$ for the terminating hydrogens in order to achieve a net charge close to zero on each of the atoms in the Si_5H_{12} cluster at the equilibrium geometry. Figure 5 shows the results of a series of calculations for the XSi_4H_{12}, $XSi_{16}H_{36}$, and $XSi_{28}H_{36}$ clusters with X=Si or O, using both the normal (dotted lines) and the modified (solid lines) hydrogen parameters. With increasing cluster size the use of the modified hydrogen parameter with identical bond lengths on differently coordinated hydrogen atoms is less successful in ensuring zero net atomic charges in the defectless cluster. Nevertheless, the polarization effect is diminished, and the top level of the cluster valence band is always of t_2 symmetry. The position of the a_1 level is very strongly influenced by the surface dipole layer. The results with the modified hydrogen parameters indicate that the a_1 level is going to converge to somewhere very near to the actual valence-band edge calculated by MNDO. This is in sharp contrast with the close to midgap position which could have been predicted using the valence band edge of the Si_5H_{12} cluster as reference. Therefore in our opinion there was not sufficient justification to force the a_1 level into the gap in

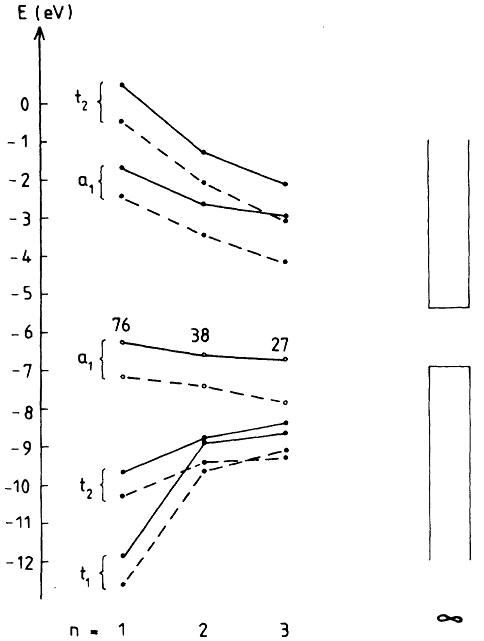

FIG. 5. MNDO-MCM calculations for the $X\mathrm{Si}_4\mathrm{H}_{12}$, $X\mathrm{Si}_{16}\mathrm{H}_{36}$ and $X\mathrm{Si}_{28}\mathrm{H}_{36}$ clusters with X=Si or O. The topmost two occupied levels (t_1 and t_2) and the two lowest unoccupied levels (a_1 and t_2) of the X=Si clusters are displayed together with the a_1 level in the vicinity of the gap related to the on-center substitutional oxygen (X=O). Dashed and solid lines connect results with normal hydrogen parameters and with modified hydrogen parameters (see text), respectively. For comparison, the band edges obtained from a periodic calculation are shown on the right-hand side. The numbers in the figure show the degree of localization inside to the first-neighbor shell in %.

Ref. 37.

Finally we note that the *ab initio* HF calculation resulted in an almost complete localization of the sulphur a_1 defect state into the first-neighbor shell. This allows the use of this small molecular cluster for locating the defect level relative to the gap. The ionization energy of the a_1 level has been computed as 4.6 eV. The dipole correction is about -0.2 eV. Since we have supposed the MP3 results to be close to "experimental data," we compare the computed level with the experimentally known position of the silicon gap: between -5.4 and -4.3 eV. The computed *ab initio* position of the defect level after correction is about 0.1 eV below the conduction-band edge. At this level of approximation this is in fairly good agreement with experiment.

V. CONCLUSION

Semiempirical quantum-chemical methods are widely used to calculate the properties of molecular clusters in order to simulate defects in silicon. It is generally assumed in the solid-state physics community that from methods like CNDO/S, MINDO/3, and MNDO, a similar accuracy can be expected in predicting equilibrium geometries and energy levels of defects as is often found for organic molecules. Based on such considerations, MNDO is also often regarded as superior to MINDO/3. However, the very nature of the approximations used in such methods forbids the *a priori* assumption of satisfactory predictions for systems far from the realm of molecules for which the parameters have been determined.

In this paper we have provided a test of the CNDO/S, MINDO/3, and MNDO methods on a basic molecular cluster used to describe defects in silicon. Such a test was necessary because very few calculations on molecules containing silicon exist, and the number of available experimental data is even less. We used *ab initio* techniques to provide reference data.

We have shown that the original silicon parameters of MNDO are not only inferior to MINDO/3 in predicting geometries, as is the case for smaller molecules,[20] but MNDO gives also an incorrect relative sequence for the ionization energies of the vacancy, the substitutional oxygen and sulphur in silicon. The absolute MNDO ionization energies are also quite different, especially for sulphur, from the *ab initio* values obtained by using third-order Moeller-Plesset perturbation theory. On the other hand, the CNDO/S and MINDO/3 ionization energies are in fair agreement with the *ab initio* results. Therefore, even though MNDO has proven very successful in organic chemistry, for silicon-based systems MINDO/3 appears to be preferable.

We have demonstrated that in some cases the equilibrium conformation of the defect can be qualitatively affected by the approximations involved in the semiempirical methods. The computed nearly on-center location of oxygen in a $\mathrm{Si}_4\mathrm{H}_{12}$:O cluster obtained by MINDO/3 and MNDO is characteristic to these methods. A double-zeta *ab initio* Hartree-Fock calculation gave essentially the same relaxation as that obtained by DeLeo *et al.*[9] with attached "springs" to the cluster in an MNDO calculation.

In using methods like CNDO/S, MINDO/3, and MNDO for molecular cluster calculations, it is also often ignored that the calculated one-electron energies are supposed to supply the negatives of the ionization energies on an absolute scale. Consequently, gap levels are usually located with respect to the highest occupied level of the defectless cluster, which is thought to represent the top of the valence band.

We have shown that while the position of levels associated with relatively well localized defect states such as the a_1 level of a vacancy do not change very much when the cluster is increased from one silicon neighbor shell to four, there is considerable change in the position of the valence-band edge of the defectless cluster. The potential of the dipole layer arising due to the termination of the cluster also shifts the levels. The shift depends on the localization of the corresponding wave function. As demonstrated with the cases of the ideal vacancy and the oxygen substitutional, the location of "gap levels" based on the "gap" of hydrogen-terminated small clusters is highly unreliable. We suggest that defect levels corrected for the polarization effect should be related to the valence-band edge obtained from a band-structure calculation using the same semiempirical method. We present approximate CNDO/S, MINDO/3, and MNDO band structures of silicon in the following paper.[28] The comparison of the ionization energy of the highly localized a_1 state of substitutional sulphur is computed very accurately by *ab initio* techniques relative to the experimentally known position of the silicon gap. This supports the correctness of the proposed procedure.

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*Permanent address: Physical Institute of the Technical University of Budapest, Budafoki ut 8, H-1111 Budapest, Hungary.

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