

Self-consistent treatment of effective electron correlation at localized dangling-bond defect states in silicon

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1992 J. Phys.: Condens. Matter 4 9971

(<http://iopscience.iop.org/0953-8984/4/49/024>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 12:38

Please note that [terms and conditions apply](#).

Self-consistent treatment of effective electron correlation at localized dangling-bond defect states in silicon

Sergey S Moliver

Moscow State University branch in Ulyanovsk, 42 L N Tolstoy Street, Ulyanovsk, 432700 Russia

Received 18 October 1991, in final form 20 March 1992

Abstract. A semiempirical local approach to the problem of electron correlation at localized defect states in solids is presented. The approach modifies any quantum-chemistry scheme by adding a certain correction to the Fock matrix, thus permitting one to obtain self-consistently correlation corrections to all ground-state parameters of the defect. The theory has been applied to the large-unit-cell models of the dangling-bond defects $\text{Si}:\text{V}^0$ and $\text{Si}:(\text{VH}_3)^-$. The results of the calculations are useful for investigation of negative- U properties.

1. Introduction

The quantitative description of electron correlation (e.g. calculation of corrections that make a picture of independent electrons suitable) is an outstanding problem of solid-state physics. Semiconductor physics contains an important topic in this regard: the properties of certain defects are defined by electron correlation. One such defect is the negative- U centre, one local deep state of which does not contain electrons; if an equilibrium is defined by low values of chemical potential E_F , but a shift of E_F upwards maintains a new equilibrium, the deep level acquires an electron pair. The occupation of the deep level by a single electron is unstable at any E_F position. The interaction between electrons of the deep-level pair provides a correlation correction U to the total energy of the one-electron approximation. The negative- U properties are produced by different influences of deep-level occupation-number on the two energy-reconstruction terms (correlation term and electron–lattice term).

This paper reports a self-consistent field (SCF) calculation scheme that yields corrections to the Hartree–Fock (HF) total energy, electron density, energy levels and other ground-state characteristics of a defect in a solid. All corrections are related only to the effective electron correlation at localized defect states, i.e. the energy correction is part of the total correlation energy of the solid (this part may be positive). So, the approach designed is a practical way to modify the HF SCF method for electronic structure calculations of deep centres in solids.

The present method is theoretically based on a local approach (LA) to the electron correlation problem (Stollhoff and Fulde 1980). By contrast with molecular *ab initio* methods (configuration interaction, generalized valence-bond methods) applicable only to molecules or to cluster models of solids, the LA is model-independent. On the other hand, the powerful *ab initio* density-functional approach to electron correlation

in solids adapts poorly to defect calculation problems, such as adiabatic energy curves of lattice reconstruction. The LA method permits one to carry out defect calculations with fewer difficulties.

This paper also deals with the application of the modified HF SCF method to the large-unit-cell (LUC) models of two vacancy-hydrogen (V-H) centres in Si. The purpose was to describe the effective electron correlation at Si dangling bonds (DB). In addition to their well known practical importance (Pearton *et al* 1987), Si V-H centres are appropriate for testing a new calculation scheme, because they have been thoroughly investigated by several theoretical approaches.

Si:V. Experimental data for the Si vacancy (Watkins 1986) are explained by negative- U centre phenomenology (Baraff *et al* 1980), which in turn uses the results of density-functional calculations of an unreconstructed neutral vacancy (Baraff and Schlüter 1979, Bernholc *et al* 1980) and of its multiplet and Jahn-Teller analysis (Lannoo *et al* 1981). The electron correlation effect at Si unreconstructed vacancy DBs has also been investigated by a generalized valence-bond method (Surratt and Goddard 1978). The numerical results of the two *ab initio* approaches disagree because (i) they are applied to opposing models, and (ii) their correlation approximations are constructed differently—either with only bound DB states or with all defect electrons. Application of the semiempirical LA method to the LUC model of reconstructed Si:V⁰ in this work demonstrates the features of both *ab initio* methods. Only two electrons of the bound DB state are assumed to correlate, but still the SCF process involves other states in correlation corrections (first of all, the unbound state resonant with the valence band).

Si:VH₃. The isolated DB of this centre is the main subject of amorphous Si (a-Si) theoretical investigations. A theoretical prediction about its negative- U properties (Bar-Yam and Joannopoulos 1986) has no clear experimental evidence (Pantelides 1988). Calculations of the present work support the negative- U theory, but insist on the effective correlation energy parameter U being small, which agrees with recent experiments on intrinsic a-Si (Essick and Cohen 1990).

2. Theory: a simple semiempirical local approach to the Fock matrix

A semiempirical local approach (LA) to electron correlation derives from the *ansatz*

$$\psi_0 = \exp(S)\psi_{\text{HF}} \quad (1)$$

where ψ_{HF} is a many-electron wavefunction of the HF approximation, and ψ_0 is a ground-state wavefunction of correlated electrons (Stollhoff and Fulde 1980). The semiempirical calculation procedure is defined in a rather general way with the use of a correlation operator S . First, the local regions $\langle r | m \rangle$ are introduced as one-electron linear combinations of atomic orbitals (LCAO) of the chosen model:

$$\langle r | m \rangle = \sum_{\mu a} \gamma_{m\mu a} \langle r | \mu a \rangle. \quad (2)$$

Here μ denotes atomic orbital (AO) type—usually it means a set of the main, orbital and magnetic quantum numbers—and a denotes the atom on which the AO is centred. For example, in the LUC model (section 3) $\langle r | \mu a \rangle$ is a sum of AOs centred on the

ath atom of every R th LUC (R is the Bravais vector of the lattice in which LUC is the primitive unit cell). Coefficients $\gamma_{m\mu a}$ make up a set of parameters. A second set of parameters $\eta_{mm'}$ is defined by the chosen type of electron correlation in the local regions:

$$S = \sum_{m,m'} \eta_{mm'} (|m\rangle O_{mm'} \langle m'|). \quad (3)$$

For example, $O_{mm'}$ may have Hubbard form $O_{mm'} = \delta_{mm'} n_{m\alpha} n_{m\beta}$ where n_{ms} is the occupation number of the local region m with spin s (α means spin up, β means spin down).

After setting up the basic correlation *ansatz* (1)–(3), the LA proceeds to second-order expansion of the state (1) energy and minimization of this expansion by varying the coefficients $\eta_{mm'}$. Though the correlation *ansatz* (1)–(3) is similar to *ab initio* methods, because the energy expansion includes two-electron matrix elements of the Coulomb interaction, the LA is not a rigorous many-electron method, obtained from perturbation theory. Thus, if the empirical coefficients $\gamma_{m\mu a}$ are not optimized, it makes no sense to carry out the difficult calculation of two-electron integrals. Besides, application of the LA is only recently possible for some atoms, molecules and a few perfect crystals (Stollhoff 1990).

So, we see good reason to simplify the LA, conserving its HF reference and self-consistent nature. Two steps of such simplification are presented in this section (Moliver 1988, 1991).

The first simplifying step reduces the parameter set by use of the following assumption: the local regions of strong correlation coincide with some of the molecular orbitals (MO) of a defect. This implies that MOS can be produced by some quantum-chemistry procedure. The MOS labelled by $i = 1, 2, \dots, N$ and spin $s = \alpha, \beta$ are LCAO:

$$\langle r | is \rangle = \sum_{\mu a} c_{\mu a}^{is} \langle r | \mu a \rangle. \quad (4)$$

The LCAO coefficients $c_{\mu a}^{is}$ form the electron density matrix

$$P_{\mu a \mu' a'} = \sum_s P_{\mu a \mu' a'}^s \quad P_{\mu a \mu' a'}^s = \sum_{i=1}^{N_F} c_{\mu a}^{is} c_{\mu' a'}^{is'} \quad (5)$$

where N_F is the highest occupied MO (MOS are ordered by HF one-electron energies). The HF method does not need spin-non-diagonal elements of the type $P_{\mu a \mu' a'}^{s \bar{s}}$, but, bearing in mind the correlation problem, we shall distinguish them and conserve the unusual double spin index in (5). Introducing a localization criterion for every MO,

$$p_{is} = \sum_{\mu a \in S\{\mu a\}} (c_{\mu a}^{is})^2 - p \quad 0 < p < 1 \quad (6)$$

we obtain a new set of local regions with a single parameter p , instead of (2). In fact, (6) means the following: do AOs from the subset $S\{\mu a\}$ make up more or less than part p of the i s-th MO (4)? So, the local regions are defined as those MOS for which $p_{is} > 0$. The localization threshold p separates localized MOS occupied by strongly

correlated electrons from delocalized ones (such as crystal valence-band or resonant defect states) that contribute negligibly to the defect correlation energy. For example, studying the negative- U centre energy dependence on reconstruction, one can omit the constant crystal part of the correlation and take into account only the effective correlation of localized electrons (Baraff *et al* 1980).

The second simplifying step retains as a calculation basis the HF SCF energy-minimization procedure for the LCAO coefficients of (4), instead of the minimization procedure for the LA *ansatz* coefficients of (3). Since HF SCF minimizes the total electron energy, approximated by the bilinear form of the density matrix (5), the correlation correction to the HF energy must take the form

$$\Delta E = \sum P_{\mu a \mu' a'}^s A_{\mu a \mu' a'}^s + \frac{1}{2} \sum P_{\mu a \mu' a'}^s P_{\mu'' a'' \mu''' a'''}^{s''} B_{\mu a \mu' a' \mu'' a'' \mu''' a'''}^{s''} \quad (7)$$

(summing over all indices). Quantum-chemistry calculation schemes minimize (7), using the eigenvalue and eigenvector procedure for the Fock matrix and LCAO coefficient vector. Variation of (7) by LCAO coefficients (see (5)) gives an eigenvalue problem with the Fock matrix correction

$$\Delta F_{\mu a \mu' a'}^s = A_{\mu a \mu' a'}^s + \sum B_{\mu a \mu' a' \mu'' a'' \mu''' a'''}^{s''} P_{\mu'' a'' \mu''' a'''}^{s''} \quad (8)$$

(summing over repeated indices).

In order to express (8) through the localization criterion (6), we need some model for the electron correlation at the localized MOs (such as model (3) of the LA). The well known Hubbard model Hamiltonian

$$\Delta H = U \sum_i^{\text{loc}} n_{i\alpha} n_{i\beta} \quad (9)$$

is appropriate for the effective electron correlation at the localized defect states (Baraff *et al* 1980). In (9), U is the effective correlation energy, $n_{i\alpha}$ is the electron occupation operator for i st MO, and summation is limited to localized MOs. The correspondence between (7) and (9) may be established by

$$\Delta E = U \sum_{i=1}^{N_f} \vartheta(p_{i\alpha}) \vartheta(p_{i\beta}) \quad (10)$$

$$\vartheta(x) = \begin{cases} 0 & x < 0 \\ 1 & x > 0 \end{cases}$$

$$\vartheta(x) \simeq \frac{1}{2} + \frac{1}{2} \frac{x}{(x^2 + \gamma^2)^{1/2}} \quad |x| \gg \gamma.$$

Correlation correction (10) is defined by all doubly occupied MOs, and through expressions (6) and (5) ΔE obtains a density-functional character (a good argument in favour of a semiempirical approximation). In addition to U , there appears here a new parameter γ —a smoothing constant for the step function ϑ .

The set of localization parameters—threshold p , smoothing constant γ and localized defect state AO subset $S\{\mu a\}$ —must be found empirically during HF calculations. The subset $S\{\mu a\}$ includes AOs of defect neighbours, so that linear

combinations of these AOs describe rather well only localized defect states but not delocalized ones. As to γ , it must be chosen so that variations of threshold $p \pm \gamma$ would not change the separation of MOs on localized and delocalized types previously established by criterion (6). A value of γ with this property always exists, since the energy levels of localized defect states are separated from the continuous spectrum of delocalized states of the solid. Therefore, we can use a smooth approximation of the step function in (10).

Putting (6) into (10) and changing ϑ by a γ -smoothed function, we obtain a LCAO correction to the total energy

$$\begin{aligned} \Delta E = & \frac{U}{4} \sum_{i=1}^{N_F} \left[\left(1 - \sum_{s=\alpha}^{\beta} \frac{p}{(p_{i_s}^2 + \gamma^2)^{1/2}} + \frac{p^2}{(p_{i_\alpha}^2 + \gamma^2)^{1/2} (p_{i_\beta}^2 + \gamma^2)^{1/2}} \right) \right. \\ & + \sum_{\substack{\mu\alpha \in S\{\mu\alpha\} \\ s=\alpha, \beta}} (c_{\mu\alpha}^{is})^2 \left(\frac{1}{(p_{i_s}^2 + \gamma^2)^{1/2}} - \frac{p}{(p_{i_\alpha}^2 + \gamma^2)^{1/2} (p_{i_\beta}^2 + \gamma^2)^{1/2}} \right) \\ & \left. + \sum_{\mu\alpha \in S\{\mu\alpha\}} \sum_{\mu'a' \in S\{\mu\alpha\}} \frac{(c_{\mu\alpha}^{i\alpha})^2 (c_{\mu'a'}^{i\beta})^2}{(p_{i_\alpha}^2 + \gamma^2)^{1/2} (p_{i_\beta}^2 + \gamma^2)^{1/2}} \right]. \quad (11) \end{aligned}$$

Now we have to transform (11) into the quantum-chemistry form (7). Staying within the semiempirical calculation scheme, it makes no sense to look for some elaborate conversion of (11). The simplest solution is just to take MO averages instead of those expressions in (11) which are multiplied by density-type functions of the LCAO coefficients:

$$\sum_{\mu\alpha \in S\{\mu\alpha\}} (c_{\mu\alpha}^{is})^2 \quad \text{and} \quad \sum_{\mu\alpha \in S\{\mu\alpha\}} \sum_{\mu'a' \in S\{\mu\alpha\}} c_{\mu\alpha}^{i\alpha} c_{\mu'a'}^{i\beta}.$$

So, if we introduce averages

$$\begin{aligned} \Delta_{1s} &= \frac{1}{N_F} \sum_{i=1}^{N_F} \frac{1}{(p_{i_s}^2 + \gamma^2)^{1/2}} \\ \Delta_2 &= \frac{1}{N_F} \sum_{i=1}^{N_F} \frac{1}{(p_{i_\alpha}^2 + \gamma^2)^{1/2} (p_{i_\beta}^2 + \gamma^2)^{1/2}} \\ D_{\mu\alpha\mu'a'}^s &= \frac{1}{N_F} \sum_{i=1}^{N_F} \frac{c_{\mu\alpha}^{is} c_{\mu'a'}^{is'}}{(p_{i_\alpha}^2 + \gamma^2)^{1/2} (p_{i_\beta}^2 + \gamma^2)^{1/2}} \end{aligned} \quad (12)$$

and use density-matrix definition (5), ΔE will become a linear function of density, i.e. we obtain the first term of (7):

$$\begin{aligned} \Delta E = & \frac{U}{4} \sum_{\substack{\mu\alpha s \\ \mu'a' s'}} P_{\mu\alpha\mu'a'}^s \left\{ \delta_{\mu\mu'} \delta_{\alpha\alpha'} \delta_{ss'} \left[\left(\frac{1}{2} - p\Delta_{1s} + \frac{1}{2}p^2\Delta_2 \right) \right. \right. \\ & + \delta_{\mu\alpha, S\{\mu\alpha\}} \left(\Delta_{1s} - p\Delta_2 + \frac{w}{2} \sum_{\mu''\alpha'' \in S\{\mu\alpha\}} D_{\mu''\alpha''\mu''\alpha''}^{-s} \right) \left. \right] \\ & \left. + \delta_{\mu\alpha, S\{\mu\alpha\}} \delta_{\mu'a', S\{\mu\alpha\}} \delta_{s, -s'} \frac{1-w}{2} D_{\mu\alpha\mu'a'}^s \right\}. \quad (13) \end{aligned}$$

Here $\delta_{\mu a, S\{\mu a\}}$ equals 1 if $\mu a \in S\{\mu a\}$, and 0 otherwise. The weight w , $0 < w < 1$, is introduced because the last term of (11) can be converted with the use of averages (12) by two different arrangements (during calculations it was assumed that $w = 0.5$). The first arrangement contains a diagonal element of the density matrix (term proportional to w in (13)); the second contains a non-diagonal element (term proportional to $(1 - w)$).

The correlation correction (13) to the HF energy is a linear function of the electron density; the bilinear term of (7) is not used. Of course, there is a way to extract this bilinear term from (11), but it seems to be useless, because expression (11) itself is rather crude, being based on a one-site approximation (9) with a single parameter U .

It has to be underlined that correlation correction (13) really has some features of electron correlation: as was mentioned above, the HF approximation does not need spin-non-diagonal density-matrix elements, while (13) contains them.

Finally, we can write down the Fock matrix correction for practical use in the framework of standard quantum-chemistry calculations of defect systems with localized states. The following sections of this paper investigate only closed-shell defect models (the restricted HF approximation). Coefficients (12) in this approximation do not depend on spin indices; therefore, the closed-shell Fock matrix is

$$\begin{aligned} \Delta F_{\mu a \mu' a'} = & \frac{U}{4} \left\{ \delta_{\mu \mu'} \delta_{a a'} \left[\left(\frac{1}{2} - p \Delta_1 + \frac{1}{2} p^2 \Delta_2 \right) \right. \right. \\ & \left. \left. + \delta_{\mu a, S\{\mu a\}} \left(\Delta_1 - p \Delta_2 + \frac{w}{2} \sum_{\mu'' a'' \in S\{\mu a\}} D_{\mu'' a'' \mu'' a''} \right) \right] \right. \\ & \left. + \delta_{\mu a, S\{\mu a\}} \delta_{\mu' a', S\{\mu a\}} \frac{1-w}{2} D_{\mu a \mu' a'} \right\}. \end{aligned} \quad (14)$$

Self-consistency is the most useful property of correction (14). Though electron density is absent in (14), the averages (12) are defined by the density matrix, and therefore they vary at every step of the SCF process. Thus, the calculation tactics will be successful if correction (14) is not invoked during the first iteration step, but only after achieving a certain degree of HF self-consistency. With these tactics, variations of (12) at every step will be small and will decrease step by step, the total electron energy will converge to a minimum, and all HF ground-state characteristics (one-electron energies, electron density) will obtain correlation corrections. Calculations described in section 4 prove this.

3. The MO LCAO HF calculation scheme, large-unit-cell model and INDO parametrization for Si

The HF ground-state electron structures of perfect and defect Si crystals have been obtained in this work by the SCF LCAO method (Pople and Beveridge 1970) with a modified intermediate neglect of differential overlap (INDO) parametrization (Shluger and Kotomin 1981). The basic LUC crystal model included 16 Si atoms: the two-atom primitive unit cell of a crystal (FCC diamond lattice) was doubled along each of the (110) basic Bravais vectors. All defect LUCs have been derived from this ideal crystal Si16 LUC.

The electron structure of a LUC, as a molecule with cyclic boundary conditions on every MO, may be calculated, yielding all electron states with wavevectors k in several high-symmetry points of the Brillouin zone. This approach is called the quasi-molecular LUC model or cyclic-cluster model, in order to distinguish it from band calculations at k -points of a crystal with a LUC as the primitive unit cell (supercell). Using the quasi-molecular LUC model (Evarestov and Lovchikov 1979), we classify the MOS of Si16 according to their degeneracy and obtain energy band values in Γ , X and L points (figure 1(a)).

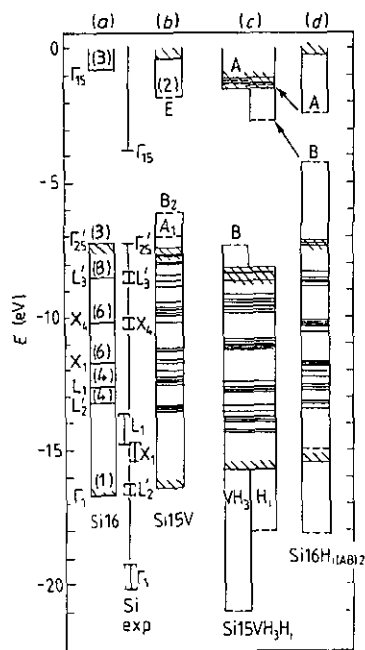


Figure 1. Electron structure of (a) perfect and (b-d) defect Si crystal LUC models. Defect levels are dashed. Crystal energy band edges are shaded. Experimental values for Si (a) are shifted in accordance with Γ'_{25} . The occupied levels are collected into the lower bands, the empty ones into the upper bands in every spectrum. Orbital degeneracies of crystal LUC MOS stand above their levels. Arrows show H_i level changes after 'doping' VH_3 centre.

The Si 3s and Si 3p AO parameter set—electronegativity $E_{neg}(\mu a)$, radial part exponent constant $\zeta_{\mu a}$ and bonding parameter $\beta_{\mu a}$ (Pople and Beveridge 1970)—has been optimized to valence band structure, cohesive energy and bulk modulus (Harker and Larkins 1979). Using these optimal complete neglect of differential overlap (CNDO) values, the author has calculated the lattice constant d_0 and hybridization parameters $P_{\mu a \mu a}^{(0)}$ that provided a minimum of the crystal LUC total energy E_{tot} . The hybridization parameters enter the diagonal matrix elements of the mutual potential energy of valence electrons and atomic cores in the following way:

$$\langle \mu a | H^{(1)} | \mu a \rangle = -E_{neg}(\mu a) - \sum_{\mu'} P_{\mu' a \mu' a}^{(0)} [(\mu a \mu a | \mu' a \mu' a) - \frac{1}{2}(\mu a \mu' a | \mu' a \mu a)] \quad (15)$$

where

$$(\mu a \mu' a | \mu'' a'' \mu''' a''') = \int d^3 r' \int d^3 r'' \frac{\langle \mu a | r' \rangle \langle r' | \mu' a' \rangle \langle \mu'' a'' | r'' \rangle \langle r'' | \mu''' a''' \rangle}{|r' - r''|}$$

The HF nature of (15) permits one to adjust atomic values of electronegativity to the crystal calculations (Shluger and Kotomin 1981, Stefanovich *et al* 1990).

During E_{tot} minimization for Si16, while d_0 was fixed, the hybridization parameters of (15) were varied, with the purpose that the input $P_{\mu\alpha\mu\alpha}^{(0)}$ values would become equal to the output self-consistent diagonal density-matrix elements $P_{\mu\alpha\mu\alpha}$ of (5). Only after exit from this feedback loop of the SCF iterations was a new point added to the graph $E_{\text{tot}}(d_0)$. As a result, this graph with a high precision (better than 10^{-4} au) gave a parabolic curve of adiabatic compression with optimal d_0 and $P_{\mu\alpha\mu\alpha}^{(0)}$ at the minimum point, where the internal pressure of a crystal model is zero.

All parameters of the calculations may be found in table 1. After optimization of Si16 we get a model of almost the same quality as had been achieved by CNDO (Harker and Larkins 1979). For example, the energy spectrum is shown on figure 1(a). Of course, it is not the best model within its class of computations (Deak and Snyder 1987), but is still a suitable one to test the theory proposed in section 2. In the course of Si DB defect calculations it is very important to exclude the intrinsic pressure of the crystal model. That is why the minimization of d_0 described above seems to be necessary for any quantum-chemistry calculations.

Table 1. Parameters of MO LCAO modified INDO calculations.

Parameter	Units	This work	Other work
$\zeta_{\text{Si } 3s}$	au ⁻¹	1.54 ^a	1.93 ^b
$\zeta_{\text{Si } 3p}$	au ⁻¹	1.54 ^a	1.76 ^b
$E_{\text{neg}}(\text{Si } 3s)$	eV	6.3 ^a	23.03 ^b
$E_{\text{neg}}(\text{Si } 3p)$	eV	4.5 ^a	16.03 ^b
$\beta_{\text{Si } 3s} = \beta_{\text{Si } 3p}$	eV	-6.4 ^a	-4.5 ^b
$P_{\text{Si } 3s, \text{Si } 3s}^{(0)}$	au	1.0144	0.93 ^a , 0.63 ^b
$P_{\text{Si } 3p, \text{Si } 3p}^{(0)}$	au	0.9952	1.023 ^a , 0.59 ^b
d_0	au	10.68	10.34 ^a , 10.26 ^c
$\zeta_{\text{H } 1s}$	au ⁻¹	1.2 ^b	
$E_{\text{neg}}(\text{H } 1s)$	eV	7.18 ^b	
$\beta_{\text{H } 1s}$	eV	-9.0 ^b	
$P_{\text{H } 1s, \text{H } 1s}^{(0)}$	au	0.8 ^b	

^a Crystal optimization, CNDO (Harker and Larkins 1979).

^b Molecular and SiO₂ crystal optimization, modified INDO (Shluger 1985).

^c Experimental value.

It is well known that the HF method systematically overestimates the gap value of narrow-gap insulators and semiconductors, and does not reproduce conduction band dispersion in contrast with rather good valence band reproduction (figure 1(a)). For example, one cannot find the Si minimal indirect-gap value $E_g \simeq X_1-\Gamma'_{25}$ on any HF-calculated spectrum (Deak and Snyder 1987). The direct-gap value $E_{\text{opt}} = \Gamma_{15}-\Gamma'_{25}$ is a better optimization criterion for the HF scheme than E_g , but not the most important one in studies of the ground-state properties (Harker and Larkins 1979). While HF-calculated values of energy gap and lattice constant are greater than the experimental ones, the local density approximation (LDA) usually underestimates them. This systematic discrepancy of HF and LDA has been studied for a long time, and it is assumed now that if one chooses HF or LDA as a basic approximation, one must define correctly a set of properties for comparison with the experimental data (Maksimov *et al* 1989, Pisani *et al* 1988). For example, LDA is used for reliable calculations of energy levels, electron density and electron-lattice constants of defects,

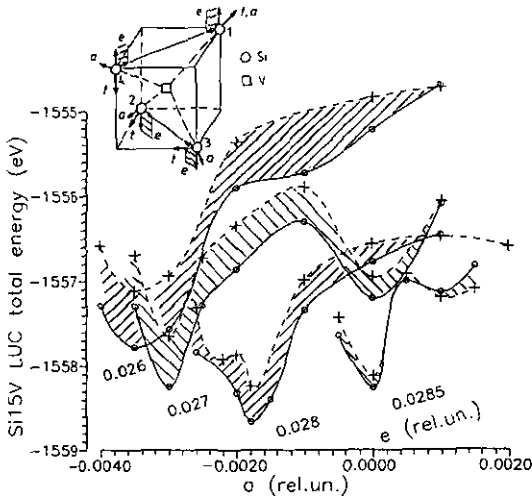


Figure 2. E_{tot} adiabatic curves of Si15V: (O) HF; (+) HF with semiempirical LA, $U = 0.25$ eV. Each pair of curves united by shading represent the reconstruction with constant tetragonal distortion e written nearby in relative units. Absolute vectors of atomic displacements (inset) are: tetragonal $\frac{1}{2}ed_0[221]$ and symmetrical $ad_0[111]$.

while the *ab initio* or semiempirical HF approximation is applicable to problems of property trends in defect series, sophisticated defect complexes, etc., especially in cases explained by interactions of a chemical bond type.

4. Results of Si: V^0 and Si:(VH_3) $^-$ calculations: reconstruction and effective correlation

4.1. Si: V^0 (reconstructed neutral vacancy)

Taking one atom out of Si16, we get an ideal (unreconstructed) neutral vacancy model, ready for the closed-shell HF calculations, Si15V. This ideal V is unstable, owing to the Jahn–Teller (JT) effect, which demands a reconstruction to take place as the superposition of three main lattice distortions near V: relaxation (a), tetragonal (e) and trigonal (t) distortions. By the way, the SCF iteration process did not converge for ideal V. Non-convergence, which arises in computations using the HF scheme, has been named HF instability. For ideal Si: V^0 , HF instability stems from partial occupation of the orbital triplet DB state T_2 . In the first step of the HF iteration process three MOs of T_2 acquire slightly different energies because of computer precision limitations. According to the HF scheme the electron pair will be placed on that MO of the triplet which occasionally has the lowest energy. After calculation of electron density during the next iteration cycle, the occupied DB MO energy level may be pushed up (in order to minimize E_{tot}) and may become higher than the energy level of the empty (in previous cycle) DB MO. If this takes place, the electron pair will be transmitted from one DB MO to another. The next iterations may repeat this swapping of occupancy and energy level ordering of two DB MOs, making the iteration process unstable. The easiest way to bypass HF instability of the type considered is to distort the lattice in order to break the degeneracy of the DB state, i.e. to work only with a JT-reconstructed defect.

Distortions a and e have been applied to the four nearest neighbours of V, and only then has the Si15V minimal E_{tot} been found (figure 2). According to experimental data (Watkins 1986), trigonal distortion is negligible: even a small t distortion increased E_{tot} too much.

The electron structure of V (figure 1(b)) is in agreement with both experimental and theoretical data (Baraff and Schlüter 1979, Bernholc *et al* 1980). The MO A_1 has a small binding energy and is rather delocalized. This points to the resonant nature of this state (symmetrical s and sp^3 combination of V neighbour AOs). The partially occupied triplet T_2 of ideal V, after JT reconstruction, splits into the occupied singlet B_2 and empty doublet E. The bonding DB state B_2 consists of two pairs of sp^2 -p type hybrids, each pair of which binds two atoms adjacent to V, which become closer if e distortion is positive (atomic pairs 1-4 and 2-3 on figure 2). The doublet E is antibonding: the AOs of V neighbours (mainly p) interfere destructively between atoms.

With good precision it has been found that the V^0 electron-lattice interaction is linear near the equilibrium reconstruction. The binding energies of three vacancy levels and the (B_2 -E) splitting are proportional to the deviations ΔQ from equilibrium values $Q(0)$ of distortions that give the minimum E_{tot} (figure 2):

$$\begin{aligned}
 E_{A_1} &= E_{A_1}(0) + V_{eA_1} \Delta Q_e + V_{aA_1} \Delta Q_a & Q_a &= 2\sqrt{3}ad_0 \\
 E_{B_2-E} &= E_{B_2-E}(0) + 1.5V_e \Delta Q_e & Q_e &= 2\sqrt{6}ed_0 \\
 V_{eA_1} &= -0.8 \text{ eV } \text{\AA}^{-1} & V_{aA_1} &= +1.3 \text{ eV } \text{\AA}^{-1} & a(0) &= -0.0018 \text{ ru} \\
 V_e &= -1.2 \text{ eV } \text{\AA}^{-1} & & & e(0) &= 0.028 \text{ ru.}
 \end{aligned} \tag{16}$$

(Coordinate relative units (ru) are preferable, because the lattice constant d_0 is an adjustable parameter. In order to find the atomic displacements, one must multiply ru by d_0 and by the crystallographic vector of distortion; e.g. the Si-Si crystal bond is 0.25 ru.)

The parameters of tetragonal distortion in (16) are in good agreement with band calculations of Baraff *et al* (1980), who obtained $V_e = -1.12 \text{ eV } \text{\AA}^{-1}$ and $e(0) = 0.023 \text{ ru}$. No references were found for electron-lattice parameters of the resonant A_1 state. Though the equilibrium relaxation $a(0)$ is small (less than 1% of crystal bond), it plays an important role in correlation correction.

The localization criterion (6) of effective correlation works well for all V reconstructions shown on figure 2. For the subset $S\{\mu a\}$, defining DB MOs, it is enough to take Si 3s and Si 3p AOs of the four atoms near V. For $p \pm \gamma = (23 \pm 1)\%$ only the bonding DB state B_2 is separated from all other occupied MO as a localized state (figure 1(b)). Correlation corrections have been calculated with the Fock matrix correction (14) and with $U = 0.25 \text{ eV}$, which is the effective correlation energy from the phenomenology of Baraff *et al* (1980). Theory for the multiplet

$$A_1^2 T_{2x}^a T_{2y}^b T_{2z}^c \quad a + b + c = 2 \tag{17}$$

of V^0 shows that near equilibrium reconstruction the ground-state term differs from the nearest excited term by more than U (Lannoo *et al* 1981). Thus, the ground-state self-consistent correction of section 2 makes sense. Figure 2 clearly demonstrates the semiempirical nature of the LA: energy correction of DB effective correlation ΔE (shown as shaded energy difference on figure 2) is not constant—it depends on reconstruction. It is important that $\Delta E \simeq 2U$ in equilibrium, varies with both distortions e and a , and even disappears at certain reconstructions. On the

other hand, ΔE is small in comparison with adiabatic lattice reconstruction energy variations (see figure 2)—a negative- U centre property.

Energy minima of adiabatic curves on figure 2 occur for the same lattice distortions, regardless of whether or not the correlation correction is included, though the depths of the minima are changed. Thus, we conclude, in agreement with negative- U phenomenology, that the electron-lattice term in E_{tot} is a leading one for Si:V⁰.

4.2. Si:H_i (interstitial hydrogen atom in antibonding (AB) position)

This centre plays an assisting role here, being a 'doping impurity' for the V-H defect LUCs with an odd number of electrons. After the 'doping' we get a LUC with an even number of electrons, and the closed-shell HF method can be applied (α and β spin electrons occupy equivalent pairs of MOs). The problem of the hydrogen atom state in Si crystal is a very complicated one (Deak *et al* 1988, 1990), but here we have the simple task to find such a position of the H atom that slightly perturbs the electron density of a crystal.

The INDO parameters of H simulate the H₂ molecule (Shluger 1985), and they can be found in table 1. Two H atoms have been inserted into Si16 in equivalent AB interstitial positions, i.e. forming straight lines Si-Si-H_i-T_d, where T_d means a symmetrical tetrahedral interstitial site. The interaction between H_i atoms has been found to decrease greatly when two AB directions inside the LUC were non-parallel and spaced by the largest possible distance. This Si16Hi(AB)₂ LUC has been used for H_i calculations.

All the Si atoms have been preserved in their crystal sites; the single variation parameter was the Si-H_i distance $d(\text{Si-H})$. E_{tot} minimum configuration has been found at $d(\text{Si-H}) = 0.13$ ru, but for the 'doping' purpose a value 0.16 ru fitted better, because it gave a small electron density perturbation. For $d(\text{Si-H}) = 0.16$ ru, atomic charges were +0.03 au on H_i and -0.07 au on the adjacent Si. The electron spectrum of H_i (figure 1(d)) differs from that calculated by the more precise (modified) MINDO/3 technique with first- and second-neighbour Si atom positions left free in the course of the search for the E_{tot} minimum (Deak *et al* 1988). The bonding MO (named B on figure 1(d)) must have a resonant energy level with valence band, and the antibonding MO A must be almost resonant with the conduction band. Certainly, if the Si atoms of the Si-Si-H_i line were free in this work to take positions predicted by MINDO/3, then $d(\text{Si-H})$ would decrease, tightening this bond and therefore increasing A-B splitting (figure 1(d)). The second reason for the non-resonant deep-level electron structure of H_i may result from the valence bandwidth ($\Gamma'_{25}-\Gamma_1$) underestimation by INDO parametrization of this work and overestimation by MINDO/3 (Deak and Snyder 1987).

So, as a 'doping impurity' we take the unrealistic interstitial H_i, which slightly perturbs the crystal electron density and weakly interacts with the V-H centre of interest.

4.3. Si:(VH₃)⁻ (reconstructed single dangling bond)

Inserting three H atoms into Si15V in the DB-passivating positions (as shown on figure 3), we get an ideal neutral DB model (Bar-Yam and Joannopoulos 1986). In order to stay within the closed-shell HF framework, a 'doping' H_i was added (i) at the largest possible distance from and (ii) with AB direction not parallel to the single

DB of VH_3 . It has been found, similarly to the ideal V case, that the electron structure of this Si15VH3H_i LUC could not be calculated without distortion of the V neighbourhood. During computations three Si atoms with passivated DB were excluded from the t distortion and preserved in their crystal sites. This simplification assumes that overlap of passivated DB is energy-unprofitable. Conformation properties of the model are depicted on figure 3: trigonal displacement t of the Si atom with DB and passivation distance $d(\text{Si-H})$ both greatly influence the equilibrium reconstruction.

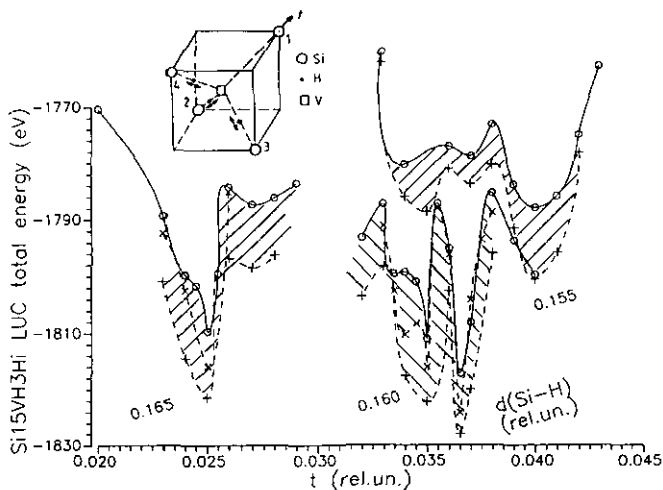


Figure 3. E_{tot} adiabatic curves of Si15VH3H_i : (O) HF; (x) HF with semiempirical LA, $U = 0.01$ au; (+) $U = 0.02$ au. Each set of curves united by shading represents the reconstruction with constant $d(\text{Si-H})$ written nearby in relative units. The absolute vector of $\text{Si}(1)$ atom displacement is $td_0[111]$.

From the not-less-than-two-dimensional character of the adiabatic energy surface, it may be concluded that one-dimensional calculations of VH_3 properties cannot be precise (Singh *et al* 1977).

The Si15VH3H_i spectrum (figure 1(c)) shows that H_i acts like a donor impurity, because the deep-level state B of H_i (figure 1(d)) passes its electron to the DB bonding state of VH_3 . Therefore, the DB state of VH_3 in this LUC is doubly occupied, and figures 1(c) and 3 show the properties of the charge state $(\text{VH}_3)^-$, known also as T^- or D^- in a-Si theory (Allan and Joannopoulos 1984). Of course, the LUC used is not large enough to diminish the parasitic effect of the $\text{VH}_3\text{-H}_i$ interaction. This effect shows itself by raising the deep level B of the periodic H_i model (figure 1(d)) about 20% E_{opt} , if every second H_i is changed to VH_3 (figure 1(c)). ($E_{\text{opt}} = \Gamma_{15}\text{-}\Gamma'_{25}$ varies slightly from one defect LUC to another. Since the HF method systematically overestimates the gap value (figure 1(a)), relative units (per cent of E_{opt}) fit better for deep levels.) However, the remaining $\text{VH}_3\text{-H}_i$ interaction seems not to be crucial for a conclusion about $(\text{VH}_3)^-$ properties, because the DB state B (figure 1(c)) is almost pure hybrid sp^3 of non-passivated Si and contains a negligible amount of H_i and its neighbouring AOs, and because the atomic charge of Si with DB is the largest in the LUC and varies slightly (-0.58 ± 0.01 au for all reconstructions of figure 3).

Although a two-dimensional reconstruction model has an E_{tot} minimum, the energy variations and barriers of the adiabatic surface on figure 3 are unrealistically large. In practice, Si V-H centre computations show that taking into account more lattice degrees of freedom makes adiabatic minima less sharp and lowers barriers. But the author could not obtain enough computer power to improve the results.

In contrast with E_{tot} the electron structure of $(\text{VH}_3)^-$ does not change greatly with reconstruction, e.g. the DB level B rises by about 1% of E_{opt} , if the reconstruction shifts from the main minimum $d(\text{Si-H}) = 0.160$ ru to the 'metastable' ones 0.165 or 0.155 ru (figure 3).

The localization criterion (6) works very well in the whole reconstruction range of figure 3. The subset $S\{\mu a\}$, defining a single DB, consists of unpassivated Si 3s and Si 3p. The threshold parameter $p \pm \gamma = (48 \pm 8)\%$ separates a single well localized DB state. The Fock matrix correlation correction (14) has been applied with $U = 0.02$, 0.01 and 0.005 au. The first value has been taken according to supercell calculations of Si DB (Bar-Yam and Joannopoulos 1986). The two other reduced values give better convergence of the SCF process and higher precision, which permits one to check the calculations. From figure 3 it is seen that correlation corrections ΔE calculated with different U values behave similarly, when the reconstruction changes, though the precision of self-consistency is proportional to U .

Comparing ΔE for V^0 and $(\text{VH}_3)^-$ we find some important differences.

(i) ΔE has the same order as U for V^0 , but for $(\text{VH}_3)^-$ in its adiabatic trigonal distortion minima $\Delta E \simeq 20U$.

(ii) ΔE is positive for V^0 and negative for $(\text{VH}_3)^-$. Knowing the sign of ΔE is not enough to judge the effective correlation sign of a centre; however, $\Delta E < 0$ is a very strong argument in favour of negative- U behaviour (section 5).

(iii) Not only E_{tot} but also the DB state B level of $(\text{VH}_3)^-$ has a non-negligible correlation correction in contrast with V^0 . For the equilibrium reconstruction (figure 1(c)) $\Delta E_B \simeq -60\% U$.

The large value of ΔE seems to be unrealistic, so the effective correlation energy U , as a matrix element of the Hamiltonian (9), cannot be identified with the correlation correction to E_{tot} of VH_3 ; otherwise, for V such identification is possible.

5. Discussion: analysing negative- U centres with the semiempirical local approach

In order to outline the applications of the semiempirical LA, devised above, we shall compare the results of *ab initio* methods with those reported in section 4.

The generalized valence-bond (GVB) method permits one to calculate ΔE_{corr} , the full difference between the HF and the *ab initio* values of a correlated finite electron system E_{tot} . This difference is the rigorous definition of 'correlation energy' and is always negative, because the GVB minimizes a many-electron wavefunction containing two-electron valence bonds, while the more restricted HF wavefunction (Slater determinant) consists of one-electron MOS. For the cluster model of unreconstructed Si:V⁰ (Si4H12V) the GVB calculations have been performed with two valence bonds, i.e. four electrons of the V DB have made up a correlated subsystem (Surratt and Goddard 1978). In other words, the localized electrons have formed a multiplet

$$A_1^d T_{2x}^a T_{2y}^b T_{2z}^c \quad a + b + c + d = 4 \quad (18)$$

where A_1 is a singlet state with full V symmetry and T_2 is a tetragonal triplet state. For the ground term of (18) it has been found that $\Delta E_{\text{corr}} = -2.0$ eV (figure 4). How can we compare this with the semiempirical LA correlation correction ΔE shown on figure 2?

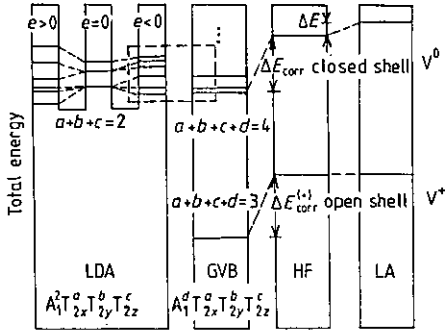


Figure 4. Schematic view of correlation corrections obtained by different methods. V^0 and V^+ are charge states with four and three electrons on DB (V^+ corrections are not actually calculated by either method). The LDA multiplet structure is shifted to match the GVB one.

(i) ΔE estimates the correlation effect of repulsion between two electrons localized at the V bound state. It is well known that a full description of the effect by the HF is impossible.

(ii) Being non-equivalent to the correlation energy ΔE_{corr} , the semiempirical ΔE may be positive (figure 2) or negative (figure 3), depending on type, neighbourhood and self-consistent properties of a defect.

(iii) ΔE_{corr} has 'absolute' nature; it shows the error of the HF calculation for a defect with a certain number of localized electrons. In contrast, ΔE has 'relative' nature; it shows the error of the HF calculation of energy difference between two defect charge states—with single and double occupation of the localized state. Figure 4 shows this situation schematically. The closed-shell LA of this work gives the correction only to the V^0 charge state with doubly occupied DB MO, while the GVB would modify any charge state HF energy.

Alternatively to the GVB, the *ab initio* method of the density functional (local density approximation (LDA)) permits one to calculate not only E_{tot} (including correlation) but also multiplet structure and Jahn–Teller properties of a defect (Lannoo *et al* 1981). Since the correlation energy cannot be extracted from E_{tot} of the LDA, we can compare only multiplet splittings of LDA and GVB (figure 4). There is almost identical splitting of the three lower terms of multiplets (17) and (18) of V^0 , calculated by LDA and GVB, outlined by the dashes on figure 4. The LDA predicts this splitting for two strongly correlated V^0 electrons and for some far-from equilibrium JT tetragonal distortion, while GVB predicts almost the same splitting for four correlated electrons of non-distorted V^0 . It seems that the semiempirical LA can fill the gap between two *ab initio* correlation approximation constructions: (i) it takes into account only correlation of the strongly localized electrons (two DB electrons in the case of V^0), but (ii) the correlation corrections are self-consistent and thus the resonant V^0 electrons of the A_1 state influence the corrections. The latter is confirmed by the same order of electron–lattice coefficients of resonant and bound states (16) and by the contribution of symmetrical JT distortion to ΔE (figure 2). Therefore, we can recognize in the semiempirical LA description of the reconstructed V^0 features of both *ab initio* approaches: of the LDA (electron correlation of two DB

bound electrons is compensated by the JT reconstruction, giving negative- U effective correlation, defined mainly by the conformation properties of the vacancy) and also of the GVB (correlation corrections depend self-consistently on two DB resonant electrons through their sensitivity to the reconstruction).

Now we shall turn to the problem of Si:VH₃ negative U . Can we prove that the (VH₃)⁺ state, stable at certain E_F , changes to (VH₃)⁻ with increase of E_F , i.e. that (VH₃)⁰ is unstable at any E_F ? The proof is not easy, because the total energies of the closed-shell and of the open-shell HF approximations are not comparable. Besides, there is a non-controlled 'doping' H_i contribution. However, using the scheme of figure 4 and the spectrum of figure 1(c), we can transform a negative- U condition

$$E((\text{VH}_3)^0; d', t') > E((\text{VH}_3)^-; d, t) - E_F \quad (19)$$

to the 'closed-shell' one

$$E_{\text{os}}^*((\text{VH}_3)^0; d', t') - E_{\text{os}}((\text{VH}_3)^0; d', t') < -\Delta E + E_{\text{os}}((\text{VH}_3)^-; d', t') - E_{\text{os}}((\text{VH}_3)^-; d, t). \quad (20)$$

Here (d', t') and (d, t) are the equilibrium distortions of the charge states 0 and -; E^* is a non-self-consistent energy of the charge state 0 calculated with the MO of the state -. In (20) Koopmans's theorem (Pople and Beveridge 1970) for $[E_{\text{os}}^*((\text{VH}_3)^0; d, t) - E_{\text{os}}((\text{VH}_3)^-; d, t)]$ is used. From figure 3 data, the right side of (20) can be evaluated. Thus, the condition (20) bypasses the problem of direct comparison (19) between the open- (os) and closed-shell (cs) forms of HF. If the right side of (20) exceeds the open-shell HF self-consistency correction $(E^* - E)_{\text{os}}$, then the centre has negative U . It is clear that even for $U = 0.01$ au (figure 3) the negative ΔE values are rather large, making (20) very probably true. Besides, the conformation contribution to the right side of (20) $(E - E)_{\text{os}}$ can be estimated from figure 3 as having the same order as ΔE .

6. Conclusions

The simple semiempirical local approach, based on the localization criterion for the molecular orbitals, modifies any quantum-chemistry calculation scheme so that effective electron correlation at the defect states can be estimated self-consistently. Technically, the approach gives a correction to the usual Fock matrix of the closed- or open-shell Hartree-Fock method.

The problem of dangling-bond negative- U centres in Si has been considered. The large-unit-cell model has been found to be rather realistic—crystal valence band structure, defect structure of the vacancy and of the vacancy with three passivated dangling bonds, vacancy reconstruction and electron-lattice parameters all fit theoretical and experimental data. Models of Si:V⁰ and Si:(VH₃)⁻ demonstrate the self-consistent and reconstruction-dependent nature of the dangling-bond effective correlation correction ΔE .

ΔE calculated for V⁰ near the equilibrium reconstructions can be identified with the correlation energy U of two electrons occupying a dangling-bond bound state. However, ΔE depends on two Jahn-Teller distortions and self-consistently depends on a resonant dangling-bond state, thus making negative- U phenomenology

unreliable, especially when applied to the far-from-equilibrium reconstructions (like in migration or reorientation processes).

ΔE calculated for $(\text{VH}_3)^-$ cannot be identified with a correlation parameter U and, therefore, negative- U phenomenology for this centre must meet certain difficulties. In fact, such is the situation around a dangling bond in a-Si:H. The present work confirms negative- U theory for Si:VH₃, but shows that the parameter U cannot be simply linked to the total energy. For example, values of U , having the same order as for Si:V, give an unrealistically large correlation correction to the total energy of Si:(VH₃)⁻.

Acknowledgments

This paper is part of the author's dissertation work and has been carried out at the computer centre of Riga Technical University. The basic quantum-chemistry program set CLUSTER and all necessary help were received from Alexander Shluger. I also wish to thank him and all the colleagues from his seminar at the University of Latvia for fruitful discussions. I am grateful to Peter Deak for his interest in this work and helpful comments.

References

- Allan D and Joannopoulos J D 1984 *The Physics of Hydrogenated Amorphous Silicon II (Topics in Applied Physics 55)* (Berlin: Springer)
- Bar-Yam Y and Joannopoulos J D 1986 *Phys. Rev. Lett.* **56** 2203
- Baraff G A, Kane E O and Schlüter M 1980 *Phys. Rev. B* **21** 3563, 5662
- Baraff G A and Schlüter M 1979 *Phys. Rev. B* **19** 4965
- Bernholm J, Lipari N O and Pantelides S T 1980 *Phys. Rev. B* **21** 3545
- Deak P, Heinrich M, Snyder L C and Corbett J W 1990 *Conf. on Quantum Chemistry of Solids (November 1990)* (Riga: Latvian University) Abstracts, p 161
- Deak P and Snyder L C 1987 *Phys. Rev. B* **36** 9619
- Deak P, Snyder L C and Corbett J W 1988 *Phys. Rev. B* **37** 6887
- Essick J M and Cohen J D 1990 *Phys. Rev. Lett.* **64** 3062
- Evařestov R A and Lovchikov V A 1979 *Phys. Status Solidi B* **93** 469
- Harker A H and Larkins F P 1979 *J. Phys. C: Solid State Phys.* **12** 2497
- Lannoo M, Baraff G A and Schlüter M 1981 *Phys. Rev. B* **24** 943
- Maksimov E G, Mazin I I, Savrasov S Yu and Uspenski Yu A 1989 *J. Phys.: Condens. Matter* **1** 2493
- Moliver S S 1988 *USSR J. Phys. Chem.* **62** 2518
- 1991 *USSR Solid State Phys.* **33** 929
- Pantelides S T 1988 *Acta Phys. Polon. A* **73** 861
- Pearson S J, Corbett J W and Shi T S 1987 *Appl. Phys. A* **43** 153
- Pisani C, Dovesi R and Roetti C 1988 *Hartree-Fock Ab Initio Treatment of Crystalline Systems (Lecture Notes in Chemistry 48)* (Berlin: Springer)
- Pople J A and Beveridge D L 1970 *Approximate Molecular Orbital Theory* (New York: McGraw-Hill)
- Shluger A 1985 *Theor. Chim. Acta Berlin* **66** 355
- Shluger A L and Kotomin E A 1981 *Phys. Status Solidi B* **108** 673
- Singh V A, Weigel C, Corbett J W and Roth L M 1977 *Phys. Status Solidi B* **81** 637
- Stefanovich E, Shidlovskaya E, Shluger A and Zakharov M 1990 *Phys. Status Solidi B* **160** 529
- Stollhoff G 1990 *Conf. on Quantum Chemistry of Solids (November 1990)* (Riga: Latvian University) Abstracts, p 26
- Stollhoff G and Fulde P 1980 *J. Chem. Phys.* **73** 4548
- Surratt G T and Goddard III W A 1978 *Phys. Rev. B* **18** 2831
- Watkins G D 1986 *Deep Centers in Semiconductors* (New York: Gordon and Breach) p 147