Theoret. Chim. Acta (Berl.) 66, 355-363 (1985)

THEORETICA CHIMICA ACTA

Application of molecular models to electronic structure calculations of defects in oxide crystals. I. Parametrization of the modified INDO method

Alexander Shluger

Chemical Faculty, Latvian State University, Rainis Blvd. 19, Riga, USSR

A modified calculation scheme of the INDO method is applied for calculating the electronic structure of perfect and imperfect oxide crystals. In order to obtain a flexible scheme permitting reliable calculation of both the electronic structure and the defect conformations, the INDO parameters for H, Li, Mg, Si, O are fitted directly to reproduce one-electron energies as well as the vicinity of the potential energy curve minima for a series of diatomic molecules and the electronic structure of MgO and β-crystoballite form of SiO_2. The method is tested on the Li_2SiO_3 crystal calculated within the framework of the large unit cell model.

Key words: SCF LCAO method for solids—INDO—parametrization—MgO—SiO_2—Li_2SiO_3

1. Introduction

So far there have been a number of CNDO (INDO) SCF calculations of the electronic structure of perfect 3D crystals [1-10] as well as their surface [11] and defects therein [1, 5, 12-15]. However, perfect ionic crystal calculations have yielded results which are not in good agreement with the known characteristics of their band structures [3, 6-8, 10]. Head et al [16] were the first to point out that these flaws could be due to a choice of empirical parameters (e.g. [17]), which was not appropriate for such highly ionic systems as alkali halide crystals. Some other authors [4, 5] also focused their attention on this point, attempting to find new parameters that could account for the *crystalline peculiarities* of ionic solids starting from the properties of diatomic homo- and heteronuclear molecules, which is in line with the standard parametrization by Pople and Beveridge [17]. Another approach is to modify the *calculating scheme* itself (e.g. incorporating the non-orthogonality of the Bloch functions [2]). The calculations of the properties of *defects* in crystals complicate the problem since ionic relaxations around defects along with one-electron energy spectrum should be obtained.

Bearing this in mind, we have recently suggested [6-9] improving *both* the parametrization and calculation schemes of the zero differential overlap methods. Thus, we were able to consider successfully not only the optical properties of defects in alkali halides [9, 12, 13], but also to simulate *processes* of defect creation [13], their interaction [15] and tunneling recombination [18]. In our opinion, the latter could be a very promising field for applying these methods efficiently.

The present paper sets out to carry out similar investigations on *oxide* crystals, which are now being intensively studied both theoretically and experimentally (e.g. [19-21]). Two *molecular* models will be widely used here - the *molecular cluster* and the quasi-molecular large unit cell (LUC) (supercell) [3-5, 22, 23].

A feature they have in common is the necessity to treat rather large crystalline fragments (>20 atoms) in order to obtain reliable results. It is due to necessity to find the eigenvalue spectrum at several Brillouin zone points $\boldsymbol{k}$ in the case of LUC model (in order to obtain the correct density matrix and to estimate the dispersion law $E(\boldsymbol{k})$) or else an attempt to weaken the effects of boundary conditions if the cluster model is used. The conclusion itself suggests that a series of such calculations could be carried out with quantum chemical *semiempirical* methods such as CNDO (INDO). Since quantum chemical methods usually treat *sets* of similar molecules, we shall consider a perfect crystal and as many *defects* in it as possible, thus obtaining more reliable results than by means of a single calculation.

Both theoretical calculations and experimental estimates show the oxygen effective charge to differ considerably from oxide: 1.6-$1.8e$ in MgO [24, 25], 1.0-$1.5e$ in SiO_2 [26], $\approx 0.8e$ in Al_2O_3 [27]. At any rate, it essentially *exceeds* that for organic compounds ordinarily used for the CNDO (INDO) parametrization which inevitably results in unrealistic MgO, α-quartz band structure features (first of all, absolute energies of band edges) if standard INDO parameters for Mg, Si, O [28] were used. On the other hand, the above mentioned large scattering of oxygen charges in oxides requires a flexible calculating scheme, which, as we believe, has been developed in [7-9].

In this paper we deal with the *optimization* of H, O, Mg, Si, Li INDO parameters which are then tested on the electronic structure calculations of perfect Li_2SiO_3 (in the present paper) as well as Li_2O crystal and number of defects in MgO and SiO_2 (in the forthcoming paper).

Since strictly speaking, any semiempirical parameters should be used in the framework of the *same* calculating scheme, which was employed in their derivation, the latter is briefly described below.

2. Modified INDO calculating scheme

The matrix elements of Fockian for the INDO-LUC model are given, e.g. in [3, 4, 8]. Since our modified calculating scheme has been described earlier [8, 9] we shall point out here its most important deviations from the standard one [17]. (i) The orbital exponents ζ (and sometimes bonding parameter β) are taken to be *different* for **s** and **p** AO's, which only permits to obtain the upper **np**-valence band wider than **ns**-valence band which is violated in the standard parametrization[1] (e.g. [3]). (ii) The one-exponential basis set is used, where ζ-values are varied during the parameter optimization and all one-centre exchange and Columb integrals are calculated *exactly* [29]. Two-centre Columb integrals $(\mu\mu|\nu\nu)$ and $(Z_B|\nu\nu)$ are also exactly calculated but if $\mu(\nu)$ are **p**-kind AO's their angular dependence is neglected. (This permits to retain the invariance with respect to the rotation of a general coordinate system.) It should be stressed that the use of appropriate formulae for two centre integrals presented, e.g. by Mataga and Ohno, along with large cut-off radius of summation (see point (iv)) leads to noticeable errors, in particular for the Madelung field on ions [7–9]. (iii) The diagonal matrix elements of the interaction of an electron occupying the μth valence AO on atom A with its own core are taken in the form

$$U^A_{\mu\mu} = -E^A_{\mathrm{neg}}(\mu) - \sum_\nu \left(P^{(0)A}_{\nu\nu}\gamma_{\mu\nu} - \tfrac{1}{2}P^{(0)A}_{\nu\nu}K_{\mu\nu}\right) \tag{1}$$

where $P^{(0)A}_{\nu\nu}$ are the diagonal elements of the density matrix ($=\nu$th AO populations), $\gamma_{\mu\nu}$ and $K_{\mu\nu}$ are one-centre Coulomb and exchange integrals, $-E^A_{\mathrm{neg}}(\mu)$ is the initial guess of the μth AO energy (ion's electronegativity). Therefore the effective potential $U^A_{\mu\mu}$ depends on E_{neg}, ξ_μ, $P_{\mu\mu}$ whose choice is discussed below. (iv) The matrix elements of an interaction of an electron on the μth AO belonging atom A with the core of another atom B are

$$V_{\mu B} = Z_B\{1/R_{AB} + [(\mu\mu|\nu\nu) - 1/R_{AB}]\,\mathrm{e}^{-\alpha_B R_{AB}}\}, \tag{2}$$

where R_{AB} is the distance between A and B, Z_B is the core charge of atom B, α_B is an additional adjustable parameter characterizing the *non*-point nature of the B's core. (The advantages of (2) as compared with other relations, e.g. standard Goeppert-Mayer and Sclar, $V_{AB} = Z_B\gamma_{AB}$, were discussed in [9]). Due to the cyclic boundary conditions the matrix elements of the LUC-Fockian contain lattice sums

$$S_{\mu\nu} = \sum_j S_{0\mu,j\nu}, \tag{3}$$

$$V^M_\mu = \sum_j \left(\sum_\nu{}^B P^B_{\nu\nu}\gamma_{0\mu,j\nu} - V_{\mu B}\right) \tag{4}$$

$$P_{\mu\nu}\Gamma_{AB} = P_{\mu\nu}\sum_j \gamma_{0\mu,j\nu}. \tag{5}$$

---

[1] As is known (e.g. [30]) different *s*- and *p*-parameters permit to improve considerably the conformations of molecules which is also important for the relaxation around defects in crystals

Here j denotes the summation over the whole crystalline lattice with the LUC basic vectors ($j=0$ for the cluster model). Summation over overlap integrals $S_{\mu\nu}$ is rapidly convergent due to exponential fall-off of the overlap with a distance. The Coulomb integrals $\gamma_{0\mu,j\nu}$ entering Eq. (4) mean $(\mu\mu|\nu\nu)$ with μ belonging atom A from the zero LUC whereas ν belongs atom B from the jth LUC. Therefore the matrix elements of the crystalline field V_μ^M could be easily calculated by standard methods known for bulk solids [32]. Finally, summation (5) in off-diagonal elements entering Fockian (instead of $P_{\mu\nu}^{\alpha}\gamma_{AB}$ for molecular calculations) is nothing but the effect of non-local exchange in the Hartree–Fock method (as well as its derivatives CNDO, INDO). Its recent careful analysis [33] has revealed that the use of several $\boldsymbol{k}$ points in the Brillouin Zone (typical for the LUC model) necessitates incorporation of the *weighting function* in (5) which sometimes can be approximated by the step-function with cut-off radius $R_{\mathrm{ex}} \simeq \frac{1}{2}$ length of the LUC translation vector.

Therefore our calculating scheme require the optimization of the *five* parameters for each atom: ξ_μ, $E_{\mathrm{neg}}^{A}(\mu)$, $P_{\mu\mu}^{(0)A}$, β_A, α_A.

3. Parameter optimization

The optimization of our INDO parameters consists of reasonable compromise between their fitting for reproducing *both* the one-electron energies, charge distribution and conformations of a series of diatomic molecules as well as band structure of perfect crystals (MgO and β-crystoballite in the present case). Namely, *absolute* energies of the edges of the upper valence bands, their midpoints, E^m, and widths, E^w, the gap, E_g, effective charges for ions, $\boldsymbol{q}$, in crystals and the equilibrium distances, R_e, and potential energy curves in the vicinity of their minima for molecules are considered as their mean features [7–9] (cf. [5]). As is well known [34, 35], a direct comparison of the gap and midpoints of bands calculated within the Hartree–Fock method (or its simplification as the INDO is) with the experimental data is not justified since so-called *correlation corrections* should be added preliminary to the calculated one-electron energies. These corrections consist of short-range and long-range components [34, 35]. Since short-range corrections (which in fact have atomic character) are effectively taken into account in the course of our parameter optimization, the *sum* of the calculated one-electron gap, E_g^{th}, and long-range corrections should be fitted to the experimental gap. (In our opinion, these long-range corrections *cannot*, in principle, be taken into account through atomic parameters since they arise due to crystal polarization by an electron and hole obviously having *many*-centre nature.) The long-range corrections are calculated for MgO [25], but unfortunately are absent for SiO_2. The latter calculations are greatly complicated by a mixed nature of valence bands in SiO_2 (unlike alkali halides and MgO). However we believe that a whole *trend* holds for all wide-gap insulators: the upper valence band rises whereas the conduction band is lowered thus reducing the Hartree–Fock forbidden gap by a sum of long-range corrections ($2.4+2.1=4.5$ eV for MgO).

The electronic structure for most of molecules and their R_e are calculated by means of the *ab initio* GAUSSIAN-70 method employing 6-31G Gaussian basis set for O and H and 6-21G [36] for Li and Si. When calculating the electronic structure of the perfect MgO and SiO_2 (β-crystoballite), the LUC's Mg_8O_8 and Si_8O_{16} were used permitting to obtain the energies at Γ, X, L points of the Brillouin Zone.

As a starting point the INDO parameters for H $E^{H}_{neg} = 7.18$ eV, $\zeta_H = 1.2$ a.u., $\beta_H = -9$ eV were used. Two other parameters, $P^{(0)}_{\mu\mu}$ and α_H, were fitted to reproduce R_e and the ionization potential of the H_2 molecule. Then the preliminary oxygen parametrization was achieved making use of OH and H_2O molecules (cf. [37]). Their further optimization was done trying to get a *compromise* between the electronic structure of MgO, SiO_2 crystals and the properties of a number of molecules: O_2, O_2^-, LiO, Li_2O, SiO, SiO^+, SiO_2, SiO_2^-, MgO (see below). The additional data for Li_2, LiSi molecules were also used for the Li parametrization, Si_2, Si_2^+, SiH - for Si, and Mg_2 molecule - for the Mg parametrization.

The initial choice of parameters corresponds to ions O^{2-}, Si^{2+}, Mg^{2+}, Li^+. Since the O^{2-} ion could be stable in a crystalline field only, an initial guess for the E^{2p}_{neg} is taken in a positive energy spectrum due to which the corresponding AO's are delocalized as compared to those in a free atom O. In their turn, the initial guesses for cations are lower as compared to the free atom whereas AO's are compressed. Such a behavior of parameters correctly reproduce a trend of the AO's asymptotics when an ion is substituted for an atom. (These parameters are physically transparent for Si^{2+} only, since they describe the state of two remaining electrons. For Mg^{2+} and Li^+ they describe *virtual* (vacant) states, determining the bottom of the conduction band, which have not so clear an interpretation.) The parameters $P^{(0)A}_{\mu\mu}$ entering the diagonal matrix element $U^{(A)}_{\mu\mu}$ (Eq. (1)) were varied in the course of the parameter optimization in order to obtain $P^{(0)A}_{\mu\mu}$ values coinciding with the diagonal elements of the self-consistent density matrix for MgO and SiO_2 crystals. The values $U^{A}_{\mu\mu}$ thus obtained were *fixed* during further calculations. The parameters derived are given in Table 1.

Despite the "ionic" character of the initial guess for parameters, use for their optimization of *both* ionic and covalent compounds still permits to reproduce

Table 1. The optimized INDO parameters[a]

Atom		ξ_μ (a.u.)$^{-1}$	$E^{A}_{neg}(\mu)$, eV	$-\beta_A$, eV	α_A (a.u.)$^{-1}$	$P^{(0)}_{\mu\mu}$, e
H	1*s*	1.2	7.18	9.0	0.3	0.8
Li	2*s*	0.9	2.5	1.1	0.3	0.1
O	2*s*	2.27	4.5	16.0	0.0	1.974
	2*p*	1.86	−12.6	16.0	0.0	1.96
Mg	3*s*	1.4	16.0	1.1	0.25	0.15
Si	3*s*	1.93	23.03	4.5	0.1	0.63
	3*p*	1.76	16.03	4.5	0.1	0.59

[a] These parameters were derived to minimize the sum of deviations of the bond lengths, $(R_e^{th} - R_e^{exp})^2$, for 14 molecules shown in Table 2.

Table 2. Calculated equilibrium distances for diatomic molecules (a.u.)[a]

Molecule	OH	O_2	O_2^-	Li_2	LiO	Li_2O	Si_2	Si_2^+	SiO	SiO^+	SiO_2	SiLi	Mg_2	MgO
Ground state	$^2\Pi_i$	$^3\Sigma_g^-$	$^2\Pi_g$	$^1\Sigma_g^+$	$^2\Pi$	$^1\Pi_u$	$^3\Sigma_g^-$	$^2\Pi_u$	$^1\Sigma^+$	$^2\Sigma^+$	$^1\Pi_g$	$^2\Pi$	$^2\Sigma^+$	$^1\Sigma^+$
R_e^{th}	1.9	2.4	2.5	4.6	3.23	3.1	3.3	5.1	2.95	3.1	2.95	4.9	6.3	3.3
R_e^{exp} [38]	1.83	2.28	2.53	5.05	3.3	3.1	4.24	4.6	2.85	3.1	2.93	5.1	7.35	3.31

[a] The underestimations of the bond lengths of some homopolar molecules (except for O_2) is probably due to greatly limited basis set (see Table 1) and too compact wavefunctions.

quite adequately the properties of systems with different nature of chemical bonds (Table 2). However, an "ionic" character of the optimized parameters *prevails* on the whole, and this is required to reproduce correctly the electronic structure of *ionic* crystals MgO and SiO_2. In its turn, good simultaneously obtained for the purely *covalent* molecules O_2, Si_2, etc. bear witness to a successful choice of the parameters of an effective potential (1).

4. Discussion

The derived parameters are given in Table 1, whereas the equilibrium distances for molecules[2] and the electronic structure of MgO crystals and β-crystoballite are summarized in Tables 2, 3. The conclusion may be drawn that R_e values in Table 2 are close to the experimental data except for Mg_2 and Li_2. However, the potential energy curves of these molecules are rather flat (e.g. the dissociation energy of Mg_2 is 1.154 kcal/mol only) and the deviation of the R_e^{th} that from R_e^{exp} does not affect essentially the R_e values for complexes containing Li, Mg. The nature of valence bands of MgO and SiO_2 crystals is in good agreement with other band structure calculations [20, 35]. (This will be discussed in more detail in the second part of the paper.)

Making use of the derived parameters, the electronic structure of Li_2SiO_3 crystal in the LUC model is calculated for the first time. Its spatial structure is given in [39] and presents a set of distorted tetrahedral [LiO_4] and [SiO_4] tied by their vertexes. A primitive cell is rather large and contains 12 atoms which makes calculation of the four-fold LUC (48 atoms = 144 basic functions) beyond our possibilities. Thus, we confined ourselves to the primitive cell, i.e. the Γ point of the Brillouin Zone, was treated only (Table 3). The top of the valence bands is

Table 3. Electronic structure properties obtained with the LUC model for three oxide crystals[a]

	Crystal				
	MgO		SiO_2		Li_2SiO_3
Property	theor.	exp.	theor.	exp.	theor.
$-E^m$, eV	8.8	8.8	13.5	13.2	12.7
E^w, eV	4.6	6.0	9.4	10.0	8.1
E_g, eV	11.4	7.8	10.6	11.5	8.6
q, e	1.8	≈ 1.4	1.56[b]	1.2	1.5

[a] Correlation corrections are *not* taken into account here, i.e. the calculated E_g are overestimated by about 4 eV (see text).
[b] The oxygen charge.

---

[2] For compactness the R_e values are given in Table 2 only. Note that the calculated INDO one-electron energies are also in good agreement with the *ab initio* calculations

high than that for the β-crystoballite and consists mainly of π-oxygen states. The upper valence band width is slightly reduced as compared to the β-crystoballite which however may be also due to smallness of the cell used. Respectively the bottom of the conduction band is lowered and consists of 35% Li AO's, 40% of Si AO's and 25% O AO's. It is in line with the experimental data indicating that the bottom of the conduction band of alkali silicates has a large contribution of *metal* states [38]. Despite the fact that it represents the Γ point only and that its extension could alter the results obtained they nevertheless are in good qualitative agreement with the available experimental data [40]. The next part of the paper deals with the comparison of cluster model and the LUC for MgO and SiO_2 znd point defects in them.

References

1. Hayns, M., Dissado, L.: Theor. Chim. Acta (Berl.) **37**, 147 (1975)
2. Perkins, P., Marwaha, A., Steward, J.: Theor. Chim. Acta (Berl.) **57**, 1 (1980)
3. Evarestov, R. A., Lovchikov, V. A.: Phys. Status Solidi **B89**, 743 (1977); **B93**, 469 (1979)
4. Harker, A. H., Larkins, F. P.: J. Phys. C: Solid State Phys. **12**, 2487, 2497, 2509 (1979)
5. Itoh, N., Stoneham, A. M., Harker, A. H.: J. Phys. C: Solid State Phys. **10**, 4197 (1977)
6. Shluger, A. L., Kotomin, E. A., Ermoshkin, A. N., Dzelme, Yu.: Izv. Akad. nauk Latv. SSR, fiz., No. 3, 116 (1979)
7. Shluger, A. L., Kotomin, E. A., Dzelme, Yu.: Phys. Status Solidi **B96**, 91 (1979)
8. Shluger, A. L., Kotomin, E. A.: Phys. Status Solidi **B108**, 673 (1981)
9. Shluger, A. L., Kotomin, E. A.: Teor. Eksp. Khim. **19**, 630 (1983)
10. Matos, M., Maffeo, B., Zerner, M. C.: J. Phys. C: Solid State Phys. **15**, 7351 (1982)
11. Ermoshkin, A. N., Shluger, A. L., Kotomin, E. A.: J. Phys. C: Solid State Phys. **15**, 847 (1982)
12. Kotomin, E. A., Shluger, A. L., Dzelme, Yu.: Phys. Status Solidi **B98**, 427 (1980)
13. Kotomin, E. A., Shluger, A. L.: Phys. Status Solidi **B109**, 75 (1982)
14. Kotomin, E. A., Shluger, A. L.: Solid State Commun. **40**, 669 (1981)
15. Kotomin, E. A., Shluger, A. L., Tāle, I. A.: Solid State Commun. **46**, 625 (1983)
16. Head, J. D., Mitchell, K. A. R., Williams, M. L.: Molec. Phys. **29**, 1929 (1975)
17. Pople, J. A., Beveridge, D. L.: Approximate molecular orbital theory, New York: McGraw-Hill 1970
18. Shluger, A. L., Kotomin, E. A., Kantorovich, L. N.: Solid State Commun. **42**, 749 (1982)
19. Hughes, A. E., Henderson, B. in: Point defects in solids, p. 381, New York: Plenum Press 1972
20. Chelikowsky, J. R., Schluter, M.: Phys. Rev. **B15**, 1020 (1977)
21. Batra, I. P.: J. Phys. C: Solid State Phys. **15**, 5399 (1982)
22. Evarestov, R. A.: Quantum chemical methods in solid state theory. Leningrad: State University Press 1982
23. Evarestov, R. A., Kotomin, E. A., Ermoshkin, A. N.: Molecular model of point defects in wide-gap solids. Riga: Zinātne 1983
24. Batsanov, S. S.: Zh. neorg. khim. **20**, 2595 (1975)
25. Ermoshkin, A. N., Kotomin, E. A., Evarestov, R. A.: Phys. Status Solidi **B72**, 787 (1975)
26. Hübner, K.: Phys. Status Solidi **(a)40**, 133 (1977)
27. Lewis, J., Schwarzenbach, D., Fiack, H. D.: Acta Crystallogr. **A38**, 733 (1982)
28. Gubanov, V. A., Zhukov, V. P., Litinskii, A. O.: Semiempirical methods of molecular orbitals in quantum chemistry. Moscow: Nauka 1976
29. Guseinov, I. I.: J. Chem. Phys. **67**, 3837 (1977)
30. Gineitite, V. L., Balavichus, L.-M.: Zh. str. khim. **23**, 68 (1982); Teor. Eksp. Khim. **19**, 432 (1983)
31. Zakharov, I. P., Litinskii, A. O., Balavichus, L.-M.: Teor. Eksp. Khim. **18**, 16 (1982)
32. Ziman, J.: Principles of the theory of solids. Cambridge: Univ. Press 1972
33. Evarestov, R. A., Lovchikov, V. A., Tupitsin, I. I.: Phys. Status Solidi **B117**, 417 (1983)

34. Pantelides, S. T., Mikish, D. J., Kunz, A. B.: Phys. Rev. **B10**, 2602 (1974)
35. Pantelides, S. T., Mikish, D. J., Kunz, A. B.: Phys. Rev. **B10**, 5203 (1974)
36. Gordon, M. S., Binkley, J. S., Pople, J. A.: J. Amer. Chem. Soc. **104**, 2797 (1982)
37. Yip, K L., Fowler, B.: Phys. Rev. **B10**, 1400 (1974)
38. Handbook of molecular constants of inorganic compounds, ed. Krasnov, K. S., Leningrad: Khimiya 1979
39. O'Keeffe, M., Hyde, B. G.: Acta Crystallogr. **B34**, 3519 (1978)
40. Trukhin, A. N., Tolstoi, M. N., Glebov, L. B., Savel'ev, V. L.: Phys. Status Solidi **B99**, 155 (1980)

Received December 12, 1983/April 25, 1984