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Quantum-Chemical Calculations of Electronic and Hole Centres and Surface of NaCl Crystals (I)

By

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A new parametrization scheme for electronic structure calculations of defects in alkali halides by the CNDO semiempirical method is presented and developed. The model of a molecular cluster is used taking into account, for the first time, the non-point nature of ions *outside* the cluster, which considerably reduces the surface effect. The derived parameters reflect the ionic nature of the NaCl crystal. An attempt to calculate the F centre properties (first of all the position of its ground state level within the gap and the spin density on the neighbouring ions) indicates the necessity to extend the valence basis set by introducing an additional wave function centered at the vacancy. The parameters of the latter are derived.

Предложена новая схема параметризации полуэмпирического метода ПШДП, предназначенная для расчета электронной структуры дефектов в щелочно-галогенидных кристаллах. Использована модель молекулярного кластера. Впервые учитывается при этом неточность ионов *вне* кластера, что значительно уменьшает поверхностный эффект. Полученные параметры отражают ионную природу кристалла NaCl. Попытка вычисления характеристик F центра (прежде всего, положения уровня основного состояния в запрещенной зоне и спиновой плотности на ближайших ионах) показывает необходимость расширения валентного базиса добавлением волновой функции, централизованной на вакансии. Получены параметры последней.

1. Introduction

Most theoretical papers dealing with the electronic structure of defects in crystals focus their attention mainly on the calculation of optical transition energies, but very rarely defect level positions in the band scheme of a perfect crystal are considered. For instance, numerous F centre calculations based on different models yield, as a rule, good absorption energies but very different *absolute* energies of the ground state [1]. On the other hand, the position of the defect level within the gap determines directly the efficiency of such processes as the tunneling recombination of defects, carrier ionization into the conduction (valence) band, chemiluminescence arising when a coloured crystal is dissolved.

Modern calculations of defect properties along with atomic (ionic) defect properties usually take into account the electronic structure of ions surrounding a defect, which appears to be important for both covalent and ionic (e.g. alkali halide) crystals. The latter approach is usually realized in the form of molecular defect models (molecular cluster (MC) [2], large unit cell (LUC) [3]). This approach permits to calculate the electronic structure of such non-point defects as molecular ones, aggregate centres, crystal surface, etc. Unlike the traditional variational methods [4], the above models permit, in the framework of the same calculation scheme, to consider *both* a perfect and defect

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containing crystal, and this is necessary for placing defect levels within the gap of the perfect crystal.²⁾

A distinctive feature of the molecular models is the consideration of systems containing a large (several tens) number of electrons of atoms surrounding a defect. Due to this the molecular models are usually realized by some semiempirical quantum-chemical method. Their relative simplicity results from the use of a number of empirical parameters in the calculation scheme. Semiempirical methods have been successfully employed to calculate molecules with chemical bonds of widely differing nature.

One of the most popular methods of quantum chemistry — the CNDO (complete neglect of differential overlap) [6] — recently has been also applied to defect calculations in crystals [7]. However, in order to take into account the peculiarity of the crystal both the existing calculation scheme and the parameters have to be modified (cf. [8 to 11]).

In the first part of this paper we consider the principles of the new parametrization illustrated on the perfect NaCl crystal and the bulk F centre. The second part of the paper deals with bulk hole (H , V_K) centres and surface defects (including the surface as a defect). The positions of defect levels within the perfect crystal gap are determined and electron density and spin distributions are analysed.

Our results for the F centre are compared with those obtained by the Mulliken-Ruedenberg semiempirical method, which differs essentially from the CNDO method.

2. Calculation Scheme and CNDO Parametrization

2.1 Choice of parameters

In recent years several attempts have been made to derive CNDO parameters capable of yielding values close to the experimentally observed features of the perfect alkali halides [8 to 10]. As a rule, the traditional way (widely used for organic molecules) to obtain parameters has been to fit them so as to reproduce certain features of *diatomic* molecules (Me_2 , X_2 , MeX). However, the analysis [8] shows that such a way of fitting parameters usually gives rather poor values for the forbidden gap, the valence band widths, and the cohesive energy of the crystal. This is because such an approach to the parametrization problem fails in taking into account the peculiarity of the crystal. In particular, the effective charges of atoms in a diatomic heteronuclear molecule are less ionic than in the respective alkali halide crystal. (This is even the more so because the parameters are often fitted to *homonuclear* molecule properties.) In both cases the internuclear separation differs considerably from that in a crystal. The basis set of calculations is usually very restricted (as a rule, valence AO's only) and its choice affects the results. At first sight it seems reasonable to employ the *ionic* AO's for alkali halides. However, the real functions of ions in crystals differ from those of *free* ions (e.g. [12]). As is well known, the ionization potentials of atoms essentially differ from those for ions, and this is to be reflected by the electronegativity parameters. Ions with closed shells interact chemically in a way different from atoms, which again is to be seen in the bonding parameters β .

It follows from what has been said above that a change of the traditional parametrization scheme is necessary in order to calculate ionic (e.g. alkali halide) crystals. We propose to fit the CNDO parameters by calculating a MC which simulates the perfect crystal. The MC is embedded into an electrostatic field of ions outside the MC keeping in mind that, contrary to the general view, we are dealing with non-point ions.

²⁾ The same problem can be considered in terms of the much more complicated Green's function method [5] which does not eliminate the use of semiempirical parameters either.

The parameters being fitted to the experimentally observed features of the perfect crystal are then used for calculating the *defect* properties and *no* additional parameters are required.

Our parametrization scheme is in line with the principles of the semiempirical approach to the electronic structure calculations. On the other hand, preceding parametrizations [8 to 10], developed in a more indirect way, reproduce unsatisfactorily the band features of the perfect crystal (Table 1) (which are indispensable for defect calculations).

Table 1

Results of calculations for NaCl crystal based on the MC CNDO approach for different parametrizations (energies in eV)

feature	[6]	[7b]	[8]	[11]	present paper	<i>f</i>	exp. [17]
E_w^p	0.61 ^{a)} 0.31 ^{b)}	1.8	2.02 ^{c)}	1.1	1.92 ^{b)} 3.38 ^{e)}	4.1	4.1
$-E_m^p$	8.84 ^{a)} 5.06 ^{b)}	6.0		10.22	9.48 ^{b)} 10.5 ^{f)}	11	10.5
ΔE_g	8.95 ^{a)} 21.97 ^{b)}		13.50 ^{c)} 10.57 ^{d)}	7.2	8.82 ^{b)} 8.70 ^{f)}	8.5	8.6
$q(e)$	0.91 ^{a)} 0.97 ^{b)}		0.6 ^{c)} 0.9 ^{d)}	0.94	0.93 ^{b)} 0.90 ^{f)}	0.87	0.76 [18]

a) Point ion model, 16-atom MC. b) Non-point ion model, 4-atom MC. c) 27-atom MC. d) 80-atom MC. e) Non-point ion model, 16-atom MC. f) Non-point ion model, 27-atom MC.

In order to take into account the polarization effect, in our calculations the polarization correction for the valence band (1.5 eV [19]) is added to E_m^p and the sum of corrections for the valence band and conduction band (2.5 eV [19]) is subtracted from the calculated gap value.

To obtain parameters one has first to obtain the relations between the perfect crystal features and the parameters sought for. These relations depend, however, on the model of the electrostatic field of the rest of a crystal outside the MC.

Therefore, let us first consider this problem.

2.2 Electrostatic field of non-point ions

The MC simulating the perfect or imperfect crystal is traditionally embedded in the electrostatic field of the *point* ions outside the MC ("reduced Madelung") [2] whose energy in the site A is (in atomic units)

$$V_A = \frac{-\text{sign } Q_A M |Q|}{a_0} - \sum_{B \in \text{MC}} \frac{Q_B}{|\mathbf{R}_A - \mathbf{R}_B|}, \quad (1)$$

because the interaction of an electron localized on the ion A with other MC ions is considered in the course of the MC calculation. (Q stands for the self-consistent effective charges of ions, M is the Madelung constant).

The energy of the latter interaction is usually taken in the CNDO method as

$$V_A = \sum_{B \neq A} \{P_{BB} \gamma_{AB} - V_{AB}\}; \quad P_{BB} = \sum_{\mu \in B} P_{\mu\mu}, \quad (2)$$

where $P_{\mu\mu}$ are density matrix elements, γ_{AB} two-centre Coulomb integrals. The V_{AB} term, describing the interaction energy of the A atom electron with a core of the B

atom, is usually employed in the Gipert-Mayer-Selvar approach, that is $V_{AB} \approx Z_B \gamma_{AB}$, where Z_B is the core charge. Thus, one gets

$$V_A = \sum_B Q_B \gamma_{AB}, \quad (2a)$$

where $Q_B = P_{BB} - Z_B$ are the self-consistent ion charges.

Such different approaches in considering interaction of electrons with ions inside and outside the MC are obviously inconsistent and lead to a surface effect. In our opinion it is more reasonable to calculate the quantity desired also taking into account the non-point nature of ions *outside* the MC, that is

$$V_A = \sum_{B \in MC} Q_B \gamma_{AB}. \quad (3)$$

This leads to a marked difference in the absolute values of the field energy on cation and anion lattice sites; the former is 0.57 at. units but the latter -0.11 at. units,³⁾ whereas the point-ion energies are ± 0.298 at. units. It is obvious that the role of the non-point-ion field of the rest of a crystal is minimal for a central ion in the symmetrical MC because this effect is appreciable within 3 to 4 spheres around a given ion. The crystal field is calculated below by (3).

2.3 NaCl crystal parameters

We fitted the CNDO parameters first using the small $[\text{Na}_2\text{Cl}_2]$ MC, which permits to estimate semi-quantitatively the relation between these features and the parameters sought for. The analysis of these relations permits rapid fitting of parameters for the greater neutral MC $[\text{Na}_8\text{Cl}_8]^{4)}$ (similar to Fig. 2c in [14]).

Let us consider the relations in question. The widths of the p-valence band, E_w^p , and the forbidden gap, ΔE_g , are usually regarded as the distinctive features of the perfect crystal [8 to 10]. However, the CNDO method is not capable of reproducing exactly the vacant states of the conduction band and we shall use the absolute value of the p-band middle, E_m^p , (well-studied experimentally [17]) rather than ΔE_g as a more reliable test.

Mainly due to the non-point potential, the MC calculations with "standard" parameters [6] lead to unreasonable features of the perfect crystal, e.g. $E_m^p = -6.56$ eV, $E_w^p = 0.31$ eV, $\Delta E_g = 26$ eV (cf. Table 1, first column).

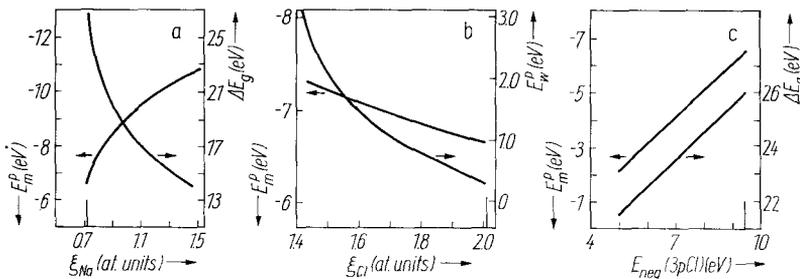


Fig. 1. Dependence of distinctive crystal features on CNDO parameters. Marks indicate standard parameters [6]

³⁾ γ_{AB} is calculated by the Ohno relation [13], $\gamma_{AA(BB)}$ as in [6] with the ξ value from Table 2. Other ways of $\gamma_{AA(BB)}$ calculation yield a similar result, $Q = 0.9$.

⁴⁾ As is shown in [15, 16], further increase of the MC size slightly changes the perfect crystal features. A neutral MC reproduces better the absolute energies and the number of its electrons is independent of the effective ion charges [14].

The relations obtained for E_m^p , E_w^p , and ΔE_g versus the parameters varied are plotted in Fig. 1. (The initial values of the parameters are taken from [6].) The variation of the parameters shows that the E_m^p value is determined mainly by the orbital exponent ξ_{Na} and the electronegativity $E_{neg}(Cl)$ ($= \frac{1}{2}$ (ionization potential + electron affinity)). The considerable influence of the first parameter is due to the dependence of the non-point-crystal field upon the effective ion radius. The latter is characterized by ξ_{Na} , ξ_{Cl} values which determine the $\gamma_{AA(BB)}$ values employed then in the field calculation (equation (3)).

From Fig. 1a one can conclude that the E_m^p , ΔE_g values are close to the experiment (Table 1) when ξ_{Na} is considerably increased (hereafter changes mean deviation from the standard parameters [6]). The effective charges of ions are not actually changed simultaneously whereas E_w^p increases from 0.31 to 0.42 eV. The decrease of the ξ_{Cl} value slightly affects E_w^p , but considerably improves the agreement of E_w^p with the experiment (Fig. 1b). It should be noted that if the point-ion field is used, the increase of ξ_{Na} leads to an increase of ΔE_g and does not noticeably change E_m^p (unlike the present case).

E_{neg} of anions is less than that for neutral atoms (the opposite effect is observed for cations), which has to be taken into account in the parametrization of an ionic crystal. The increase of $E_{neg}(Na)$ leads to a decrease of ΔE_g , but other (e.g. E_m^p) parameters are slightly changed. Again, the decrease of $E_{neg}(3p Cl)$ leads to an increase of E_m^p and to a decrease of ΔE_g (Fig. 1c).⁵⁾

Similarly, in considering an ionic crystal, the bonding parameters β_{Na} , β_{Cl} have to be decreased, which leads to a decrease of the widths of s, p valence bands whereas E_m^p remains constant, the ΔE_g change is less than 1.5 eV.

After the above-described trends were clarified, the 16-atom MC $[Na_8Cl_8]$ calculations were performed by fitting simultaneously all the parameters until the calculated features were in good agreement with the experimental values.

Table 2
The parameters derived for NaCl crystal

species	ξ (at. units)	E_{neg} (eV)	β (eV)
Cl 3p	1.51	8.6	— 4.2
3s		21.7	
Na 3s	1.21	4.1	—16.4
F centre	0.543	0.24	— 5.7

The derived parameters are given in Table 2. One can conclude that the obtained ξ_{Cl} values are rather close to the orbital exponent of the 3p Cl^- wave function in the NaCl crystal [12]. The 3s Na exponent shows also ionic trend. Thus, the optimized parameters reflect the ionic character of the chemical bonding in an ionic crystal.⁶⁾

In Table 1 we have compared the features of the NaCl crystal, calculated by different parametrizations, with the experimental data. One can conclude that the quite recent NaCl parametrization [8] is also not a satisfactory one and better perfect crystal features can be obtained by combining these parameters with those from [6].

Concluding this section it should be stressed that in order to compare ΔE_g with the experiment the polarization corrections have to be taken into account (e.g. as in [14]) which appreciably decreases the calculated ΔE_g and often breaks down the agreement with the experiment.

⁵⁾ A similar procedure has been used in [20] for a LiF crystal and it noticeably improved the calculated features.

⁶⁾ Jain [8] presented $\xi_{Cl} = 2.07$ at. units *exceeding* the chlorine atomic value [6] which contradicts what has been said before. A trend similar to ours of the ξ_{Cl} , β_{Na} , β_{Cl} parameters was recently obtained in [10] for KCl crystal by rather complicated fitting (involving perfect crystal features).

3. Bulk F Centre

The recent semiempirical F centre calculations for MgO and alkali halide crystals based on the Mulliken-Ruedenberg method (assuming no a priori distribution of the unpaired electron density and the symmetry of local states — contrary to the traditional variational method [4]) have yielded correct symmetries of the ground and first excited states as well as a very reasonable absorption energy [14 to 16]. Thus, these properties of the F centre are due to the crystalline environment of a vacancy (unlike the impurity case).

However, the *positions* of the one-electron F centre ground and excited states within the gap are reproduced unsatisfactorily (the only exception is KCl crystal) ([14, 15] and Table 3), and the share of the electron charge inside the nearest-cation sphere around a vacancy is rather small.

To reproduce correctly the desirable features it is reasonable to extend the basis set by introducing an additional function (AF) centered at a vacancy. Such a calculation *combines* the advantages of the traditional variational method [4] and of the molecular methods taking into account the electronic structure of the ions surrounding the defect.⁷⁾

Therefore, we performed the F centre calculations employing both the valence basis set (3s, 3p Cl, 3s Na AO's given in Table 2) and the extended one (including the AF). In the MC model the F centre has been simulated by an anionic vacancy surrounded by three ionic spheres directly introduced into the MC and the rest of the crystal as described in Section 2.2.

To relate the F centre ground state to the perfect crystal band scheme we have matched the middle energies of the deep 3s ClAO's in two MC's (simulating the perfect and imperfect crystals) assuming that a defect perturbs these deep states negligibly (Section 2.2 in [14]). This procedure permits to relate the one-electron energies of MC's of different sizes, point symmetries, and total charges.

To introduce the AF one has to assign three CNDO parameters: ξ_F , β_F , $U_{\mu\mu}^F$. In [10] the latter has been fitted through E_{neg} to obtain the experimental absorption energy, ξ_F corresponds to the point-ion model, $\beta_F = 2U_{\mu\mu}^{\text{Mc}} - \beta_{\text{Mc}}$. In our view it is reasonable to choose the parameters in another way.

When considering $U_{\mu\mu}^F \equiv \langle \mu | -\Delta/2 + V_A | \mu \rangle$ ($|\mu\rangle$ is the AF) as a fitting parameter, one can write

$$U_{\mu\mu}^F = \frac{1}{2} \xi_F^2, \quad (4)$$

because $V_A = 0$ for a vacancy, that is the field in which an electron moves is produced only by electrons and ions around a vacancy.

The diagonal element of the Fock matrix for the AF in the CNDO approximation reads

$$F_{\mu\mu}^\alpha = U_{\mu\mu} + (P_{AA} - P_{\mu\mu}^\alpha) \gamma_{AA} + \sum_{B \neq A} \{P_{AA} \gamma_{AB} - V_{AB}\} +$$

+ the potential energy produced by the non-point ions outside the MC. (5)

Here $P_{AA} = \sum_{\mu \in A} (P_{\mu\mu}^\alpha + P_{\mu\mu}^\beta)$, where $P_{\mu\mu}^{\alpha(\beta)}$ are the density matrix elements for $\alpha(\beta)$ spin, V_{AB} is usually taken as $Z_B \gamma_{AB}$.

The first term in (5) is the electron kinetic energy, the second one the difference of the one-centre Coulomb and the exchange energies, the third one the energy of the non-point interaction of the AF electron with the MC ions.

⁷⁾ Quite recently this approach has been realized in [10] for the KCl crystal. However, the authors fitted the AF electronegativity to obtain the optical absorption energy and did not consider the properties we are interested in.

As has been pointed out, our calculation of the electrostatic lattice energy in an anionic vacancy is less than the point-ion Madelung energy. These energies indicate that the ξ_F value, calculated in the point-ion model, is an overestimate. We estimated the ξ_F value, taking into account the non-point nature of the MC ions and the charge distribution of an excess electron, to be 0.543 at. units (cf. 0.64 at. units value for the point-ion model). This estimate is close to the 0.521 at. units obtained in the model of the hydrogen-like F centre absorption [21] and the estimate based on the ENDOR data (≈ 0.5 at. units) [22].^{a)} However, unlike the ξ_F , $U_{\mu\mu}^F$ parameters, β_F depends considerably on the parameters of the *perfect* crystal. As is shown in [11], the assumption of a weak interaction of an excess electron with the MC ions (indirectly used in [8, 10] and giving small β_F values; e.g. -2.5 eV in NaCl [8] and 0.8 eV in KCl [10], whereas typical β values for atoms are 10 to 40 [6]), leads to an underestimate of the spin density on the nearest ions by an order of magnitude [11]. (Besides, the β_F change affects the F centre level position within the gap.)

Table 3
F centre calculations in NaCl crystal (energies in eV)

feature	present paper	Mulliken-Ruedenberg method [11]		exp.
		MC	LUC	
$E_F - E_m^P$	9.2(7.7) ^{a)} 11.9(10.4) ^{b)}	(6.1) ^{a)} (9.67) ^{b)}	(5.96) ^{a)}	7.4 [4]
$E_c - E_F$	5.4(2.9) ^{a)} 2.6(0.1) ^{b)}	(2.5) ^{a)} (-2.34) ^{b)}	(4.96) ^{a)}	3.1 [4]
spin density (at. units) on nearest:				
cations	0.02 ^{a)}			0.0528 ^{c)} [22]
anions	0.01 ^{a)}			0.0236
AF	0.74 ^{a)}			—

^{a)} With AF in basis set. ^{b)} Without AF in basis set. Figures in parentheses are given with the band polarization corrections. ^{c)} We did not try to reproduce the spin densities exactly because the CNDO method itself is not suitable for this purpose. The spin densities for the point ion model are 0.1 and 0.0628, respectively [4, 23].

E_F denotes the one-electron energy of the F centre, E_c is the bottom of the conduction band.

We have listed in Table 3 the energetic separation between the F centre ground state from the bands of the perfect crystal. For comparison the results of the Mulliken-Ruedenberg method [14] (realized in the form of both MC and LUC) are also given from [11]. One can conclude that in both models the ground state energy level lies too high, if the AF is not used. Its inclusion reduces the electron level almost down to the experimental value. At the same time the electron spin density on the nearest cations and anions becomes of the order of the experimental value. The interaction of the F centre electron with the nearest non-point ions raises its position by ≈ 2.5 eV as compared to as the point-ion model [4] which considerably improves the agreement with the experiment.

^{a)} Evarestov [23] and Harker [23] have shown that if one takes into account the ion-size corrections within the pseudopotential method, the spin density and the absorption energies of the F centres are in much better agreement with the experiments than in the point-ion model.

4. Conclusions

The popularity of the LUC model for calculations of the electronic structure of crystals (both perfect and imperfect) is growing [3, 9b]. However, for ionic crystals the calculations performed within MC and LUC models yield close results. The main difference is that the MC model gives an underestimate of the valence band width (obviously due to a rather restricted number of the interacting halides inside the MC). This disagreement may be made less if one knows the correlation between the widths of the valence band for both the MC and LUC models. (Such a correlation is known for the Mulliken-Ruedenberg method [15] but has not been reliably established for the CNDO method due to a small number of comparable calculations.)

Moreover (i) the MC remains an effective approach for calculating charged defects or those of low symmetry (e.g. hole or aggregate centres) which needs very great LUC, (ii) the choice of parameters is a problem *common* to both the models (cf. [9b]).

In the first part of this paper we have presented the new parametrization scheme for calculating ionic crystals (by the MC CNDO approach) taking into account the non-point nature of ions outside the MC. This leads to: (i) different energies of the crystal field energy on anion and cation sites (unlike the point-ion model), (ii) in its turn, these energies are the same for either anions or cations inside the MC irrespective of their position in the MC. The latter greatly reduces the surface effect. For example, the 27-atom MC with standard parameters [6] indicates splitting of a "surface" level from the p-valence band of the order of 1.5 eV whereas *no* effect is observed in our calculations.

We followed the "standard" CNDO calculation scheme [6] in order to clarify its advantages and shortcomings. In particular, despite the right (ionic) trend obtained for optimized orbital exponents, the latter contradict the well-known fact that the effective ionic radius of Cl^- (1.86 Å) exceeds that for Na^+ (0.965 Å) [24].⁹⁾ (This disagreement considerably increases if the parameters [6, 8] are employed.)

Besides, the calculated width of the 3s valence band (4.1 eV for a 16-atom MC) exceeds that of the 3p band (3.38 eV) unlike the band structure calculations. This directly results from the use of the same ξ , β parameters for both s and p AO's in the standard scheme [6].

Despite these shortcomings the parameters derived due to a cancellation of errors, known for semiempirical methods, reproduce the distinctive band features of the perfect crystal.

An applicability of the derived parameters and calculation scheme to predict properties of a number of defects will be investigated in the second part of the paper.

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⁹⁾ The same trend is observed for the ionic sizes in the crystal, however, here divergence of sizes is considerably reduced [25].

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