MODIFICATION OF THE INDO METHOD FOR CALCULATING THE CHARACTERISTICS OF POINT DEFECTS IN IONIC CRYSTALS

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At the present time, semiempirical methods of quantum chemistry have been widely used in the calculation of properties of perfect and imperfect crystals [1-3]. Two models are predominantly used for this purpose: the molecular cluster model (MC) and the quasimolecular extended unit cell model (QEUC) [3]. As a rule, the use of both models requires calculation of fragments containing more than ten atoms. This is possible on the basis of semiempirical quantum-chemical methods. Some of the most correct methods are the zero differential overlap (ZDO) methods — CNDO, INDO [1, 4]. However, while these are effective for calculating properties of nonpolar molecules [4], within the framework of the standard calculation scheme and parametrization [4] they lead to unrealistic results for the electronic structure of ionic crystals [5, 6]. The goal of this work is a modification of the INDO method for calculation of the electronic and spatial structure of point defects in ionic crystals. The numerical calculations were carried out for intrinsic hole H-, V_K^-, V_2^-, V_3^--centers in a KCl crystal.

Comparison of the Results of Calculations with Experimental Data

The predictive power of semiempirical quantum-chemical methods as a rule is apparent in the investigation of a number of similar systems (see, for example, [7]). In this case, we consider a perfect crystal and all possible intrinsic point defects in its crystal structure. The proposed approach is based on preliminary calibration of the parameters of the method for reproducing the experimental characteristics of the electronic structure of the perfect crystal MeX, the dissociation energies, and the equilibrium distances of the corresponding diatomic molecules (MeX, X_2^-, etc.), with the goal of using them further in calculations of intrinsic defects. If the defect is an impurity defect (for example, Tl in KCl), its parameters are optimized in the calculation of the corresponding crystal (for example, TlCl) and the diatomic molecules.

As follows from [8, 9], in order to compare the forbidden gap width of a perfect crystal calculated by the Hartree—Fock method within the framework of band or molecular models with the experimental data, we need to take into account correlation effects associated with the appearance of a hole in the valence band and an electron in the conduction band and leading to an increase in the (one-electron) energy of the top of the valence band and a lowering of the bottom of the conduction band by an amount equal to the so-called "correlation correction," ΔE^c. This leads to a decrease in the forbidden gap width, calculated from the difference in the one-electron energies, by 4-10 eV. In principle, compensation of errors in the semiempirical method may reproduce some characteristics of the molecules and the crystals which may be impossible to obtain by nonempirical methods without taking correlation into account. Therefore it is not surprising that the difference between one-electron levels may be found to be in good agreement with the experimental forbidden gap width [10, 11]. However, in our opinion, the ZDO methods can successively take into account (upon optimization of parameters) only correlation effects between valence electrons and core electrons (the so-called short-range correlation, which in fact has a one-center character [8]). The long-range correlation of valence electrons between themselves should additionally be taken into account, for example by the method in [8, 9]. This means that upon optimization of parameters, the forbidden gap width obtained in the quasimolecular extended unit cell model (which most adequately reproduces the characteristics of a perfect crystal) should be higher than the experimental value [5, 12] by the sum of the long-range correlations ($\sim$4-5 eV in alkali halide crystals [8, 9]).

Among the characteristics of isolated defects, the most important are their optical absorption and photoionization energies.* The former may be calculated from the difference between the total energies of the defect in the ground and excited electronic states (or more accurately, from taking into account configuration interaction [13]). There are approximation methods for calculating the energies of optical transitions, using the difference between the one-electron energies of the defect states (see, for example, [12]). Calculation of the photoionization energy involves: 1) determination of the one-electron defect levels relative to the band limits of a perfect crystal; 2) calculation of the interaction energy between a "hole" in an ionized defect and the crystal. In the Condon approximation, this means taking into account the noninertial repolarization of the crystal upon photoionization of the defect [14]. Then the photoionization energy (assuming that the correlation correction to the conduction band takes into account the interaction of the electron at the bottom of the band with the rest of the electrons of the crystal, accurate up to the defect core polarization is determined by the relationship

$$\Delta E_{pi} = \varepsilon_{\Gamma} - \varepsilon_{D} - \Delta W_{p},$$

where ε_{Γ} is the energy of the bottom of the conduction band, ε_D is the energy of the defect level, ΔW_p is the difference between the total energies of noninertial polarization of the crystal by the defect before and after ionization. In calculating ε_D, we also need to take into account the interaction between electrons of the defect and the induced polarization.

An important disadvantage of the cluster model is the dependence of the results of calculation of the characteristics for a perfect or imperfect crystal on the shape, size, and total charge of the cluster used [3, 15]. As a result of this dependence, it is impossible to directly compare one-electron levels of the cluster containing the defect and those modeling the perfect crystal, i.e., we cannot directly calculate $\varepsilon_{\Gamma}-\varepsilon_D$. In order to determine the position of the defect levels relative to the band limits of the crystal, in [16, 17] it was proposed to combine the centers of gravity of the deep s-valence bands of the cluster with the defect in the perfect crystal. The experiment shows that in such a comparison it is expedient to consider a perfect crystal in the quasimolecular extended unit cell model [17]. In this case it is assumed that, as the size of the cluster with the defect increases, the defect levels are shifted like the band limits of the perfect crystal obtained for the molecular cluster modeling the perfect crystal. Since our calculations for the defects in alkali halide crystals modified by the INDO method (see below) showed that the direction of the shift in the level of the defect ground state and the band limits may be opposite, we used the technique of extrapolation of the results for calculation of the characteristics of the cluster with the defect for an infinite increase in its size, based on taking into account the difference between the charges of the ions in an analogous cluster without a defect and in the quasimolecular extended unit cell modeling the perfect crystal. This leads to an easily calculated "Coulomb" correction to the diagonal matrix element of the crystal field on the AO of the defect. Comparison of the charges of the ions of the cluster without a defect and with a defect from the charges of the ions in its environment [15, 18], as a rule prove to be quite close. That is, defects in ionic crystals do not lead to substantial rearrangement of electron density between ions of the matrix. (Taking into account the redistribution of the density is associated with analysis of the change in the off-diagonal elements of the density matrix, and is quite complicated.) This technique was used for calculations of the recombination energy for defects in alkali halide crystals [14, 15, 18].

Modified Calculation Scheme and Parametrization

The matrix elements of the Fockian for the INDO (and CNDO) methods in the quasimolecular extended unit cell and molecular cluster models are given in [6, 10, 19, 20]. They include the diagonal matrix element of the crystal (Madelung) field $V_{\mu A}^{M}$ for the electron at the μ-th orbital of atom A. We suggested [19] that this quantity should be calculated within the mo-

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*In order to calculate the recombination energies for electron and hole defects, the electronic structure of which is determined independently, we need to correctly reproduce the ionization energies of the electronic centers and the electron affinities of the hole center, i.e., the positions of their levels relative to the band limits.

lecular cluster model like in the quasimolecular extended unit cell model* (i.e., taking into account the nonpoint character of the ions in the entire crystal)

$$V_{\mu A}^{M} = \sum_{B \neq A} \left(\sum_{\lambda}{}^{B} P_{\lambda \lambda} \gamma_{\mu \lambda} + V_{\mu B} \right).$$ (1)

The first term in Eq. (1) describes the interaction of the electron in the μ-th AO of atom A with the valence electrons of atom B, where $P_{\lambda \lambda}$ are the diagonal elements of the density matrix, $\gamma_{\mu \lambda}$ are the Coulomb integrals, and $V_{\mu B}$ are the interaction energies for this electron with the core of atom B. In the traditional CNDO/2 calculation scheme, the Geoppert-Mayer and Sklar approximation [4] is assumed. This approximation is not rigorously substantiated and was introduced to better reproduce the dissociation energies and the equilibrium distances in nonpolar molecules:

$$V_{\mu B} = V_{AB} = Z_B \gamma_{AB},$$ (2)

where Z_B is the charge on the core of ion B.

In the investigation of various methods for calculating $V_{\mu B}$, in [19, 20] we have shown that the approximation in Eq. (2), which is most frequently used in crystal calculations [6, 10, 11, 19-21], leads to incorrect values for the matrix elements of the crystal field: Their values differ considerably (by about a factor of 2) from the results calculated in a basis taking into account the core AO's (such as was done in calculations of the surface states of alkali halide crystals [19, 22]). Physically, this is connected with the underestimate within the Geoppert-Mayer and Sklar approximation of the interaction energy between valence electrons and the cores of other atoms.

In this paper, we have used a simple expression which takes into account the nonpoint character of the ion cores and allows us to calculate both the matrix elements of the crystal field and the spatial characteristics of the system (see [23])

$$V_{AB} = Z_B [1/R_{AB} + (\gamma_{AB} - 1/R_{AB}) \exp(- \alpha_B R_{AB})],$$ (3)

where R_{AB} is the distance between atoms, α_B is a parameter which takes into account the nonpoint character of the core of atom B. Joint study of the electronic and spatial characteristics is necessary for self-consistent calculation of the lattice relaxation around the defects, calculation of the tunneling recombination energies, and modeling of the processes of formation and motion of defects in crystals [2, 11, 14, 15, 24].

For optimization of the parameters of the ZDO methods, the calculated characteristics were compared with known experimental data for perfect ionic crystals MeX [absolute value of the energy for the s, p valence band centers $E_{s,p}^{m}$ and their half-widths $E_{s,p}^{w}$, the forbidden gap E_g (taking correlation effects into account), effective charges of ions Q, the lattice constant a_0], the dissociation energies D_e and equilibrium distances R_e of the corresponding diatomic molecules MeX, X_2^-. The connection between the characteristics of the crystals and the ZDO parameters is discussed in [10, 11, 19].

The parameters obtained for the KCl crystal are given in Table 1. The parameters for the cation are close to those obtained by the CNDO method in [10], while the parameters for the anion are substantially lower. However, this may be due to the difference between the calculation schemes for the CNDO and INDO methods, which requires further investigation.

In order to check the suitability of the obtained parameters for other systems, we calculated the electronic structure of LiCl and KF crystals (the parameters Li^+, F^- for were obtained in [20]). From Table 2 it follows that the calculated characteristics of the LiCl crystal agree well with the experimental values, while in KF the width of the valence band is somewhat underestimated. This is evidently connected with the substantially larger interionic distance in KF compared with Lif, and is evidence for the need to correctly account for the asymptotic behavior of the optimized AO's.

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*In such an approach, similar ions are equivalent (from the viewpoint of the electrostatic field) independently of their position in the molecular cluster. However, in the molecular cluster model (in contrast to the quasimolecular extended unit cell model), the exchange and resonance interactions are limited by the size of the molecular cluster and destroy the equivalency of the similar ions. In ionic crystals, the latter effects are not great, and use of Eq. (1) almost completely removes the "surface" effect which is characteristic for the molecular cluster [19].

TABLE 1. Optimized Parameters for the INDO Method

Parameter	K+ [10]	K+ this work	Cl− [4]	Cl− [10]	Cl− this work
ζ_s, (bohr)$^{-1}$	1,1	1,1	2,03	2,07	2,0
ζ_p, bohr^{-1}	1,1	—	2,03	2,07	1,76
E^s_{neg}, eV	2,3	3,4	21,6	22,35	22,35
E^p_{neg}, eV	1,25	—	8,71	9,47	2,7
$-\beta$, eV	1,1	1,1	22,33	14,15	14,2
α, a. u.	—	0,4	—	—	0

TABLE 2. Characteristics of the Electronic Structure of LiCl and KF Crystals, Obtained in the Quasimolecular Extended Unit Cell Model [Me$_n$X$_n$]

Characteristic	LiCl calc.*	LiCl exp. [25]	KF calc.*	KF exp. [25]
ε_Γ, eV	1,6	—4,6; 2,5	—1,5	—2,3; —0,5
$-E^m_p$, eV	11,4	—	10,7	—
E^w_p, eV	5,85	4,5—5,0	1,0	3,7
E_g, eV	10,1	7,7—9,9	8,2	10,3—11,4
$|Q|$, e	0,9	0,72	0,96	0,96

*In the calculations, we take into account the following long-range correlation corrections (in eV): $\Delta E^C_{Li} = 2.3$; $\Delta E^C_F = 1.8$; $\Delta E^C_K = 2.0$; $\Delta E^C_{Cl} = 1.8$ [8].

TABLE 3. Characteristics of the ClF Molecule, Obtained by the Modified INDO Method

MO	This work $-\varepsilon_i$, eV	F 2s	F 2p	Cl 3s	Cl 3p	Nonempirical calc. [13] $-\varepsilon_i$, eV	F 2s	F 2p	Cl 3s	Cl 3p
3π	13,8	0	16	0	84	13,4	0	13	0	87
7σ	17,8	1	66	2	31	18,0	2	60	7	31
2π	18,3	0	84	0	16	19,4	0	87	0	13
6σ	33,3	26	2	72	0	30,1	8	7	84	0
5σ	38,4	72	0	26	2	44,4	89	2	6	3
$Q_{Cl}=-Q_F$, e	0,31									
R_e, Å	1,69 (1,63)*									

*Experimental value [13].

The energies of the one-electron states of the ClF molecule are given in Table 3. The one-electron energies and the composition of the MO's agree well with the results of the nonempirical calculation [13]. It is important that the parameters for Cl and F, optimized independently, can reproduce the relative properties of these ions in the compound (the fractional contribution to the MO of the ClF molecule). The equilibrium distance and the charge distribution in the Cl_2^- molecule (the "base" of the so-called V_2 centers in alkali halide crystals) are given in Table 4. In this molecule, the chemical bond differs considerably from the systems used for the optimization of the parameters. The values given in Table 4 are in agreement with the results of nonempirical calculations [26], while unsatisfactory results are obtained when using the standard CNDO scheme [27].

Characteristic	Cl_2^-	Cl_3^-	V_K	H	V_2	V_3
R_e, Å	2,4 (2,65)*	2,3 (2.22)†	2,8 (2,93)*	2,3 (2,5)*	2,1	2,1
Q_1, e	—0,5	—0,537 (—0,537)†	—0,4	—0,53	—0,625	—0,622
Q_2, e	—	0,074 (0.074)†	—	—	0,25	0,24
$\Delta E(^2\Sigma_u \to {}^2\Pi_g)$, eV	1,6 (1,65)*	—	1,5 (1,65)*	2,4 (2,38)*	—	—
$\Delta E(^2\Sigma_u \to {}^2\Sigma_g)$, eV	3,8 (3,39)*	—	3,6	3,9	—	—
$\Delta E(^1\Sigma_u \to {}^1\Sigma_g)$, eV	—	9,1 (5.06)†	(3,39)* —	(3,69)* —	9,03	9.8

*Experimental data [2] and calculation [28].
†Results of calculations [26].

Electronic and Spatial Structure of Radiation Defects in KCl

The model for the intrinsic hole H-, V_K-centers in alkali halide crystals with the NaCl lattice type is the quasimolecule X_2 (X is halide), oriented along the <110> axis (the direction of closest packing for the anions) and occupying respectively one or two anionic lattice points [2]. The model for the V_2- center is the X_3^- ion, occupying one cationic and two anionic lattice points and oriented along the <100> axis. We have carried out self-consistent calculations for the electronic and spatial structure, the H-, V_K-, V_2-centers using clusters containing ∿30 ions (close to that presented in [11]). We took into account the finite dimensions of the ions of the rest of the crystal in accordance with Eq. (1). Due to the tediousness of the calculations, for the H-, V_K-centers the total energy of the molecular cluster was minimized only with respect to the equilibrium distance in X_2^-. The shifts of other ions are chosen to be equal to those obtained by the ENDOR method and atom—atom potentials [28]. The calculated spatial and optical characteristics of hole centers and the charges of their component chlorine ions (Q_1 are the charges at X_2^- and the noncentral chlorine atoms in the quasimolecule X_3^-; Q_2 are the charges of the central ions in X_3^-) are given in Table 4.

The redistribution of electron density at the H-center is substantial. The contribution to the MO of the H-center of AO's centered on the two ions of the quasimolecule is ∿70%. The remaining part of the "hole" is localized predominantly on the two anions following along the <110> axis, which agrees with EPR data and supports the refined model for the H-center — $(X_4)^{3-}$. We observed this for H-centers also in NaCl [29]. In V_K-, V_2-centers, the hole is practically completely localized (95%) on the quasimolecules X_2^-, X_3^-.

Due to the strong localization of the hole in such quasimolecular centers, an increase in the size of the cluster from 10 to 32 ions insignificantly affects the distribution of electron density, but leads to appreciable change in the absolute energies of the levels.

One possible model for the so-called V_3-centers is two nearest mutually perpendicular V_2-centers. The calculations showed that within the framework of such a model, the energy of the absorption band maximum is shifted relative to the V_2-center by ∿0.8 eV toward higher energies, which agrees with experimental data.

The calculation results show that the proposed approach is applicable for investigation of both the electronic and the spatial structure of free molecules and point defects in ionic crystals. The general parametrization idea is applicable to crystals with different kinds of chemical bonding (see [10]), and modification of the calculation scheme is suitable for another ZDO method such as CNDO [19].

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KRAMERS' THEORY FOR THREE-ATOM REACTIONS

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Analysis of kinetic phenomena in gas and plasma media involves examining numerous coupled processes. Much attention is given in the literature to dissociation and recombination [1], and these reactions and exchange are some of the most important components of kinetic processes in active media under substantially nonequilibrium conditions. Kramers [2] proposed a very simple, clear, and effective model for describing these reactions and others. The starting point of Kramers' theory is provided by the equations of motion for the reacting particles in the presence of a random force due to the action of the environment on the reactants. The state of the system is represented in this model by a point on a phase plane, while the reaction itself is treated as diffusion in phase space. The motion of the probability density in phase space is described by the Fokker-Planck kinetic equation with initial and boundary conditions specific to each reaction. There are considerable difficulties in constructing a general solution to this equation. Therefore, the first results with this model were obtained by making various physical assumptions for a fairly narrow class of reactions and concerned mainly the probability of the system passing through a potential barrier in unit time.

Subsequent results obtained in Kramers' theory are associated with the use of time-asymptotic solutions to the Fokker-Planck equation. The processes described by this equation are of Markov character, and therefore it is difficult to overestimate the role of time-asymptotic solutions in the kinetics. Two approaches have been developed to constructing these. The first is based on representing the solution as a series in terms of eigenfunctions (EF) and eigenvalues (EV) for the corresponding boundary-value problem [3, 4], while the second has been called the quasistationary distribution (QD) method and involves representing the solution as a series in powers of a certain evolution operator [5]. In [6, 7], the first approach has been used in refining formulas derived previously for the probability of overcoming a potential barrier, and to examine the application limits of these. However, the difficulty caused by solving the EF and EV problem is that this could be done only for potentials of special form having little relation to actual physical situations. In [8, 9], the QD method was used in considering dissociation and recombination for a diatomic molecule. The theoretical and experimental reaction rates were in relatively good agreement.

Here we present a diffusion theory of three-atom reactions, which provides formulas for the rate constants in exchange and association in a triatomic molecule, and a comparison is made with experimental data. The approach enables one to put the calculation of rate constants for numerous reactions on a practical basis.

1. Formulation and Basic Equations

We consider a simplified model for a reaction in which the motion of the atoms A, B, and C occurs along a straight line joining the centers of mass. The environment affects the system via random forces acting on the end atoms A and C, while the atom B between them is screened from collision with the environmental particles. As in the theory of Brownian mo-