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Theoretical analysis of hole self-trapping in ionic solids: Application to the KCl crystal

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A method for the calculation of the hole self-trapping (ST) energy in ionic crystals is proposed. It combines model-Hamiltonian and quantum-chemical approaches. An artificial path for the ST process has been suggested containing (a) a free hole not interacting with the lattice vibrations; (b) a free-hole wave packet localized in a small crystal volume in the form of the real ST state, all crystal ions being in their perfect lattice positions; (c) the final ST state of the hole, accompanied with a corresponding lattice relaxation, including strong displacements of ions belonging to the hole region. Some intermediate states might be adopted between (a) and (b) in order to simplify the calculations. The first step ($a \rightarrow b$) is calculated with the use of a simple model Hamiltonian taking into account inertial-free crystal polarization; the latter is calculated by means of Toyazawa's electronic polaron model. Quantum-chemical calculations are used for the last ($b \rightarrow c$) and all intermediate (if any) steps, and are made by means of the embedded-molecular-cluster model combined wtih a self-consistent treatment of both the crystal polarization and the electronic structure. In order to illustrate the method, a ST hole in the form of the V_k center (X_2^- quasimolecular ion) in the KCl crystal is considered and the ST energy is calculated as carefully as possible. In particular, the semiempirical intermediate neglect of the differential overlap modification of the unrestricted Hartree-Fock-Roothaan method is employed for actual calculations. The hole ST energy in the KCl crystal is found to be near -2.4 eV.

I. INTRODUCTION

For a long time the small-radius polaron phenomenon has remained quite a fundamental problem in solid-state physics.[1-3] Of special interest is the effect of *self-trapping* (ST) of carriers, both electrons and holes. It happens when a particle-lattice interaction exceeds some critical value leading to a large self-induced distortion of the solid and strong localization of the wave packet of the particle.[2,4] As a result (absolute temperature $T=0$ is assumed), the ST particle acquires a very large effective mass and can be treated as being almost completely localized within a small crystal volume, jumping quite rarely from one position in the lattice to another due to a thermal activation.

Whether free holes or electrons can be self-trapped or not is a very important property.[1] A quantitative criterion providing such information is the so-called *ST energy*.[2] Usually it is defined as the energy difference between a *fully relaxed* ST state[2,5] and the bottom of the *free-particle band* (the lowest energy state of the particle without coupling with the lattice distortions). If it is *negative*, the particle can *spontaneously* self-trap in a material; otherwise, it is not the case, or the ST state might be metastable.[2,6] The larger the absolute value of the negative ST energy, the more stable the ST state.

Since the observations presented above are rigorously valid only for strongly localized polarons, let us introduce a more general definition of the ST energy. It should be noted that a degree of localization of a ST polaron depends closely on its bandwidth B_{ST}. Let us define the energy of the ST state E_{ST} as the energy at the *middle* of the ST band. Then the following definition of the ST energy can be stated,[7-9] $\Delta E_{\mathrm{ST}} = E_{\mathrm{ST}} - E_F$, where E_F represents the energy in the *bottom* of the free-particle band. This more correct definition of the ST energy works even for quite mobile ST polarons having not so narrow ST bands. However, it is well known that the inequality $\Delta E_{\mathrm{ST}} \gg B_{\mathrm{ST}}$ holds for the ST hole (STH) in alkali-halide crystals, in which the STH effective mass is enormously large and hence B_{ST} is very small[2,4] ($T=0$ is assumed). Only STH's in ionic crystals are considered in this paper.

Due to a very large *local* relaxation of the lattice in the

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ST state, the hole represents a sort of a point defect in a crystal. The most well-known example of the STH is the V_k center in alkali-halide crystals.[1] This defect has been investigated intensively both experimentally[10,11] and theoretically.[1,12–14] Traditionally it is treated as a negatively charged diatomic halide molecule X_2^- occupying two anion sites and oriented in the [110] direction.[12,13] Quite recently, this model was checked by means of semiempirical[15] and *ab initio* Hartree-Fock[16–18] cluster simulations. Thus the V_k center geometric structure, and its optical, spin-resonance, and other static properties have been investigated quite well.

Despite a long history of theoretical studies of carrier self-trapping in polar media (e.g., 1, 2, 4, 5, and 12–24), at present there is no clear and reliable model of a process of hole self-trapping in alkali halides. Starting from Gilbert[1,22] the process of the V_k-center creation from a free particle (electron or hole) state in which the lattice is *undistorted,* is usually *qualitatively* estimated using a hypothetical *three-stage procedure:* (i) localization of a wave packet made up of free polaron states on several lattice sites, (ii) relaxation of the surrounding lattice induced by the localized hole wave packet (crystal *polarization*), though both V_k anions are still in their perfect lattice positions, and (iii) the relaxation of the V_k anions toward each other forming a strong *chemical bond.* The first step is characterized by a *positive* energy $E_{\rm loc}$, whereas the second and the third result in *negative* contributions.[22–25] A very simple estimate[1,2] yields $E_{\rm loc}$ to be a *half* of *the width* of the upper valence band in alkali-halide crystals (typically, 1.5 eV) giving a total hole ST energy that is *negative,* i.e., such a process seems to be *favorable* in ionic solids with rather *narrow* upper valence bands. Despite the correct physical picture, which can be drawn by means of this method, its main disadvantage consists in its *qualitative* character. The most weak and delicate points are the calculation of the localization energy $E_{\rm loc}$ and an artificial division between the second and the third steps in the path connecting the free and the localized ST state, since both these steps depend on each other and in fact cannot be *correctly* separated.

Another approach, which is based on the pioneering ideas of Toyozawa,[4] has also been proposed in a series of papers.[5,21,26] In this method both states (free and ST hole) are considered by means of one and the same *model Hamiltonian* (MH), which makes it possible to calculate the ST energy in some consistent way, taking correctly into account the lattice polarization as well. However, at present such a method does not allow us to take into account the *microscopic structure* of the STH (i.e., both the electronic density redistribution around the STH and the large displacements of surrounding ions), which is possible *only* by using quantum-chemical methods. The latter methods fail, however, to consider hole states delocalized through the whole crystal.

Strictly speaking, in order to calculate the hole ST energy we have to use a *unified* method suitable for *both* localized and completely delocalized hole states. The MH approach is good for delocalized states, while quantum-chemical methods are well suited for describing local chemical interactions. In a number of recent papers[7–9] a novel method has been suggested, based on a combination of *both* techniques mentioned above–the MH and the *embedded-molecular-cluster quantum-chemical* methods. It was assumed there that the difference of energies at various points of an adiabatic potential energy surface of the hole ST process are reproduced quite well *independently* by both methods.

In this paper we have made an attempt to gather all useful ideas proposed in these papers and generalize them in order to develop a quite *general quantitative* approach suitable for hole ST energy calculations in *any* material. With the help of the rigorous formal analysis made here we have shown how *the inertia-free polarization* of the crystal produced both by the free and the ST hole can be taken into account. This point has been missed in previous studies[7–9] although, as is shown here, it might be quite important in calculating the hole ST energy. As a particular example we have calculated as carefully as possible the hole ST energy for the V_k center in a KCl crystal. Although it is known[1] that *one*-center hole localization in alkali halides does not exist (although it exists in some other crystals such as AgCl, for instance[8,27]), we study also this vague state in KCl to demonstrate the general advantages of the approach proposed here as a useful tool to choose the most *favorable* ST state.

The plan of the paper is as follows. In Sec. II we discuss the basic concept of the approach proposed in the paper for *any ionic crystal.* A microscopic model for the hole self-trapping in *alkali-halide* crystals is considered in Sec. III. Methods used during the calculations, both the MH and the quantum-chemical, are described in Sec. IV, while actual calculations of the ST energy in KCl are represented in Sec. V. General conclusions are drawn in Sec. VI, where the main steps of the approach are given as generally as possible.

II. BASIC IDEAS OF THE METHOD

Let the state F with an energy E_F correspond to a free hole (hole polaron). It is followed by the electronic (inertia-free) polarization only, since as is well known,[2,4] the value of inertial (ionic) polarization is negligibly small for the free polaron having a small coupling with lattice vibrations and so can be completely neglected.

Since there exists no clear method of how to calculate *directly* $\Delta E_{\rm ST}$, following the main ideas of the papers,[7–9] we suggest here the introduction of a number of auxiliary stages between completely delocalized (F) and localized (ST) states. Thus we consider the passage $F \rightarrow {\rm ST}$ as happening along some hypothetical path *qualitatively* just in the same way as was proposed by Gilbert, while considering the ST process for the V_k center in alkali-halide crystals.[1,22]

Suppose we know both the lattice relaxation near the STH and the hole distribution in the defect region. It means that the STH state itself has already been obtained by means of a quantum-chemical method. Let us split all crystal ion displacements Q into two sets, namely, $Q_{\rm def}$, which belongs to the strong relaxation of the lattice *within* the defect region and (as it is assumed) contributes significantly to the ST process, and Q', which describes all *residual* lattice normal coordinates. At least three states must be introduced along the passage $F\rightarrow\mathrm{ST}$ in order to calculate the hole ST energy: (i) a free hole (F); all crystal ions are in their regular sites ($Q_{\mathrm{def}}\approx 0$, $Q'\approx 0$), (ii) the hole is localized within a small crystal volume (in the defect region) just in the same fashion as it is in the final ST state ($Q_{\mathrm{def}}=0$, $Q'=0$, since there is still no relaxation of crystal ions); we will refer to this state as state L *(localized)* in the following, and (iii) the final hole ST state ($Q_{\mathrm{def}}\neq 0$, $Q'\neq 0$).

Besides, some intermediate states might also be introduced between points (ii) and (iii), depending on the real system under consideration. These states must be *localized* (with respect to the hole distribution) just in the same way as the states L,ST. All intermediate steps except the second one (L) will be denoted by the capital letter I in this section.

Note that in all these stages the *electronic polarization* should be taken into account. The state L and possibly all I's (if any) are not stable and probably do not correspond to some *stationary* hole states in the crystal (for instance, the state L is characterized by a localized wave packet of all possible states of the free hole). However, as will be shown below, the main advantage of this hypothetical path ($F\rightarrow L\rightarrow I\rightarrow\mathrm{ST}$) is that it permits us to calculate the hole ST energy ΔE_{ST} sought for.

Indeed, let $\hat{H}=\hat{H}_r+\hat{H}_{rQ}$ be an exact Hamiltonian of the crystal; r denotes a set of electron coordinates, while Q is a set of phonon ones (ion displacements). Here $\hat{H}_r$ is the crystal Hamiltonian with undisplaced ions; it takes into account electron-nuclear and nuclear-nuclear interactions. All interactions of the hole with lattice vibrations are included in $\hat{H}_{rQ}$. As it is known,[2,28] due to the periodic symmetry of the crystal (all crystal anions are equivalent as traps for the hole) the wave function of the *intrinsic hole* in *both* states $X(=F,\mathrm{ST})$ are Bloch-like and can be represented as follows:

$$\Psi_{\mathbf{k}j}^{(X)}(r,Q)=\frac{1}{\sqrt{N}}\sum_{\mathbf{R}} e^{-i\mathbf{k}\cdot\mathbf{R}}\Phi_{\mathbf{R}j}^{(X)\mathbf{k}}(r,Q) , \tag{1}$$

where N is a number of unit cells in the main region of the crystal, $\Phi_{\mathbf{R}j}^{(X)\mathbf{k}}(r,Q)$ is a normalized function, and j numerates the branches of the corresponding hole energy bands. Let us show that for comparatively narrow bands of the STH ($B_{\mathrm{ST}}\ll|E_F-E_{\mathrm{ST}}|$) the function $\Phi_{\mathbf{R}j}^{(\mathrm{ST})0}(r,Q)$ may be approximately chosen as a *wave function* of the STH instead of the exact one, given by Eq. (1). It means, that this *localized* function can be reasonably interpreted as a *wave function* of the *defect state,* describing the hole localized *around* the site $\mathbf{R}$. Therefore, it can be obtained by means of the usual variational procedure and calculated using any cluster quantum-chemical method.

Indeed, omitting both the indices of the state (ST) and the branch (j) and expanding $\Phi_{\mathbf{R}}^{\mathbf{k}}(r,Q)$ through a set of known orthonormalized and *localized* (in the vicinity of the lattice site $\mathbf{R}$) functions,

$$\Phi_{\mathbf{R}}^{\mathbf{k}}(r,Q)=\sum_{\alpha} c_\alpha(\mathbf{k})\phi_{\mathbf{R}\alpha}(r,Q) ,$$

we arrive at the usual secular problem for the unknown coefficients, $c_\alpha(\mathbf{k})$:

$$\sum_{\alpha}\left[H_{\beta\alpha}(\mathbf{k})-E^{(\mathbf{k})}S_{\beta\alpha}(\mathbf{k})\right]c_\alpha(\mathbf{k})=0 , \tag{2a}$$

where

$$H_{\beta\alpha}(\mathbf{k})=\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\langle\phi_{\mathbf{R}\beta}|\hat{H}|\phi_{0\alpha}\rangle \tag{2b}$$

is the appropriate matrix of the Hamiltonian and

$$S_{\beta\alpha}(\mathbf{k})=\sum_{\mathbf{R}} e^{i\mathbf{k}\cdot\mathbf{R}}\langle\phi_{\mathbf{R}\beta}|\phi_{0\alpha}\rangle \tag{2c}$$

represents the corresponding overlap matrix. Since in the ST state under consideration the effective mass of the hole is much larger than that for the free one, the bandwidth of the former is much smaller than that for the latter. Besides, it is assumed here that the STH band is strongly separated from the free-hole band. Summing up all these arguments we can conclude that the dispersion of the STH is *no more important* here and can be neglected, while considering the calculation of the ST energy. The ST band can be substituted by a *single* level having an average STH band energy value. This means that to a good approximation the overlap of the functions $\phi_{\mathbf{R}\alpha}(r,Q)$ centered on different lattice sites can be treated as negligible and therefore only the largest (diagonal, $\mathbf{R}=\mathbf{0}$) matrix elements in Eqs. (2b) and (2c) are left: $H_{\beta\alpha}(\mathbf{k})\simeq\langle\phi_{0\beta}|\hat{H}|\phi_{0\alpha}\rangle$ and $S_{\beta\alpha}(\mathbf{k})\simeq\langle\phi_{0\beta}|\phi_{0\alpha}\rangle=\delta_{\alpha\beta}$. This ensures that Eq. (2a) does not depend on $\mathbf{k}$ at all and gives solely only one level instead of the whole band.

On the other hand *just the same* simplest secular problem arises if the following *localized variational ansatz* for the STH is considered:

$$\Phi_{\mathbf{R}}^{(\mathrm{ST})}(r,Q)=\sum_{\alpha} c_\alpha\phi_{\mathbf{R}\alpha}(r,Q) ,$$

where $\mathbf{R}$ is any lattice vector in the vicinity of which the hole is assumed to be localized. We can choose $\mathbf{R}=\mathbf{0}$ for the sake of simplicity. Therefore, the STH can be simulated as being strongly localized and $\Phi_0^{(\mathrm{ST})}(r,Q)$ can be used as its wave function.

Then, following the standard assumption[2,5,21,26] we admit that the dispersion of the free-hole bands coincides with that of the upper valence band of the crystal. This is usually the case in ionic crystals. For instance, in alkali halides the hole bands are formed by anion p-like atomic orbitals (AO's). Then we adopt also (although this assumption can easily be avoided and is taken here for the sake of simplicity only) that the vector $\mathbf{k}=\mathbf{0}$ corresponds to the top of the valence band and all dispersion branches degenerate at this point (as happens in alkali-halide crystals). So the branch index j can be omitted in further equations. Thus we are able to estimate the value of the ST energy considering the free-hole state belonging to the $\mathbf{k}=\mathbf{0}$ point.

Therefore, we get

$$E_F^{(\mathbf{k}=0)}=E_F^{(0)}=\langle\Psi_0^{(F)}|\hat{H}|\Psi_0^{(F)}\rangle=\langle\Psi_0^{(F)}|\hat{H}_r|\Psi_0^{(F)}\rangle \tag{3a}$$

at the bottom ($\mathbf{k}=\mathbf{0}$) of the free-hole band, and

$$E_{\mathrm{ST}} \simeq \langle \Phi_0^{(\mathrm{ST})} | \hat{H} | \Phi_0^{(\mathrm{ST})} \rangle \tag{3b}$$

as an estimate for the energy of the ST state. It has been used in Eq. (3a) that $\langle \Psi_0^{(F)} | \hat{H}_{rQ} | \Psi_0^{(F)} \rangle = 0$, which is correct for any state $\Psi(r,Q)$ with $Q=0$. The function $\Phi_0^{(\mathrm{ST})}$ must be calculated by a direct *variation* of E_{ST}. Thus, the usual *cluster quantum-chemical* philosophy can be implemented here.

Let us introduce now two additional auxiliary hole states $\Phi_0^{(L)}$ and $\Phi_0^{(I)}$ (again for $\mathbf{R}=0$) corresponding to the points L and I, respectively. Keeping in mind that $Q=0$ still holds in the state $\Phi_0^{(L)}$, we arrive at the following set of equations:

$$\Delta E_{\mathrm{ST}} = \Delta E_{F\to L} + \Delta E_{L\to I} + \Delta E_{I\to \mathrm{ST}} \ , \tag{4}$$

$$\Delta E_{F\to L} = \langle \Phi_0^{(L)} | \hat{H}_r | \Phi_0^{(L)} \rangle - \langle \Psi_0^{(F)} | \hat{H}_r | \Psi_0^{(F)} \rangle \ , \tag{5a}$$

$$\Delta E_{L\to I} = \langle \Phi_0^{(I)} | \hat{H} | \Phi_0^{(I)} \rangle - \langle \Phi_0^{(L)} | \hat{H} | \Phi_0^{(L)} \rangle \ , \tag{5b}$$

$$\Delta E_{I\to \mathrm{ST}} = \langle \Phi_0^{(\mathrm{ST})} | \hat{H} | \Phi_0^{(\mathrm{ST})} \rangle - \langle \Phi_0^{(I)} | \hat{H} | \Phi_0^{(I)} \rangle \ . \tag{5c}$$

The difference $\Delta E_{F\to L}$ is the energy needed to localize the hole in the vicinity of the defect region just *in the same fashion* as it is in a real ST state. This value is *positive* due to the large kinetic energy acquired in the state L. $\Delta E_{L\to \mathrm{ST}} = \Delta E_{L\to I} + \Delta E_{I\to \mathrm{ST}}$ represents an energy gain caused both by the chemical bonding within the defect region and the relevant strong lattice relaxation, and is *negative.* Thus whether the hole ST energy will be negative (a ST state exists) or positive (likely does not exist) depends on the balance managed by these two contributions. Note that all these energy differences are calculated by means of the different Hamiltonians ($\hat{H}_r$ and $\hat{H}$) and represent differences between mean values taken with various wave functions. However, the choice of the intermediate states I is quite arbitrary. Note also that the actual sign of the each particular contribution $\Delta E_{L\to I}$ depends on the state I chosen.

Our general idea is to calculate each difference ($\Delta E_{F\to L}$, $\Delta E_{L\to I}$, $\Delta E_{I\to \mathrm{ST}}$) by means of *different methods,* the most favorable and suitable in the given particular case. Practically it means that for each difference (each step of the path $F\to L\to I\to \mathrm{ST}$) we intend to employ different Hamiltonians (such as the Hartree-Fock Hamiltonian augmented with polarization correction, the MH, etc.) and, as a consequence, different wave functions. Particularly, in order to calculate $\Delta E_{F\to L}$ we use *the MH* method whereas, while calculating both $\Delta E_{L\to I}$ and $\Delta E_{I\to \mathrm{ST}}$ *cluster quantum-chemical* calculations are applied. The latter method can be used for these steps due to the localized nature of the wave functions in the states L,I,ST. Note also that even clusters of different sizes in principle could be used on two last steps ($L\to I$ and $I\to \mathrm{ST}$).

The wave functions which coincide for any two sequential stages [for example, $\Phi_0^{(L)}$ in (5a) and (5b)] should be the same. In practice, however, they are not identical, since various methods are used on each step as is adopted here. Thus we have to take care of at least their *physical equivalence* in order to diminish as much as possible the main error of the present approach which comes from the usage of different Hamiltonians in actual calculations. However we believe, that *energy differences* are reproduced quite well in the methods mentioned above, and therefore our approach is able to yield a comparatively good estimate of the real hole ST energy, taking into account in a physically transparent way all important contributions.

Unfortunately it is not possible to formulate our general approach further in more detail without considering a concrete system. For this reason we concentrate here on the case of alkali-halide crystals and present our estimate of the hole (V_k center) ST energy in KCl crystal.

III. MICROSCOPIC MODEL OF HOLE SELF-TRAPPING IN ALKALI HALIDES

The following auxiliary stages shown in Fig. 1 can be chosen in this particular case:

(i) a free hole (F), crystal ions are in their regular sites; $Q_{\mathrm{val}} \approx 0$ and $Q' \approx 0$, where Q_{val} is a valence vibrational mode of the X_2^- molecule,[1] while Q' is a set of residual lattice normal coordinates, as before; the point F in Fig. 1;

(ii) a hole shared by two nearest anions oriented along the [110] axis; still $Q_{\mathrm{val}}=0$ and $Q'=0$, there is no relaxation of surrounding ions; the point L in Fig. 1;

(iii) relaxation of X_2^- surrounding ions ($Q' \neq 0$), but both ions (V_k-center precursors) are still in their regular sites ($Q_{\mathrm{val}}=0$); the point LR in Fig. 1 (the point I in the notations of Sec. II);

(iv) at last, the V_k center is formed ($Q_{\mathrm{val}} \neq 0, Q' \neq 0$); the point ST in Fig. 1.

Thus, the process drawn here practically coincides with that given above for the general case. The state LR has been introduced by Gilbert[1,22] and is used here as an intermediate state. We will show however that this state appears to be useless for actual calculations and may be removed after all. As before, the difference $\Delta E_{F\to L}$ is the energy needed to localize the hole on two adjacent anions and is *positive.* $\Delta E_{L\to LR}$ is in fact *negative* due to an energy gain arising after lattice relaxation around the X_2^-

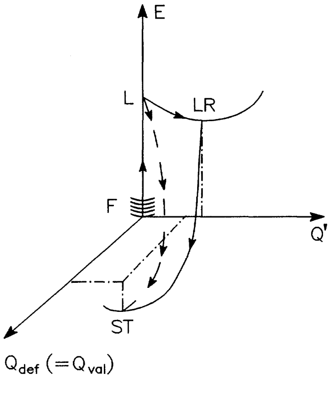

FIG. 1. Schematic representation of the path for the hole self-trapping in the alkali-halide crystals used in the present calculations.

quasimolecule. At last, $\Delta E_{LR\to \mathrm{ST}}$ represents an energy gain, caused *both* by an alteration of the chemical bonding in the X_2^- molecule and the relevant lattice relaxation, and is also *negative.*

While calculating $\Delta E_{F\to L}$ we use the MH method augmented by the inertia-free polarization treatment by means of Toyazawa's electronic polaron model,[28-31] whereas, while calculating both $\Delta E_{L\to LR}$ and $\Delta E_{LR\to \mathrm{ST}}$ the *quantum-chemical* calculations within the cluster model are applied.

Before discussing the numerical results obtained for the STH in KCl, let us consider the principal features of the methods used below for the actual calculations at each step.

IV. CALCULATION METHODS

A. Model-Hamiltonian method

When constructing the MH, one should take into account that, since the upper valence band of alkali halides is formed mainly by anion p-like atomic orbitals, the off-diagonal (in terms of lattice sites) matrix elements of the MH must differ from each other. Neglecting those differences leads to an essential overestimate of the hole localization energy.[7-9]

Accounting for all arguments discussed above, let us write down the MH for the perfect crystal in the tight-binding approximation incorporating only two anionic spheres of nearest neighbors (cf. Ref. 7). In the site representation the free-hole Hamiltonian reads:

$$\hat{H}_h=\sum_{\mathbf{R}\mathbf{R}'}\sum_{\mu\mu'}T_{0\mu,\mathbf{R}'\mu'}a^{\dagger}_{\mathbf{R}\mu}a_{\mathbf{R}+\mathbf{R}',\mu'} \tag{6a}$$

where

$$T_{0\mu,\mathbf{R}'\mu'}=-\varepsilon_0\delta_{0\mathbf{R}'}\delta_{\mu\mu'}-(1-\delta_{0\mathbf{R}'})t_{0\mu,\mathbf{R}'\mu'} \tag{6b}$$

and $\mathbf{R},\mathbf{R}'$ are lattice translational vectors ($|\mathbf{R}'|\leq 2a$, a being an interionic distance), $\mu,\mu'=x,y,z$ and $|\mathbf{R},\mu\rangle$ is the p-like function localized on the site $\mathbf{R}$ and orthogonalized to those centered on the nearest neighbors (coordinate axes are oriented along [100], [010], and [001] crystal axes); $a^{\dagger}_{\mathbf{R}\mu}$ and $a_{\mathbf{R}\mu}$ are the hole creation and annihilation operators for the orbital $|\mathbf{R},\mu\rangle$.

In order to derive rigorous expressions for the matrices $t_{0\mathbf{R}}=||t_{0\mu,\mathbf{R}\mu'}||$ used in the MH, let us consider two anions lying along the X axis. It follows from symmetry that the interaction of these anions in fact depends on the following three parameters only:[7] T_σ (interaction of two p orbitals which lie along the X axis), $T_{\pi 1}$ (p orbitals oriented along Y axis), and $T_{\pi 2}$ (p orbitals oriented along the Z axis). Note that it is necessary to distinguish both latter cases due to a different crystal environment. Thus, we found for an arbitrary vector $\mathbf{R}'$ belonging to the first sphere that the matrix

$$t_{0\mathbf{R}'}=||t_{0\mu,\mathbf{R}'\mu'}||=C^{\dagger}_{\mathbf{R}'}t_{\mathbf{R}'}C_{\mathbf{R}'}\ ,$$

where $C_{\mathbf{R}'}$ is the three-dimensional rotation matrix orienting sites $\mathbf{0}$ and $\mathbf{R}'$ along the X axis, $t_{\mathbf{R}'}$ is the diagonal matrix belonging to the ions lying along the X axis and consisting of the diagonal elements T_σ, $T_{\pi 1}$, and $T_{\pi 2}$ only. For example, for $\mathbf{R}'=a(1,1,0)$ the matrix $C_{\mathbf{R}'}$ represents an anticlockwise rotation by an angle $\pi/4$, $t_{11}=T_\sigma$, $t_{22}=T_{\pi 1}$, and $t_{33}=T_{\pi 2}$. We proceed in a similar way for anions R' from the second coordination sphere; in this case $t_{0\mathbf{R}'}$ is diagonal for all $\mathbf{R}'$, these diagonal elements are either T'_σ or $T'_\pi=T'_{\pi 1}=T'_{\pi 2}$ (their meaning is the same as for those in the first sphere). Detailed expressions for the matrices $t_{0\mathbf{R}}$ are given in an Appendix.

However the parameters T_σ, $T_{\pi 1}$, and $T_{\pi 2}$ of the hole MH introduced above are unknown. In order to obtain them,[7-9] we can match the eigenvalues of the MH with those resulted from band-structure quantum-chemical calculations. Indeed, the diagonalization of the MH given by Eq. (6),

$$\hat{H}_h=\sum_{\mathbf{k}}\sum_{\mu\mu'}T_{\mu\mu'}(\mathbf{k})a^{\dagger}_{\mathbf{k}\mu}a_{\mathbf{k}\mu'}=\sum_{\mathbf{k}j}\varepsilon_j(\mathbf{k})c^{\dagger}_{\mathbf{k}j}c_{\mathbf{k}j}\ , \tag{6c}$$

permits us to calculate the dispersion of the hole bands $\varepsilon_j(\mathbf{k})$, $j=1,2,3$. Thus, the hole energies at the Γ,X,L points of the Brillouin zone (BZ) are

$$\varepsilon(\Gamma)=-\varepsilon_0-8\alpha-4\gamma-2\delta\ , \tag{7a}$$

$$\varepsilon_{\parallel}(X)=-\varepsilon_0+8\alpha-4\gamma-2\delta\ , \tag{7b}$$

$$\varepsilon_{\perp}(X)=-\varepsilon_0+4\gamma-2\delta\ , \tag{7c}$$

$$\varepsilon_{\parallel}(L)=-\varepsilon_0+8\beta+2\delta\ , \tag{7d}$$

$$\varepsilon_{\perp}(L)=-\varepsilon_0-4\beta+2\delta\ , \tag{7e}$$

where subscripts $\parallel,\perp$ denote energy branches whose eigenvectors are parallel and perpendicular to the direction of the wave vector $\mathbf{k}$, respectively. Besides, $\alpha=\frac{1}{2}(T_\sigma+T_{\pi 1})$, $\beta=\frac{1}{2}(T_\sigma-T_{\pi 1})$, $\gamma=T_{\pi 2}$, and $\delta=T'_\sigma+2T'_\pi$.

The corresponding band-structure calculations of the KCl perfect crystal were carried out by means of the modified semiempirical method of the intermediate neglect of the differential overlap[32] (INDO) combined with the large unit-cell (LUC) model.[33] (Note that just the same INDO method was used for the V_k center calculations, discussed below.) The LUC's used allow us to get energies at least at the Γ,X,L points of the BZ. Results are presented in Table I. It is clear that the 64-atom LUC (supercell) is large enough to get the MH parameters quite reliably.

To estimate the energy of the inertia-free polarization produced by the Coulomb field of the hole, we used the electronic polaron model.[28-31] In this model the distortion of the electronic subsystem (inertia-free polarization) is described in terms of virtual Frenkel excitons created around the hole. Proceeding in this way, one arrives at the following *total MH* (i.e., the Hamiltonian of a system "the hole + Frenkel excitons"):

$$\hat{H}_r=\hat{H}_h+\hat{H}_{\mathrm{ex}}+\hat{H}_{h-\mathrm{ex}}\ . \tag{8}$$

Here $\hat{H}_h$ is the free-hole Hamiltonian, Eq. (6), without polarization; $\hat{H}_{\mathrm{ex}}=\sum_{\mathbf{q}}E_g b^{\dagger}_{\mathbf{q}}b_{\mathbf{q}}$ is the Hamiltonian of the free excitons carrying the identical energy E_g (the forbid-

TABLE I. The free-hole band energies at Γ, X, L points of the Brillouin zone and parameters of the MH, Eq. (6), for different LUC's used in the calculations: (a) $[\mathrm{KCl}]_{16}$; (b) $[\mathrm{KCl}]_{64}$; (c) $[\mathrm{KCl}]_{128}$.

	Band energies (a.u.)					Parameters of MH (eV)				
LUC	$\varepsilon(\Gamma)$	$\varepsilon_{\parallel}(X)$	$\varepsilon_{\perp}(X)$	$\varepsilon_{\parallel}(L)$	$\varepsilon_{\perp}(L)$	T_{σ}	$-T_{\pi 1}$	$-T_{\pi 2}$	$-\delta$	$-\varepsilon_0$
a	0.391	0.453	0.403	0.436	0.393	0.203	0.008	0.065	0.035	11.15
b	0.394	0.472	0.411	0.449	0.401	0.242	0.024	0.075	0.034	11.42
c	0.394	0.472	0.411	0.449	0.401	0.242	0.024	0.075	0.034	11.42

den gap width), $b_{\mathbf{q}}^{\dagger}$ and $b_{\mathbf{q}}$ are creation and annihilation operators for the excitons with the wave vector $\mathbf{q}$. Interaction of the hole with the excitons is described by an operator:[28-31]

$$\hat{H}_{h-\mathrm{ex}} = -\sum_{\mathbf{q}} \sum_{\substack{\mathbf{R}\mathbf{R}' \\ \mu\mu'}} [V_{\mathbf{R}\mu,\mathbf{R}+\mathbf{R}'\mu'}(\mathbf{q}) b_{\mathbf{q}} + \text{h.c.}] a^{\dagger}_{\mathbf{R}\mu} a_{\mathbf{R}+\mathbf{R}'\mu'} , \tag{9a}$$

where

$$V_{\mathbf{R}\mu,\mathbf{R}+\mathbf{R}'\mu'}(\mathbf{q}) = V_{\mathbf{q}} \langle \mathbf{R},\mu | e^{i\mathbf{q}\cdot\mathbf{r}} | \mathbf{R}+\mathbf{R}',\mu' \rangle , \tag{9b}$$

$$V_{\mathbf{q}} = -i \left[\frac{2\pi E_g}{V q^2} \left(1 - \frac{1}{\varepsilon_{\infty}} \right) \right]^{1/2} . \tag{9c}$$

Here $V = N v_c$ is the total crystal volume, v_c is the unit-cell volume, and ε_{∞} is the high-frequency dielectric constant. If

$$\Psi = \sum_{\mathbf{R}\nu} f_{\mathbf{R}\nu} a^{\dagger}_{\mathbf{R}\nu} |0\rangle \tag{10}$$

is the wave function of the localized hole and χ is a wave function of excitons describing electron polarization, in the Landau-Pekar approximation[5,21,26] the *total* wave function of the crystal is $\Phi = \Psi\chi$. Varying the total energy of the system $\langle \Phi | \hat{H}_r | \Phi \rangle$ with respect to χ (similarly as it has been done in Refs. 5, 21, and 26), we obtain the following expression for the total energy of the hole in the electronic polarization field

$$E[\Psi] = \langle \Psi | \hat{H}_r | \Psi \rangle + E_{\mathrm{pol}}[\Psi] = E_h[\Psi] + E_{\mathrm{pol}}[\Psi] . \tag{11}$$

The first term here corresponds to *the hole self-energy* defined via Ψ and the MH parameters in Eq. (6), while the second term in Eq. (11) is *the inertia-free polarization energy*

$$E_{\mathrm{pol}} = -\frac{1}{E_g} \sum_{\mathbf{q}} |V_{\mathbf{q}}|^2 |\langle \Psi' | e^{i\mathbf{q}\cdot\mathbf{r}} | \Psi' \rangle|^2 , \tag{12a}$$

where $\Psi' = \sum_{\mathbf{R}\nu} f_{\mathbf{R}\nu} |\mathbf{R},\nu\rangle$ is the coordinate *one-particle* representation of Ψ [cf. Eq. (10)]. To estimate the integral over the BZ in Eq. (12a), let us replace the integration over the BZ by that over a sphere with radius $q_m = \pi/a$. The result is (cf. Ref. 34)

$$\begin{aligned} E_{\mathrm{pol}} &= -(\Psi'\Psi' | \hat{g} | \Psi'\Psi') = -\int |\Psi'(\mathbf{r})|^2 \hat{g}(|\mathbf{r}-\mathbf{r}'|) |\Psi'(\mathbf{r}')|^2 d\mathbf{r}\, d\mathbf{r}' \\ &= \sum_{\mathbf{R}_1 \cdots \mathbf{R}_4} \sum_{\nu_1 \cdots \nu_4} f_{\mathbf{R}_1\nu_1} f_{\mathbf{R}_2\nu_2} f_{\mathbf{R}_3\nu_3} f_{\mathbf{R}_4\nu_4} (\mathbf{R}_1,\nu_1;\mathbf{R}_2,\nu_2 | \hat{g} | \mathbf{R}_3,\nu_3;\mathbf{R}_4,\nu_4) , \end{aligned} \tag{12b}$$

where

$$\hat{g}(z) = \frac{1}{\pi z} \left(1 - \frac{1}{\varepsilon_{\infty}} \right) \mathrm{Si} \left(\frac{\pi}{a} z \right) \tag{12c}$$

is an operator of the hole self-action via the hole-induced polarization field (the so-called dielectric screening), $\mathrm{Si}(x)$ being the usual integral sine function. Of course, the rigorous result (12a) may be used for straightforward calculation of the polarization correction instead of the approximate one given by Eqs. (12b) and (12c). In this case the method of *special points*[35] is used to perform the numerical integration over the BZ. However, one should be aware that in doing this, since $|V_{\mathbf{q}}|^2 \propto q^{-2}$, to avoid the singularity at $\mathbf{q}=0$, a special method[14] must be used.

Therefore, assuming that the hole wave function Ψ has a particular given form through its coefficients $f_{\mathbf{R}\nu}$, and using the anion orbitals $|\mathbf{R},\nu\rangle$ as Wannier functions, we can employ Eqs. (6), (11), and (12) and obtain finally the total hole electronic energy $E[\Psi]$ for any state in which all atoms occupy their regular lattice sites ($Q=0$).

It should be mentioned that the inertia-free polarization energy caused by *the free hole* (F) cannot be calculated directly with the aid of Eq. (12a), since the latter is no longer valid due to the failure of the Landau-Pekar approximation. It can be taken however from perturbation calculations also based on the electronic polaron theory.[29] For this purpose it is necessary to generalize the equations therein for the case of three free-hole p-like bands, taking correctly into account their degeneration at high symmetry **k** points (only the simplest case of a unique *s*-like band was considered in Ref. 29). This yields the following result for a shift of the threefold degenerate state at the bottom ($\mathbf{k}=\mathbf{0}$) of the free-hole band (see also Ref. 31):

$$E_{\text{pol}}(F) = -\sum_{\mathbf{q}j} \frac{|V_{\mathbf{q}}|^2}{\varepsilon_j(\mathbf{q}) - \varepsilon(\Gamma) + E_g} \times \left| \sum_{\mu} U_{\mu j}(\mathbf{q}) \langle 0,x | e^{i\mathbf{q}\cdot\mathbf{r}} | 0,\mu \rangle \right|^2 , \tag{13}$$

where $\varepsilon(\Gamma)=\varepsilon_j(\mathbf{0})$, and $\varepsilon_j(\mathbf{q})$ represents the energy of the bare (without polarization) free-hole band [see Eq. (6c)], while $U(\mathbf{q})$ is a matrix providing the diagonalization of $\mathbf{T}(\mathbf{q})$ in Eq. (6c), $|0,\mu\rangle$ is used to denote AO's as before. A corresponding correction for any **k** point of the free-hole band can be easily derived in the same way. Note that the polarization energy for a *heavy* hole calculated by means of Eqs. (12) might be either larger or smaller than the corresponding value for the free hole, Eq. (13), leading to either smaller or larger total hole localization energy value, respectively.

B. Quantum-chemical methods

To carry out the above-discussed calculations of the hole local states we need a method reproducing reliably both chemical interactions of ions nearby the V_k center and the long-range interactions known as the crystal polarization produced by the STH. The embedded-molecular-cluster[36,37] (EMC) model was used, which has been successfully applied earlier to find static properties of V_k centers in alkali halides[15] and impurity-induced hole trapping in MgO.[36] In this method a division of the defective crystal into two regions—quantum cluster containing the defect with its important neighborhood and the rest of the crystal is carried out. Then two different problems—the electronic structure of the quantum cluster embedded into the Coulomb field of the rest of the crystal and the relaxation of the surrounding crystal (its polarization, both inertial and inertia-free) induced by the defect—have to be solved in a *self-consistent* way (see also Refs. 7–9, 17, and 18). We have used here the semiempirical SYM-SYM code[38] in which the EMC method is implemented and the system symmetry is entirely taken into account.

The SYM-SYM code is based on the INDO method. This package permits one to obtain (with reasonable accuracy) the electronic structure of quantum clusters containing *several hundreds* of ions. Note that it is fully equivalent (except in the usage of the symmetry) to the CLUSTER code.[36] Besides, a special geometry optimization routine is built into the package which allows one to obtain an optimum set (or even subset) of the cluster ion coordinates. Other details of the INDO scheme implemented here can be found elsewhere.[9]

V. HOLE SELF-TRAPPING ENERGY CALCULATIONS IN KCl

A. The case of the two-site STH

At the beginning we intend to consider the two-site STH known as the V_k center; the hypothetical one-site localized hole will be considered later, in Sec. V B. In order to calculate the hole (V_k) ST energy, let us start with the localization energy, $\Delta E_{F\rightarrow L}$, which could be found with the aid of the MH method. According to Eq. (11), the free hole at $\mathbf{k}=\mathbf{0}$ has an energy $E_h(F)+E_{\text{pol}}(F)$, where $E_h(F)=\varepsilon(\Gamma)$.

In order to proceed to the next state (point *L*) it is necessary to find out the correct hole distribution in the fully relaxed (*true*) ST state, as is clear from the above given arguments. That is why we will describe in detail the STH state at the beginning.

An entirely relaxed state (point ST in Fig. 1) is obtained in the following way. Strictly speaking, the equilibrium displacements of the inner (molecular-cluster) MC ions must be obtained via the minimization of the total MC energy, evaluated in its turn within a completely self-consistent calculations by means of the EMC method, described above. Besides, the size of the MC chosen for the calculations must be large enough to be sure that *the boundary conditions* inherent to the MC model itself[33,37] are almost perfect and do not affect the positions on the MC ions thus computed. It was found, however, that it is too tedious to perform these calculations in a fully self-consistent way. In order to simplify the calculations, the following fact[39] has been used: Inclusion of the polarization practically does not contribute to the values of the *optimal* ions positions at least in the case of alkali-halide crystals. Therefore, we have simplified our calculations considerably ignoring the polarization correction while optimizing the MC geometry.

An extremely large MC $[\mathrm{K}_{74}\mathrm{Cl}_{74}]^+$, containing 148 ions and represented in Table II, has been used for these calculations, taking completely into account the hole D_{2h} point symmetry. During the calculations all MC *boundary ions* have not been displaced in order to improve the boundary conditions (see Table II). Nevertheless, the complete optimization of the MC total energy over 64 MC *inner* ion coordinates has been performed. In this respect we would like to point out that for the MC of that *very large size* the boundary conditions thus adopted in fact are almost perfect. (Indeed, removing the hole from the MC the displacements of inner MC ions have been found to be not more than $0.01-0.02a$.) The equilibrium displacements of the inner MC ions were obtained within the constraint that the defect D_{2h} point symmetry remains unchanged. Relaxations of ions surrounding V_k center found in our semiempirical calculations are summarized in Table II. They agree quite well with results of earlier calculations.[9,13]

Then using the displacements of both V_k and neighboring ions thus obtained we have worked out a completely self-consistent calculation of the V_k center electronic structure. For this purpose a smaller MC $[\mathrm{K}_{20}\mathrm{Cl}_{20}]^+$ has been used, however, containing only 40 ions (Table II).

TABLE II. The molecular clusters used in our calculations and the corresponding equilibrium geometry (in the units of interionic distance, a) of the V_k center in KCl. Only nonequivalent (with respect to the D_{2h} symmetry) ions are shown explicitly. For the largest MC used in the calculations, $[K_{74}Cl_{74}]^+$, only displaced ions are shown. The fixed boundary of this MC has been made by the additional 16 spheres of ions. The first ten spheres of the largest MC have been chosen for the MC $[K_{20}Cl_{20}]^+$ used in our self-consistent calculations.

	Perfect		V_k center	
Ion	lattice	Present work	Ref. 17	Ref. 13
Cl	0.5;0.5;0.0	0.309,0.309,0.0	0.313;0.313;0.0	0.295;0.295;0.0
K	0.5,−0.5,0.0	0.605,−0.605,0.0	0.64;−0.64;0.0	0.634;−0.634;0.0
K	0.5;0.5;1.0	0.483;0.483;1.026	0.497;0.497;1.06	0.487;0.487;1.034
Cl	0.5;−0.5;1.0	0.514;−0.514;0.99		0.509;−0.509;0.977
K	1.5;0.5;0.0	1.544;0.497;0.0	1.56;0.48;0.0	1.541;0.492;0.0
Cl	1.5;−0.5;0.0	1.522;−0.505;0.0		1.564;−0.502;0.0
Cl	1.5;0.5;1.0	1.47;0.486;0.973		1.48;0.495;0.985
K	1.5,−0.5;1.0	1.507;−0.499;1.008		1.519;−0.504;1.011
Cl	1.5;1.5;0.0	1.453;1.453;0.0	1.477;1.477;0.0	1.479;1.479;0.0
K	1.5;−1.5;0.0	1.504;−1.504;0.0		1.528;−1.528;0.0
Cl	0.5;0.5;2.0	0.494;0.494;1.987		0.494;0.494;2.005
K	0.5;−0.5;2.0	0.505;−0.505;2.004		0.507;−0.507;2.006
K	1.5;1.5;1.0	1.519;1.519;0.997		1.501;1.501;1.004
Cl	1.5;−1.5;1.0	1.51;−1.51;0.987		1.496;−1.496;0.993
Cl	2.5;0.5;0.0	2.498;0.498;0.0		2.509;0.5;0.0
K	2.5;−0.5;0.0	2.515;−0.498;0.0		2.535;−0.506;0.0

In full agreement with previous studies (see, for example, Refs. 1, 9, 13, and 40) it was found that the hole is almost completely distributed over both V_k anions (the Löwdin population analysis gave $\simeq 90\%$ of the hole located on the central Cl_2^- molecule). So, ignoring small contributions from other ions outside the V_k anions we can adopt (with reasonable accuracy) that the hole is shared equally between these two ions only.

These findings allow us to choose the following two-site ansatz for the hole wave function, while calculating the point L shown in Fig. 1 by means of the MH method (cf. Ref. 7):

$$\Phi_0^{(L)} = \frac{1}{2}(a_{0x}^+ + a_{0y}^+ + a_{1x}^+ + a_{1y}^+)|0\rangle$$
$$= \frac{1}{\sqrt{2}}(a_{0\sigma}^+ + a_{1\sigma}^+)|0\rangle \ . \tag{14}$$

The site 0 is placed at the coordinate origin, site 1 lies on the $\sigma = [110]$ axis (the anions 0 and 1 form the V_k center). The hole self-energy in this state is evidently (cf. Refs. 5, 7, and 21)

$$E_h(L) = \langle \Phi_0^{(L)} | \hat{H}_h | \Phi_0^{(L)} \rangle = -\varepsilon_0 - T_\sigma \ , \tag{15}$$

whereas the electronic polarization energy, in line with Eqs. (12), is

$$E_{\text{pol}}(L) = -\tfrac{1}{2}[(0,\sigma;0,\sigma|\hat{g}|0,\sigma;0,\sigma)$$
$$+(0,\sigma;1,\sigma|\hat{g}|1,\sigma;0,\sigma)] \ . \tag{16}$$

Note that small contributions arising from the overlap of the orbitals $|0,\sigma\rangle$ and $|1,\sigma\rangle$ occupying different lattice sites are omitted here, which lies within the ideology of the INDO method. Our calculations based on Eqs. (13) and (16) and performed with the aid of the special points method mentioned above, gave $E_{\text{pol}}(L) = -1.56$ eV and $E_{\text{pol}}(F) = -2.08$ eV. These values lead to $\Delta E_{\text{pol}}(F \rightarrow L) \simeq 0.52$ eV as the (inertia-free) polarization contribution to the hole localization energy. Thus, the hole localization into the two-site state, Eq. (14), created from its free state formed near the top of the valence band approximately requires an energy

$$E_{\text{loc}} = \Delta E_{F \rightarrow L} = [E_h(L) - E_h(F)] + \Delta E_{\text{pol}}(F \rightarrow L)$$
$$\simeq 0.47 + 0.52 \simeq 1.0 \text{ eV} \ . \tag{17}$$

At this stage the energy loss is *positive* and is associated with an increase of the kinetic energy of the localized hole (0.47 eV) and the *positive* inertia-free repolarization energy (0.52 eV), which appears to be *half* the total value of E_{loc}. Note that the inertia-free polarization contribution was omitted in previous studies[7–9] of the hole self-trapping. However, our calculations indicate the crucial importance of this term in the localization energy calculations.

Proceeding to the next stage let us estimate the relaxation energy, $\Delta E_{L \rightarrow LR}$, by means of the INDO quantum-chemical calculations. The main difficulty encountered here is concerned with the point L where it is necessary to localize the hole in the perfect crystal having all its ions on their lattice sites, since in this case there is no chance to get a proper localizing potential (recall that the states L, LR are not *true* stationary states of the system).

At least two different methods can be used at this stage to overcome this difficulty and estimate the relaxation energy for the second step of the ST path.

First of all, let us consider the smallest molecular cluster, $(X_2)^-$, comprising the two anions only, on which the hole is necessarily localized due to the *minimal cluster space.* The energy $\Delta E_{L\rightarrow LR}$ equals the total-energy difference of the cluster with inertia-free polarization *before* and *after* the relaxation of the ions outside the MC (taking into account the Coulomb interaction of the MC with the rest of the crystal), provided that both the ions of the Cl_2^- molecule are still in their perfect lattice positions. In fact the lattice relaxation energy under consideration involves only the *ionic* (inertial) component of the polarization, since its electronic (inertia-free) part practically coincides in both states L and LR. Our estimate of $\Delta E_{L\rightarrow LR}$ yields the value of -0.64 eV for this smallest MC and is covered here by the ionic polarization contribution only. It should be stressed, however, that the value obtained is underestimated (see below), since in this case the continuum approximation[41] used for the polarization energy calculations fails due to the small cluster size. Besides, the short-range contributions to $\Delta E_{L\rightarrow LR}$ (arising from the chemical interaction between the two Cl atoms of Cl_2^-) also are not included here because of the limited variational space of the cluster (only s,p orbitals were used for each Cl ion).

Another method which seems to be rather general operates with just the same MC, containing 40 ions, used before for the description of the STH state itself. The MC density matrix previously computed for the STH state has been stored in order to fix the correct localization of the hole. Now it is used for a number of proceeding calculations in which *the self-consistency* with respect to the MC electronic density is completely *ignored.* It allows us to calculate the total MC energy for any point of the path (L,LR and ST), since the MC electronic density already corresponds to the *true* STH, as it should be (see Sec. II) in particular for the L point.

Using this approach, while regarding the L point we have fixed *all* (including V_k) ions on their lattice sites and have computed the MC total energy, allowing only for the inertia-free polarization of the remainder of the MC. The latter (within the accuracy of the method) is practically the same as that obtained while calculating the ST point, though some small influence of the omitted inertial polarization ($Q=0$) is observed. Then, while regarding the next LR point, we have taken the equilibrium geometry of all MC ions as that computed before for the STH state although the V_k center ions are still fixed in their regular positions ($Q_{\text{val}}=0$). After that the full optimization (via the polarization calculations) of the crystal ionic positions outside the MC (together with accompanying inertia-free polarization) have been worked out. The total-energy difference obtained in this way represents the contribution to the second step of the ST path and is found to be -1.5 eV. This value is significantly larger than the estimate made above for the smallest MC.

At the next step $LR\rightarrow$ST only the large MC $[K_{20}Cl_{20}]^+$ has been used. At this step an appreciable energy gain $\Delta E_{LR\rightarrow \text{ST}}$ due to *chemical bonding* within the X_2^- quasimolecule accompanied by the mutual approach of two anions along the valence vibrational mode Q_{val} (Fig. 1) is expected. To calculate $\Delta E_{LR\rightarrow \text{ST}}$, the total energies of the MC's consisting of unrelaxed (point LR, $Q_{\text{val}}=0$) and relaxed (point ST, $Q_{\text{val}}\neq 0$) anions forming the V_k center have to be obtained, incorporating also additional contributions from the total polarization energy of the rest of the crystal; these latter energies differ slightly in the two cases. For the point LR just the same calculation performed before on the second step has been used. In this way we have found the value -1.9 eV for the V_k-center chemical bonding energy $\Delta E_{LR\rightarrow \text{ST}}$. Note that this value is larger than the Cl_2^--molecule dissociation energy as it must be. Indeed, an analysis shows that our value (-1.9 eV) is almost equally shared between the change in the chemical bonding *inside* the molecule associated with the passage $LR\rightarrow$ST and an alteration in the interaction of the molecule with the remaining part of the crystal. Note, that while calculating the point LR the density matrix of the ST state has been used leading to a *higher* total energy of the MC than one would expect by calculating the point LR *self-consistently* with respect to the MC electronic distribution.

At last, based on these findings, we are able to estimate the hole ST energy. It appears to be $\Delta E_{\text{ST}}=1.0+(-0.64)+(-1.9)=-1.54$ eV or $\Delta E_{\text{ST}}=1.0+(-1.5)+(-1.9)=-2.4$ eV for the case of the small and the large MC's used on the step $L\rightarrow LR$, respectively. The second value ($\Delta E_{\text{ST}}=-2.4$ eV) is more reliable, since it was obtained by means of the larger MC having better boundary conditions. Moreover, the total relaxation energy $[(-1.5)+(-1.9)=-3.4$ eV$]$ obtained in the second case agrees quite well with the value of -3.476 eV obtained by means of atom-atom potentials in Ref. 13. Therefore, we prefer -2.4 eV as an estimate of the ST energy in KCl.

As was expected, the main contribution to ΔE_{ST} comes from both chemical bonding and crystal polarization. Its quite large *negative* value confirms the well-known fact that self-trapping of a hole favored in the KCl crystal, forming the two-site charged defect, known as the V_k center. The value of ΔE_{ST} is larger than that obtained by the MH method only (-0.96 eV),[5] since the chemical bonding has been neglected there.

It should be stressed that in the second case when just the same MC has been used, while considering the passage from the point L to the point ST, introduction of the intermediate point LR along the path is of no importance here and can be omitted altogether (see the dashed line in Fig. 1). Thus, two different routes have been used here to connect points L and ST in the self-trapping path and both of them gave *qualitatively* identical results for the ST energy (i.e., large negative values). However, this, in fact *two-step* method ($F\rightarrow L\rightarrow$ST), has an additional advantage already mentioned in the Introduction. It concerns the division of the ST path into steps. This division is too artificial in the first method proposed by Gilbert,[22] whereas in the second method we dealt with a two-step procedure only which seems to be more reasonable from the physical point of view. Nevertheless, the second route used here demonstrates quite evidently the principal possibility of introducing some additional intermediate steps along the path whenever necessary.

B. The case of the one-site STH

Now let us outline briefly the calculations concerning the hypothetical one-site STH in a KCl crystal. In this case the wave function belonging to the point L reads

$$\Phi_0^{(L)}=a_{0x}^{+}|0\rangle \ , \tag{18}$$

and the corresponding hole internal and polarization energies are $E_h(L)=-\varepsilon_0$ and

$$E_{\mathrm{pol}}(L)=-(0,x;0,x|\hat{g}|0,x;0,x)\simeq-1.73 \text{ eV} \ ,$$

respectively. Therefore, the localization energy necessary to gather the free-hole wave packet on one particular lattice site of the lattice is equal to $E_{\mathrm{loc}}\simeq 1.1$ eV.

Then we must consider the passage $L\rightarrow$ST using quantum-chemical methods. For the calculation of the one-center STH the O_h-symmetry MC containing 27 ions was employed, and its equilibrium geometry was obtained allowing self-consistently for the polarization of the outer region. Then just in the same way as in the previous calculations, the density matrix thus obtained was stored and used for the total-energy calculation at the point L (the point LR has not been considered in these calculations). However, the gain in the energy acquired on the second step practically coincides with the lack of it on the first one. Thus we can conclude that one-center hole does not self-trap in KCl in complete agreement with experiment.[1]

VI. CONCLUSION

Results of our combined "model-Hamiltonian -quantum-chemical" simulations demonstrate quite clearly that the method presented in this paper is capable of giving a good *quantitative* estimate of the hole ST energy in a *real* material, like alkali-halide crystals. Quite recently[7] it has also been implemented for the study of the ST hole in the perfect MgO crystal where a comparatively small value for the ST energy was found, justifying its high mobility. The case of the mixed valence bands has been considered in Ref. 8.

Let us summarize all the important steps during the calculations of the hole ST energy by means of the approach proposed here. Formulating these stages as generally as possible we can distinguish the following steps.

(i) A model Hamiltonian enabling us to describe quite correctly the free hole bands must be derived and its parameters must be obtained using the comparison with any band-structure quantum-chemical calculations (from a LUC calculations, for example).

(ii) A guess concerning the STH structure is made (the hole is localized either on one or two sites, etc.).

(iii) Cluster calculations of the adopted STH state are made (ST point) taking into account the polarization of the remainder of the crystal in a self-consistent way; the equilibrium cluster geometry is obtained and the corresponding STH density matrix is stored.

(iv) An intermediate state L on the path between the free (F) and fully relaxed hole (ST) states is chosen in such a way that all crystal ions occupy their regular lattice sites whereas the electronic distribution of the crystal corresponds to that for the hole in the ST state.

(v) The localization energy (the energy difference between points F and L on the path) is calculated by means of the MH method, a wave function belonging to the state L is taken from the quantum-chemical calculations of the true STH, described above.

(vi) Using the density matrix of the STH stored previously, the total energy of the point L is calculated by means of the same MC used for the STH calculations. If necessary, a number of additional intermediate steps along the route $L\rightarrow$ST might be introduced; for these steps some other MC's can be used as well.

(vii) All these steps might be repeated for other possible structures of the STH in the material leading to the opportunity to choose the most favorable one (or a number of them) having the largest negative ST energy or draw the conclusion that all STH's considered are unstable or even do not exist at all if the ST energy turned out to have a small negative or positive value, respectively.

We believe that our method with some reasonable improvements (mainly concerning the localization energy calculations by means of the model-Hamiltonian method) and the choice of the ST path could be successfully applied to a wide range of materials. It is of special interest to apply it to the study of crystals with an *intermediate* character of chemical bonding such as corrundum (α-Al_2O_3) (Ref. 42) for which the issue of whether the ST hole exists or not is still a challenging problem.

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APPENDIX

In this appendix we give the detailed expressions for the matrices $t_{0\mathbf{R}}=||t_{0\mu,\mathbf{R}\mu'}||$ for the free-hole Hamiltonian $\hat{H}_h$ in Eq. (6). Let us start from anions which are nearest neighbors to the given one located in the origin, and enumerate them sequentially from 1 to 12 as follows (lattice vectors are given in units of a, the interionic distance): (1,1,0), (−1,1,0) (−1,−1,0), (1,−1,0), (1,0,1), (−1,0,1), (−1,0,−1), (1,0,−1), (0,1,1), (0,−1,1), (0,−1,−1), and (0,1,−1). Then, the matrices $t_{0,\mathbf{R}_i}$ ($i=1,\ldots,12$) have the following form

$$t_{0,\mathbf{R}_1}=t_{0,\mathbf{R}_3}=\begin{bmatrix}\alpha & \beta & 0\\ \beta & \alpha & 0\\ 0 & 0 & \gamma\end{bmatrix}; \quad t_{0,\mathbf{R}_2}=t_{0,\mathbf{R}_4}=\begin{bmatrix}\alpha & -\beta & 0\\ -\beta & \alpha & 0\\ 0 & 0 & \gamma\end{bmatrix};$$

$$t_{0,\mathbf{R}_5}=t_{0,\mathbf{R}_7}=\begin{bmatrix}\alpha & 0 & \beta\\ 0 & \gamma & 0\\ \beta & 0 & \alpha\end{bmatrix}\;;\quad t_{0,\mathbf{R}_6}=t_{0,\mathbf{R}_8}=\begin{bmatrix}\alpha & 0 & -\beta\\ 0 & \gamma & 0\\ -\beta & 0 & \alpha\end{bmatrix}\;;$$

$$t_{0,\mathbf{R}_9}=t_{0,\mathbf{R}_{11}}=\begin{bmatrix}\gamma & 0 & 0\\ 0 & \alpha & \beta\\ 0 & \beta & \alpha\end{bmatrix}\;;\quad t_{0,\mathbf{R}_{10}}=t_{0,\mathbf{R}_{12}}=\begin{bmatrix}\gamma & 0 & 0\\ 0 & \alpha & -\beta\\ 0 & -\beta & \alpha\end{bmatrix}\;.$$

Then let us enumerate six anions of the second shell as follows: (2,0,0), $(-2,0,0)$, (0,2,0), $(0,-2,0)$, (0,0,2), and $(0,0,-2)$. The corresponding matrices $t_{0\mathbf{R}_i}$ all are diagonal and have the form

$$t_{0,\mathbf{R}_1}=t_{0,\mathbf{R}_2}=\begin{bmatrix}T'_\sigma & & \\ & T'_\pi & \\ & & T'_\pi\end{bmatrix}\;;\quad t_{0,\mathbf{R}_3}=t_{0,\mathbf{R}_4}=\begin{bmatrix}T'_\pi & & \\ & T'_\sigma & \\ & & T'_\pi\end{bmatrix}\;;$$

$$t_{0,\mathbf{R}_5}=t_{0,\mathbf{R}_6}=\begin{bmatrix}T'_\pi & & \\ & T'_\pi & \\ & & T'_\sigma\end{bmatrix}\;.$$

All parameters (α, β, γ, T'_σ, and T'_π) used here are given in the text.

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