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Modeling charge self-trapping in wide-gap dielectrics: Localization problem in local density functionals

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We discuss the adiabatic self-trapping of small polarons within the density-functional theory. In particular, we carried out plane-wave pseudopotential calculations of the triplet exciton in NaCl and found no energy minimum corresponding to the self-trapped exciton contrary to the experimental evidence and previous calculations. To explore the origin of this problem we modeled the self-trapped hole in NaCl using hybrid density functionals and an embedded-cluster method. Calculations show that the stability of the self-trapped state of the hole drastically depends on the amount of the exact exchange in the density functional: at less than 30% of the Hartree-Fock exchange, only delocalized hole is stable, at 50%—both delocalized and self-trapped states are stable, while further increase of exact exchange results in only the self-trapped state being stable. We argue that the main contributions to the self-trapping energy such as the kinetic energy of the localizing charge, the chemical bond formation of the dihalogen quasimolecule, and the lattice polarization, are represented incorrectly within the Kohn-Sham based approaches.

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I. INTRODUCTION

Despite considerable progress in studies of self-trapped excitons (STE's) and polarons, the dynamics of early stages of self-trapping in specific systems is still poorly understood. The conceptual difficulty primarily lies with the fact that the quasiparticle in question undergoes a transition between the free (delocalized) state and the localized one. In case of small polarons this transition is also associated with a substantial local lattice distortion. Within an adiabatic approximation one can describe self-trapping in terms of a potential-energy surface (PES) connecting free and localized states. Then a microscopic model of self-trapping will involve a characterization of this PES, i.e., relevant atomic coordinates, relative energies of the free and self-trapped states, the energy barrier (if any) between them, as well as spectroscopic properties of free and self-trapped species.

Significant progress has been achieved in understanding the conditions for polaron and exciton localization and self-trapping, as summarized in recent reviews.[1–4] It has been suggested by Rashba[5] that in three-dimensional dielectric crystals, the free and self-trapped forms of excitons may coexist, thus implying an energy barrier separating the two states. The height of this barrier affects the dynamics and characteristic time of self-trapping process. However, atomistic modeling has only been successful in calculating the structure and properties of strongly localized systems and never in modeling transitions between delocalized and localized states. One should note that the barrier for self-trapping, if it exists, is not likely to exceed a few tenths of an electron volt.[2] Therefore its experimental verification and theoretical calculation is extremely challenging.

It has been anticipated that further development of quantum-mechanical techniques, especially density-functional theory (DFT), will allow one to close this gap and achieve predictive modeling of self-trapping or defect induced trapping process. However, recent attempts to calculate even well established models of small radius polarons have failed unexpectedly. Calculations of the triplet self-trapped exciton in NaCl using plane-wave DFT in the generalized gradient approximation (GGA) predicted no stable state[6] in direct contradiction with the experimental evidence[2] and previous Hartree-Fock calculations.[7,8] On the other hand, Perebeinos *et al.*[9] using plane-wave local spin-density (LSDA) approach predicted the existence of a marginally stable STE in this system, albeit higher in energy than the free exciton state. Song and co-workers[10–12] applied plane-wave DFT to the triplet exciton in α quartz and similarly found the free exciton state to be more stable than the localized one. The delocalized solution has also been found in LSDA calculations of the hole trapping at the Li^0 center in MgO.[13] Pacchioni *et al.*[14] and Lægsgaard *et al.*[15] considered the hole trapped at an Al impurity in silica. Both groups concluded that the predicted structure of this defect strongly depends on the density functional used in the calculations: local and GGA functionals predicted only the delocalized hole to be stable, again in contradiction with the experiment. Importantly, the nonlocal density functionals predict more localized states for this system.

An apparent bias of DFT calculations towards the delocalized electronic states was attributed to the self-interaction error inherent in the local or semilocal GGA-type approximations, which are central to the Kohn-Sham (KS) method.[16] It is unclear, however, to what extent the local approximation affects qualitative results (localized versus delocalized states), and what is the role of other factors in the calculation, such as boundary conditions, basis set completeness, and pseudopotential approximation.

In this paper, we consider a triplet exciton and a hole in the archetypal ionic insulator NaCl. These defects have been studied extensively both experimentally and theoretically[2,7,17] and thus provide good test systems. Previous calculations were carried out mainly in small embedded cluster models using the Hartree-Fock method and therefore were unable to treat delocalized states and take full account

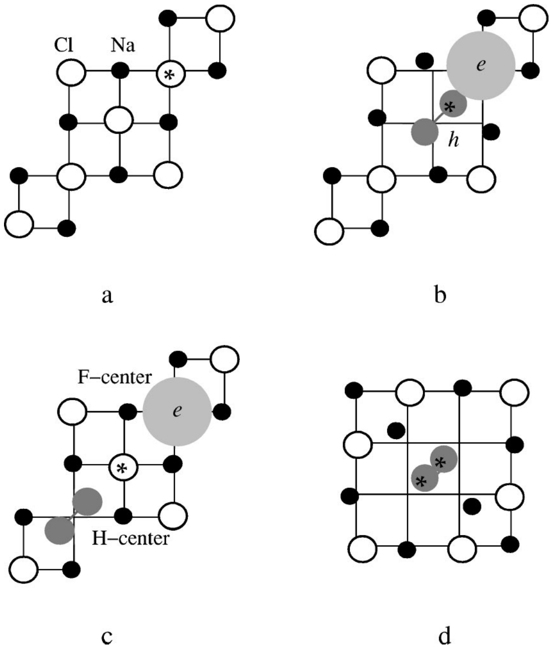

FIG. 1. Schematic representations of the perfect rocksalt structure (a); of the triplet self-trapped exciton (b), the closest separated *F*-*H* pair (c), and the V_k center (d) in an alkali halide crystal. The atoms marked with stars were constrained during the optimization procedure.

of the electron correlation. We would like to model a transition from delocalized to self-trapped exciton state and for this purpose use the plane-wave DFT method. We analyze the effect of size of a periodic supercell and the related question of spurious multipole interactions in this system and conclude that no stable self-trapped state for the exciton or a hole is predicted within the GGA DFT framework, once these factors are eliminated. To separate the localization problem from the effects of periodic boundary conditions (PBC's) we then consider a hole within the embedded cluster approach and find that the nonlocal contribution to the exchange interaction is decisive in the description of self-trapped states.

The paper is organized as follows. In the next section we give a brief account of the microscopic models of the self-trapped exciton and hole in alkali halides. Next we outline the details of the periodic plane-wave and embedded-cluster procedures used. The results of calculations for an exciton and a hole are presented respectively in Secs. IV and V, followed by discussion in Sec. VI.

II. SELF-TRAPPED EXCITON AND HOLE IN ALKALI HALIDES: BACKGROUND

Most of the alkali halides at normal pressure and temperature assume the face-centered-cubic structure [Fig. 1(a)] (except cesium halides which are simple cubic). Self-trapped excitons and holes in these crystals exhibit the features of both molecular and dielectric polaron character. In particular, the self-trapped hole (otherwise called a V_k center) is known to be localized on two adjacent halogen ions forming a $X_2{}^-$ molecular ion [Fig. 1(d)]. There is no experimental evidence pointing to existence of a barrier for the hole self-trapping in alkali halides,[2,18] suggesting that the free hole is unstable. In particular, Lushchik *et al.*[19] estimated that the mean free path of a free hole in NaCl before self-trapping does not exceed 30 a_0 (a_0 is the shortest Na-Cl distance in the perfect lattice). The hole self-trapping energy, which is the difference between the energies of the fully delocalized and localized states, is larger than the activation energy for the V_k center diffusion ($\sim$0.4 eV in NaCl).[20] Therefore it is expected that the description of such a deep state is well within the reach of the DFT theory.

The model and the geometric structure of the V_k center in alkali halides has been first proposed on the basis of the analysis of the electron spin resonance data[21,22] and later refined in numerous theoretical calculations.[17,23–25] The structure and stability of the V_k center is primarily determined by the chemical bond formation between the two halogen ions, assisted by the lattice polarization.

Self-trapped triplet excitons in alkali halides can be formed either directly by excitation in the exciton band or as a result of a localization of an electron near already self-trapped hole, V_k center. It is currently accepted that the STE in alkali halides consists of a localized hole in the form of the $X_2{}^-$ molecular ion, and an electron localized in its vicinity. The so-called on-center and off-center configurations of triplet STE's are considered in the literature.[2] In the on-center configuration the $X_2{}^-$ molecular ion equally occupies two nearest anion sites [as in Fig. 1(d)], with the electron cloud symmetrically localized around it and has the D_{2h} point symmetry group. It is therefore called a (V_k+e) configuration. Williams and Song[26] suggested that in some alkali halides at least, the on-center configuration of the STE is unstable relative to an off-center displacement of the $X_2{}^-$ ion along the $\langle 110\rangle$ crystallographic direction towards one of the anion sites [Fig. 1(b)]. The center of mass of the electron component in this configuration is localized near the other (vacant) anion site, thus giving the C_{2v} symmetry to the STE. This model of the triplet STE in alkali halides has been further developed using effective potential and embedded-cluster *ab initio* Hartree-Fock calculations, as reviewed by Song and Williams.[2] The STE in NaCl has also been studied using *ab initio* embedded-cluster methods by Puchin *et al.*,[7,27] who confirmed the existence of the off-center STE configuration and demonstrated the importance of the electron correlation in determining the properties of the STE.

Triplet STE created by irradiation may subsequently annihilate (radiatively or nonradiatively) restoring the perfect lattice, or decay into a Frenkel pair of lattice defects: an electron in an anion vacancy (*F* center) and an interstitial halogen atom in the form of an $X_2{}^-$ molecular ion occupying one halogen site, the *H* center [Fig. 1(c)]. The energy barrier between the off-center STE and the closest *F*-*H* pair has been calculated in alkali chlorides and bromides by Song *et al.*[28] and also recently in KBr by Shluger and Tanimura.[8] The dissociation barrier for the STE is found to be very low (0.07 eV for NaCl and 0.03 eV for KBr).[28] The activation energy for the STE diffusion in NaCl is somewhat larger,[20] $\sim$0.13 eV.

TABLE I. The supercells used in the exciton calculations, specified by the number of atoms, Cartesian translation vectors (given in units of the shortest Na-Cl distance a_o), and the number of irreducible k points used in the calculations. The last column shows the value of the optimized lattice constant a_0 for the ground and excited states.

Atoms (relaxed) (Ref. 29)	Translation vectors (a_0)	No k points	a_0 Å $s=0$	 $s=1$
2	(1 1 0), (1 0 1), (0 1 1)	35	2.845	
32 (26)	(4 0 0), (0 4 0), (2 2 2)	4	2.83	2.87
64 (48)	(4 0 0), (0 4 0), (0 0 4)	4	2.84	2.85
108 (28)	(3 3 0), (3 0 3), (0 6 6)	3	2.83	2.84
144 (46)	(6 0 0), (0 6 0), (0 0 4)	1	2.84	2.84

At the outset of this work we perceived the plane-wave periodic Kohn-Sham based DFT methods to be adequate for treating both delocalized and localized states and applied them to study the adiabatic potential for self-trapping of triplet exciton in NaCl. The results presented below highlight the limited applicability of the existing functionals to the localization problem.

III. CALCULATION PROCEDURE

A. Periodic DFT calculations

In order to model the triplet exciton self-trapping we consider the adiabatic coordinate corresponding to a displacement Δ of one chlorine ion (hereafter designated as Cl*) along the $\langle 110 \rangle$ crystalline axis with all other surrounding atoms[29] relaxed at each position of the Cl*. The displacement Δ is measured in units of 1/8 of the plane diagonal $(a_0\sqrt{2})$. By virtue of construction, the specified adiabatic coordinate connects the free exciton state $(\Delta=0)$ [Fig. 1(a)] with the STE configuration $(\Delta\sim 4\text{–}5)$ [Fig. 1(b)], and the closest F-H pair separated by one lattice anion, $\Delta\sim 8)$ [Fig. 1(c)]. The considered potential-energy surface (PES) allows for both on- and off-center forms of STE as well as for the transient one-center excitons proposed by Shluger and Tanimura.[8] However, it should be emphasized, that an existence of the potential-energy barrier along this coordinate does not rule out a possibility of alternative self-trapping paths with still lower energy barriers.

The PES along the coordinate Δ was calculated using the plane-wave density-functional approach implemented in the VASP code[30] with the GGA density functional due to Perdew and Wang[31] and the ultrasoft pseudopotentials[32] as supplied by Kresse and Hafner.[33] The self-consistent triplet excited state was modeled by constraining the total spin of the system to $S=1$, so as to obtain the lowest energy state of given multiplicity.

To study the effect of the supercell size, the exciton PES was calculated in unit cells containing 32, 64, 108, and 144 ions. The details of the supercells are given in Table I together with the sets of k points used and number of atoms explicitly relaxed. At each position of Cl* the specified ions were relaxed, so that the maximum force acting on any individual atom did not exceed 0.04 eV/Å.[29] Most of the calculations were performed with an energy cutoff of 285 eV.

As shall be seen below, the calculated PES for the exciton self-trapping does not display a minimum for the STE. Furthermore, the shape of PES strongly varies with the size of the supercell. In order to separate the effects of the boundary conditions and density functionals, we considered the formation of the V_k center in NaCl as described in the next section.

B. Embedded-cluster calculations

In this method, a crystal is represented by a large finite nanocluster, that is divided into several regions. Spherical region I at the center of the nano-cluster includes a quantum-mechanically treated cluster (QC) surrounded by interface ions and a region of classical shell-model ions.[34] The remaining part of the nanocluster is represented by classical nonpolarizable ions. All quantum-mechanical, interface and classical ions (both cores and shells) in region I are allowed to relax simultaneously in the course of geometry optimization. Ions outside region I remain fixed and provide an accurate electrostatic potential within region I. This approach allows one to take into account the defect-induced lattice polarization of a crystal region containing a few hundred atoms. An account of lattice polarization outside region I can be extended to infinity using a polarizable continuum model and the Mott-Littleton approach.[35] In this approximation the polarization energy is proportional to the square of the excess charge in the lattice. In the case of the V_k center, the charge is constant, so the Mott-Littleton contribution cancels out in any energy differences. Therefore this term was neglected in the current calculations.

The described scheme is implemented in the GUESS code,[36,37] which provides an interface between the GAUSSIAN package[38] for calculation of the electronic structure of the QC and a code providing the shell-model representation of the rest of the crystal. The total energy and the electronic structure of the QC is calculated by solving standard Hartree-Fock or Kohn-Sham equations which include the matrix elements of the electrostatic potential due to all classical point charges in regions I and II computed on the basis functions of the cluster. Further details for the total-energy evaluation in this approach are given elsewhere.[36]

A cubic nanocluster containing 8000 $(20\times20\times20)$ ions was used in these calculations. Spherical region I of radius 11.5 Å included 300 classical ions and a stoichiometric QC comprising 22 ions (Fig. 2).

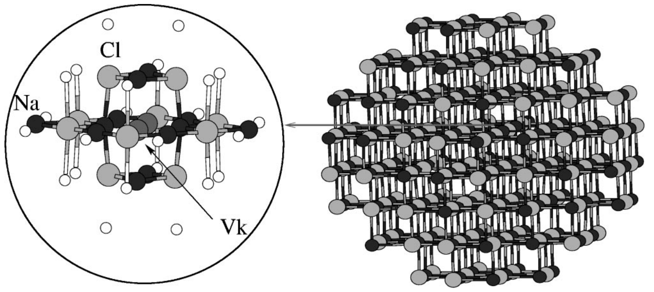

FIG. 2. Illustration of the embedded-cluster model used in the V_k-center calculation (only region 1 is shown). The quantum cluster is shown enlarged. The small white balls represent the sodium interface atoms.

In our scheme, the charge density in QC interacts with the classical atoms only electrostatically, which results in artificial polarization by the classical cations nearest to the QC.[39] To avoid this, an interface region between the QC and classical ions in region I was introduced. In the present model it includes 20 Na ions represented by effective core pseudopotentials,[40] and a single *s*-type basis function (see Fig. 2). Therefore all QC anions are fully coordinated by either quantum or interface ions. For the quantum cluster we have used an all electron Gaussian-type atomic basis[41] optimized for the NaCl crystal (8–511 G for Na and 86–311 G for Cl).

The shell-model ions in region I interact via pair potentials due to Catlow *et al.*,[42] which were slightly modified to represent more accurately the static dielectric constant. Modified potentials give a static equilibrium Na-Cl distance of 2.79 Å and fairly well reproduce the elastic, dielectric, and phonon properties of the perfect NaCl crystal.

The embedded-cluster calculations were carried out using three different density functionals: the Hartree-Fock, Becke hybrid three parameter (B3), and so-called half-and-half functionals (BH&H).[43] The latter two incorporate 20% and 50% of the Hartree-Fock exchange, respectively.[43] The hybrid exchange functionals were used in conjunction with the Lee, Yang, and Parr correlation functional (LYP).[44]

Consistency of the interactions between the classical and quantum regions was tested by calculating an ideal QC embedded into an ideal classical lattice. The optimized Na-Cl distances inside the QC and those at the cluster boundary differ from the Na-Cl distances in the rest of the nanocluster by approximately 1% and 3.5%, respectively.

IV. EXCITON SELF-TRAPPING IN NaCl

Exciton self-trapping is associated with a strong lattice relaxation. It has been suggested that this relaxation is associated with the significant volume change.[45] To account for this effect, we optimized the lattice constant of the supercells in both the ground and excited triplet states using the VASP code. The results are presented in Table I. The calculated ground-state equilibrium lattice constant $a_0 = 2.84$ Å is $\sim 2\%$ larger than the experimental value, extrapolated to 0 K, of 2.79 Å. We also observe a slight increase of the perfect lattice constant in the triplet excited state in smaller supercells.

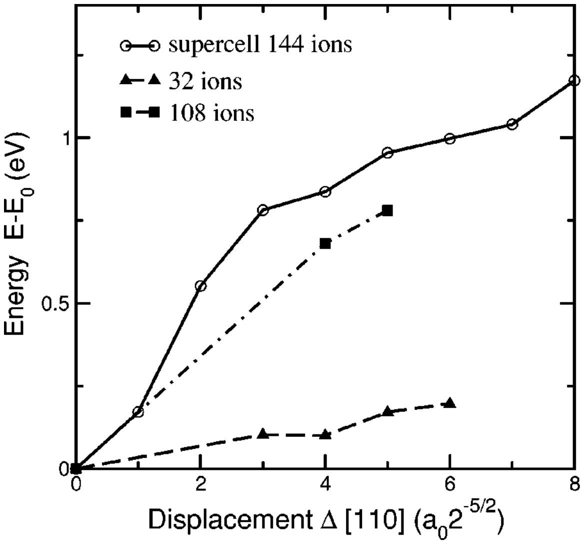

FIG. 3. The potential-energy surface for the triplet exciton as described in the text. The energies are plotted with respect to the energies of the triplet state of a perfect lattice (zero coordinate). $\Delta \sim 5$ corresponds to the expected minimum for the STE [Fig. 1(b)], $\Delta = 8$ corresponds to the next nearest-neighbor *F-H* pair [Fig. 1(c)].

Next, we calculate the potential-energy surface for the triplet exciton by displacing a selected Cl* ion along the $\langle 110 \rangle$ crystallographic axis and relaxing all the surrounding atoms at each Cl* position [Figs. 1(a)–(c)]. The PES for the triplet state calculated in different supercells is shown in Fig. 3. Additional information on the lattice relaxation and spin density changes along the Cl* displacement coordinate can be found on our web page.[46] It is seen that the obtained PES varies significantly with the size and shape of the supercell, in which it was calculated. In all calculations the free exciton configuration is predicted to be the lowest energy state, as reported previously.[6,9] The off-center STE configuration corresponds approximately to $(\Delta \sim 5)$. This state is predicted to be marginally stable only in the smallest supercell used (identical to the one used by Perebeinos *et al.*[9]). We also observe that the energy difference between the free exciton and the expected self-trapped state increases with the size of the supercell.

We have singled out most probable causes of the significant dependence of the calculated PES on the size and shape of different supercells: (i) defect volume change; (ii) spurious electrostatic interaction between the supercells; (iii) basis set completeness, and (iv) pseudopotential approximation. In the rest of this section we discuss these aspects.

To mimic the effect of the volume change associated with the self-trapping, we optimized the volume of the 144-ion supercell at each point of the adiabatic surface. The equilibrium lattice constant a_0 has increased only slightly: from 2.840 Å for a perfect lattice $(\Delta = 0)$ to 2.848 Å at the expected STE state $(\Delta = 5)$. The total energy of the STE has lowered by ~ 0.1 eV and the energy minimum for the STE did not exist.

As can be seen in [Fig. 1(b)], the charge distribution in off-center STE is associated with a substantial dipole moment. The strong dependence of the PES on the supercell size suggests that a significant contribution to the total energy may arise from the interaction between periodic multipoles persisting even for comparatively large supercells. The detailed evaluation of the correction energy within the PBC is tedious and extends beyond the scope of this paper. To give a qualitative estimation of this energy let us assume that the configurational coordinate of interest, Δ, is associated with a change of an electrical dipole moment $\mathbf{P}(\Delta)$, but not with a higher multipoles. Then, the total energy obtained within the PBC will contain the spurious interaction energy between the periodically repeated dipoles:

$$E_{PBC}(\Delta)=E(\Delta)+E_{dip}(\Delta). \tag{1}$$

Let us consider now the case when $\mathbf{P}(\Delta)$ is a nonmonotonic function and has a maximum at some value $\Delta=\Delta_x$. Then the energy $E_{dip}(\Delta)$ may also have an extremum at this point. If we shall further assume that the function of interest $E(\Delta)$ is almost constant in the interval around Δ_x, then the curvature of the $E_{PBC}(\Delta)$ may become qualitativaly different from that of the sought energy $E(\Delta)$.

To quantify the dipole-dipole interaction energy, a dipole moment of the supercell needs to be evaluated:

$$\mathbf{P}=\Omega^{-1}\int_{cell}\mathbf{r}\rho(\mathbf{r})d^3\mathbf{r}, \tag{2}$$

where the integral is taken over the volume of the supercell Ω, and $\rho(\mathbf{r})$ is a charge density (including both electrons and atomic cores). Given the value of the dipole moment $\mathbf{P}(\Delta)$, the energy E_{dip} can be evaluated using a point dipole approximation utilized in Makov-Payne formula[47] and generalized by Kantorovich[48] for noncubic supercells.

However, a calculation of $\mathbf{P}$ within the PBC is problematic, since the dipole defined by Eq. (2) is not invariant with respect to supercell's origin.[49] Therefore we consider the following simplified model. Assuming that the dipole moment of a free exciton in the perfect lattice, and that of a separated *H*-*F* pair, is zero, we approximate the dipole function $\mathbf{P}(\Delta)$ by a Gaussian, $P(\Delta)=P_{STE}\exp-[(\Delta-\Delta_{STE})^2/2\sigma^2]$, with a maximum at the expected STE configuration ($\Delta_{STE}\sim 4$). We chose $P_{STE}=4e$ Å and $\sigma=1$, which roughly corresponds to the $+/-$ unit charges separated by $a_0\sqrt{2}$ in NaCl. The dipole moment of the STE is unlikely to exceed this value. The model dipole function $P(\Delta)$ and the correspondig dipole interaction energies $E_{dip}(\Delta)$ for the supercells of 32 and 144 ions, are shown in Fig. 4. We observe that the dipole interaction energy is negative, strongly nonmonotonic, and significantly larger in absolute values for the smaller supercell. Therefore, if E_{dip} is sufficiently large, E_{PBC} (1) may exhibit a local minimum at the STE configuration while the corrected energy $E(\Delta)$ will not. We suggest, that the marginal local minimum for the STE obtained in our 32 ions supercell (Fig. 3) is precisely of this origin. The result obtained in the larger unit cell is closer to the GGA DFT accuracy limit.

We should note that the unscreened point dipole model[48] used here overestimates electrostatic interaction between supercells in PBC. Nevertheless, we believe that further refinement of the calculations will not affect the main conclusion—no stable state for the STE is predicted by the GGA DFT approach.

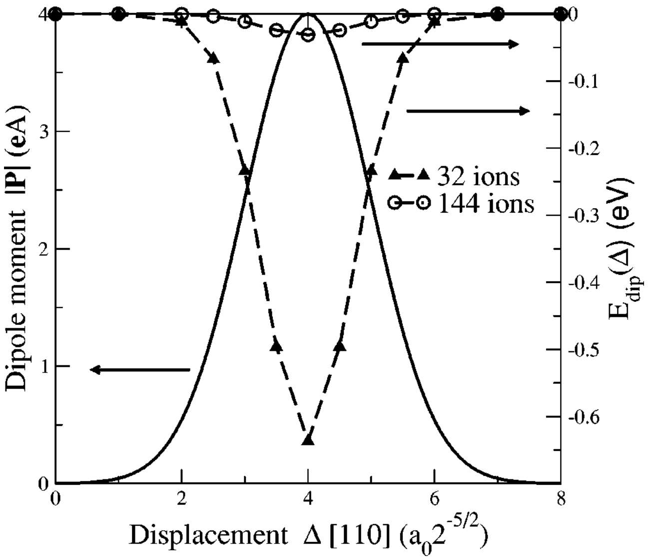

FIG. 4. The model electric dipole moment as a function of the adiabatic coordinate Δ (solid line and left *y* axis), and the corresponding energies E_{dip} (dashed lines and right *y* axis) for two different unit cells.

The reasons for the absence of a STE energy minimum in the local DFT approximation are not obvious. Several factors could result in the bias towards the delocalized solution. These include, for example, the choice of energy cutoff and *k*-point sampling. To check these issues, we compared calculations with cutoff energies of 220 and 285 eV and observed no significant difference in the STE relaxation. The *k*-point sampling is likely to affect more the energies of delocalized states. In fact we do observe a slight increase of the free exciton energy with the number of irreducible *k* points. This reduces the energy difference between the free and the self-trapped exciton, though the minimum for the STE still does not appear. Another uncontrolled factor in the calculation is the pseudopotential approximation for core electrons. In particular, we employed a large core ($1s^2 2s^2 p^6$) pseudopotential for sodium atoms. Hence the polarization of cations was virtually neglected in our calculations. To examine the role of cation polarization, we carried out the STE calculations with the helium core pseudopotential for Na atoms for selected configurations in the 64 atoms supercell. This also did not affect our qualitative conclusions—no energy minimum was obtained for the STE.

Our analysis suggests that the problem of localization lies not with the technical details of the calculations but rather more fundamentally with the approximations involved in the GGA density functional. In particular, essentially uncontrolled self-interaction error in the local density approximation is the most likely cause. However, a detailed characterization of the involved energy terms is difficult for the exciton, which comprises two strongly interacting spins with the energies near the top of the valence band and the bottom of the conduction band, respectively. It must be emphasized at this point that holes in alkali halides do self-trap in the form of V_k centers, while the electrons do not. Hence the hole self-trapping is also fundamental in the exciton localization. At the same time, self-trapping of the hole is a simpler problem in that it involves localization of a single spin. However, being charged, a hole presents some difficulty for studying within the PBC. In particular, we obtained no self-trapping of the hole within plane-wave DFT. Therefore we resorted to modeling the hole within the embedded cluster method, that has the following advantages: (i) the atomic-type basis set ensures no bias towards the delocalized states; (ii) the lattice polarization effects paramount for charged polar systems are fully accounted for; (iii) the use of the atomic basis sets allows the straightforward application of a number of local and nonlocal density functionals, so that the properties of various functionals can be studied.

V. HOLE TRAPPING IN NACL

The calculations of the hole (a total charge of the system is equal to $+1$) were performed within the embedded-cluster model discussed in Sec. III B (Fig. 2). We calculated the total energy of the system as a function of the distance between the two Cl ions equally displaced along the $\langle 110 \rangle$ axis towards each other from their respective perfect lattice sites [see Fig. 1(d)]. All other ions in region I were relaxed simultaneously to their equilibrium positions for each Cl-Cl separation.

The potential-energy surfaces calculated with different density functionals are depicted in Fig. 5. The zero energy in the top panel corresponds to the singly ionized perfect lattice calculated within each method. We observe that the shape of PES qualitatively depends on the amount of the Hartree-Fock exchange included in the density functional. The B3LYP functional predicts one global minimum corresponding to a free hole, the BH&H functional predicts two minima separated by a marginal barrier, while the Hartree-Fock method gives a single energy minimum corresponding to the self-trapped hole (V_k center) (top panel of Fig. 5). Furthermore, the energy difference between the free and self-trapped states ranges between -0.2 eV for B3LYP and 1.5 eV for the HF.

Different functionals also predict distinctly different spin localization. The analysis of the Mulliken spin population on the Cl_2^- molecule (middle panel in Fig. 5) reveals that the extent of spin localization increases faster with decreasing Cl_2^- distance when the amount of exact exchange is larger. In particular, the Hartree-Fock calculations predict the spin almost fully localized on Cl_2^- at a mere 0.05-Å displacement of two Cl ions from their respective lattice sites. The B3LYP functional, on the contrary, predicts very gradual spin localization with the decrease of the Cl-Cl distance. The variance in localization of spin in different functionals also affects the lattice relaxation. The bottom panel in Fig. 5 shows the distance between the two relaxed Na ions adjacent to the Cl_2^- molecule as a function of the Cl_2^- distance. It is seen that weak spin localization predicted in the B3LYP functional causes much smaller cation relaxation than that obtained in the Hartree-Fock method.

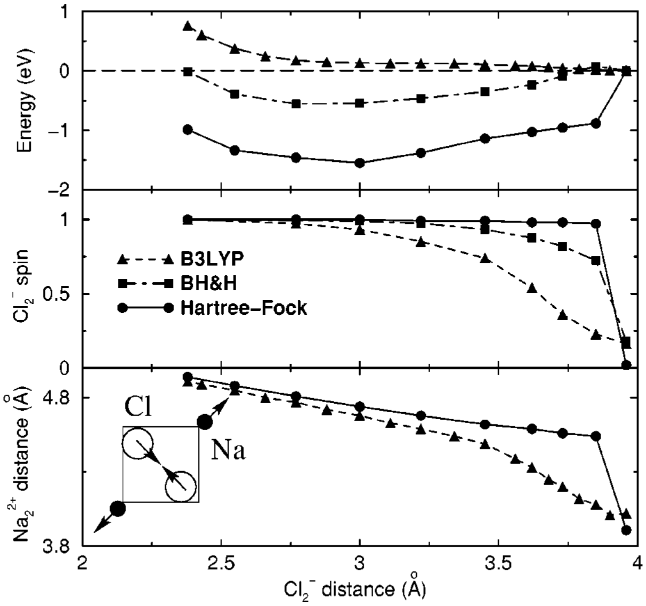

FIG. 5. The adiabatic surface for the V_k center (top panel), calculated with various density functionals. At each given Cl_2^- distance, all other atoms in the system were relaxed to the minimum-energy geometry. Zero energy corresponds to the perfect crystal configuration (the extended hole). The middle panel shows the dependence of the Mulliken spin population on the Cl_2^- molecule as a function of the same adiabatic coordinate. The bottom panel shows the relaxation of the pair of Na atoms adjacent to the V_k center.

VI. DISCUSSION

Our results highlight severe problems with applying KS DFT methods to the self-trapping problem. The LSDA and GGA density functionals yield solutions biased towards the delocalized states to such an extent that no stable self-trapped state is predicted for either a hole or an exciton, contrary to experimental evidence.

Let us emphasize that the degree of localization of a polaron is closely linked to the properties of the single-particle spectrum for the problem. For instance, spin density of the V_k center is represented almost entirely by the single-particle density of the last occupied orbital in a majority spin, $\psi_s(\mathbf{r}')$. The degree of localization of $\psi_s(\mathbf{r}')$ is related to its energy, ϵ_s, or more precisely, to the energy split of the ϵ_s from the corresponding band edge. In the KS method, ϵ_s is defined as[16]

$$\epsilon_s = \langle \psi_s | -\frac{1}{2}\nabla^2 + v_{eff}(\mathbf{r}) | \psi_s \rangle, \tag{3}$$

where

$$v_{eff}(\mathbf{r}) = v(\mathbf{r}) + \int \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}' + v_{xc}(\mathbf{r}). \tag{4}$$

Here, $v(\mathbf{r})$ represents the external potential of the atomic cores, the second term is the classical electrostatic potential due to electrons of density $\rho(\mathbf{r})$ (including the self-interaction), and $v_{xc}(\mathbf{r})$ is a local exchange-correlation po-

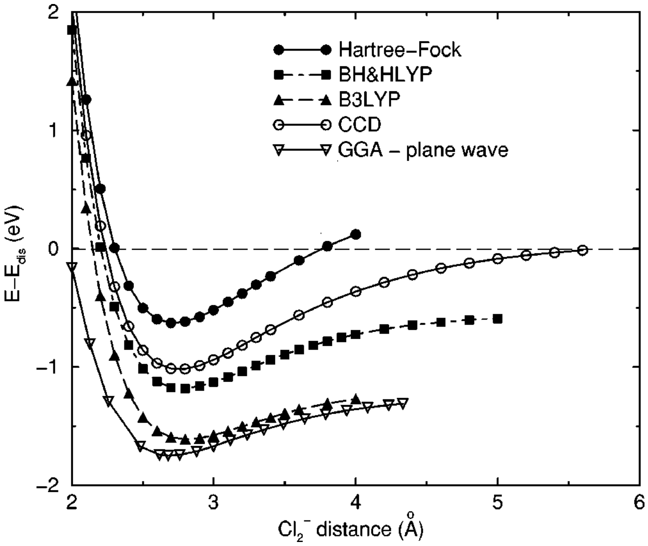

FIG. 6. The dissociation curve for the $Cl^-{}_2$ molecular ion calculated using various density functionals $[E_{dis}=E(\mathrm{Cl}^-)+E_{\mathrm{Cl}^0}]$. All the local basis calculations are done using the G86-311 Gaussian basis set.[41] In the plane-wave GGA calculations the energy cutoff 285.3 eV is used.

tential, where the self-interaction energy is partially cancelled. How do the terms in Eq. (3) contribute to self-trapping? One of the main factors facilitating self-trapping is lattice polarization. In alkali halide crystals, the second (and perhaps dominant) negative term is the energy gain due to the formation of the σ bond (localized doubly occupied orbital) in the $X_2{}^-$ molecular ion (X=F, Cl, Br, I). The factors favoring self-trapping are partially counterbalanced by an increase in the kinetic energy of localizing electrons. The latter results in a splitting of corresponding single-particle levels from the edge of the valence band. First, we note that any perturbation in the external potential $v(\mathbf{r})$ alone cannot cause self-trapping, since it does not depend on the number of electrons or their state, and self-trapping does not occur in a neutral crystal in its ground state. This is in contrast to polaron localization by defects, where the $v(\mathbf{r})$ contribution to localization is dominant. Therefore the critical localization terms for self-trapping are contained in the Hartree (electronic polarization) and exchange-correlation (bond formation) terms.

An accurate calculation of these contributions presents a serious problem for the KS DFT, for the following reasons:

(i) First, let us consider the formation of the $X_2{}^-$ quasimolecule. For that purpose we calculate the dissociation curve for the free $Cl_2{}^-$ molecular ion using different density functionals and the GAUSSIAN-98 package.[38] We shall use as a reference the energy curve obtained by the coupled cluster method with double substitutions (CCD). In Fig. 6, we observe that both the unrestricted Hartree-Fock and all studied DFT functionals do not predict the correct dissociation behavior for this open shell ion. Moreover, local as well as hybrid density functionals (but not the Hartree-Fock method) violate the energy variational principle in that the predicted dissociation curves asymptotically tend to energies significantly lower than the corresponding dissociation limit (i.e., the sum of the ground-state energies of the isolated negative chlorine ion and the neutral chlorine atom). The implication of this drawback for the self-trapping is clear—the energy gain associated with a decrease of the interionic distance in the $Cl^-{}_2$ from ~4 Å (as in a perfect lattice) to the V_k-center equilibrium configuration (~3 Å), is substantially underestimated by the DFT and overestimated by the UHF method.

Incorrect dissociation behavior of radical ions in DFT was reported by Bally and Sastry.[50] The subsequent comprehensive analysis of the $H_2{}^+$ molecular ion by Zhang and Yang[51] revealed that the self-interaction error in local density functional for such systems becomes uncontrollably large. It can be demonstrated that the self-interaction error, associated with the single-particle states, is positive and increases with their localization. Therefore self-interaction, being minimized during self-consistency, will also lead to the less localized single-particle states.

(ii) The polarization properties of a many electron system in the density functional theory are related to the exchange-correlation kernel[52] $K_{xc}(\mathbf{r},\mathbf{r}')=\delta^2E_{xc}/\delta n(\mathbf{r})\delta n(\mathbf{r}')$. The exact exchange correlation kernel is shown to possess the so-called ultranonlocality property, i.e., the diagonal element of its Fourier transform $K(\mathbf{q},\mathbf{q})$ possesses a $O(1/q^2)$ divergence at small wave numbers q. However, as demonstrated in Refs. 52 and 53, both LDA and GGA lead to $K_{xc}(\mathbf{rr}')$ which does not have the required $O(1/q^2)$ divergence. One of the implications of the nondivergent exchange-correlation kernel in KS DFT is that the macroscopic polarizability of the system (calculated as a KS polarizability) depends on the number of electrons and on the occupancy of the KS bands. That is, a calculated KS polarizability of the dielectric will be generally different in a singlet and triplet state, and for a system with or without the hole (both systems are technically metallic). Thus the reliability of polarization contribution in KS DFT for the triplet or charged systems is also essentially uncontrolled.

(iii) As mentioned earlier, the largely single-particle character of the self-trapping problem implies that the total spin density may be represented by a single-particle density of just one orbital. It is known, however, that KS orbitals do not necessarily carry this physical meaning. In particular, by virtue of construction, the KS formalism yields the single-particle eigenstates which minimize the kinetic energy (as calculated on single-particle orbitals).[16] Thus the kinetic energy contribution is always underestimated, leading generally to the least localized set of orbitals for a given density. Another delocalizing factor is the self-interaction error in the Hartree term, which is only partially cancelled in the local approximations to the exchange-correlation potentials. Apparently, a positive self-interaction grows uncontrollably as the state becomes more and more localized. Therefore any self-consistent procedure minimizing the total energy, also minimizes self-interaction by delocalizing the orbitals. It should be noted that the effects of minimization of the kinetic energy and self-interaction in KS method have the same effect and cannot be separated, since any form of nonlocal self-interaction correction leads to the single-particle equations distinct from those of KS.

Conceivably the depth of the self-trapping potential in polar dielectrics is unlikely to exceed 1 eV. It seems that the spurious delocalizing contributions inherent in the KS method always outgrow the localizing potential, so the self-trapped state cannot be predicted in this approach.

This problem is partially resolved by use of hybrid density functionals. We have demonstrated for the holes that the self-trapped solution gradually becomes energetically more stable as the amount of the exact exchange is increased. However, the conventional hybrid functionals, such as B3LYP, failed to predict a stable V_k center, let alone its localization energy. This raises the question of parametrization strategies for semiempirical functionals, which are not clear in the context of self-trapping.

Our calculations also highlighted another important methodological issue related to the calculations of the PES for polar systems within the periodic boundary conditions. The artificial multipole electrostatic interactions between supercells may drastically affect the shape of the PES, if the leading multipoles of the charge density vary along the chosen adiabatic coordinate. The dipole-dipole interaction in the triplet exciton modelled in a small supercell resulted in the appearance of the energy minimum for the STE configuration reported by Perebeinos *et al.*[9] Interestingly, the authors of Ref. 9 reported that no stable configuration could be found for the V_k center. These results can be understood by recalling that in the V_k-center calculations the leading term in the electrostatic interaction between the supercells is the monopole-monopole one. This term does not vary with the adiabatic coordinate and therefore does not affect the shape of the PES.

Although artificial delocalization in KS based DFT theory can be expected, it is difficult to assess *a priori* when a specific functional will fail in practical calculations. We suggest that the problem with the localized states in the KS method will occur in all cases where the localization potential is provided mainly by the electron-electron term. These include self-trapping phenomena, Jahn-Teller systems, low dimensional systems (e.g., Peierls instability), and systems with weak impurity perturbations. A list (by no means complete) of problematic DFT calculations where an artificial delocalization was reported includes: the hole localization in CaO doped with Li and Na and the F center in LiF as reported by Dovesi *et al.*;[13] dimerization in C_{4N+2} carbon rings;[54] the structure of the Al defect in α quartz;[14,15,55] exciton self-trappping in presence of thermal disorder;[6,56] the phase diagram of crystalline Pu (related to a localization of f-type atomic orbitals).[57–59]

On the other hand, the use of the Hartree-Fock based approaches is also limited since neglecting electron correlation favors localized states.[60] One should also note that frequently used approaches based on tight-binding methods do not fully account for the electron kinetic energy, and thus are also intrinsically biased towards localized solutions. As seen from these arguments, the DFT approach in KS formalism is unable to reliably resolve between localized and delocalized situations in systems where both types of states are possible. A more adequate many-electron theory for the self-trapping problem must go beyond the KS methods. Different forms of the density functionals free of the self-interaction error should be examined.

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