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# Charging induced emission of neutral atoms from NaCl nanocube corners

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## Abstract

Detachment of neutral cations/anions from solid alkali halides can in principle be provoked by donating/subtracting electrons to the surface of alkali halide crystals, but generally constitutes a very endothermic process. However, the amount of energy required for emission is smaller for atoms located in less favorable positions, such as surface steps and kinks. For a corner ion in an alkali halide cube the binding is the weakest, so it should be easier to remove that atom, once it is neutralized. We carried out first principles density functional calculations and simulations of neutral and charged NaCl nanocubes, to establish the energetics of extraction of neutralized corner ions. Following hole donation (electron removal) we find that detachment of neutral Cl corner atoms will require a limited energy of about 0.8 eV. Conversely, following the donation of an excess electron to the cube, a neutral Na atom is extractable from the corner at the lower cost of about 0.6 eV. Since the cube electron affinity level (close to that a NaCl(100) surface state, which we also determine) is estimated to lie about 1.8 eV below vacuum, the overall energy balance upon donation to the nanocube of a zero-energy electron from vacuum will be exothermic. The atomic and electronic structure of the NaCl(100) surface, and of the nanocube Na and Cl corner vacancies are obtained and analyzed as a byproduct.

## 1. Introduction

Displacement, or detachment of ions, atoms or molecules from a bulk alkali halide crystal is generally an energetically costly process. For instance, the energy required to remove a NaCl molecule from bulk NaCl is  $\sim 1.8$  eV per molecule [1]. Nonetheless, following addition or removal of an electron to the crystal, individual neutral atoms may be extracted from an alkali halide surface with greater ease. On account of the absence of Coulomb binding, and of the resulting low stability of the surface neutralized atom, such a process will be energetically less expensive.

For the extraction of a neutral halogen atom there is the initial cost of the preliminary neutralization process, requiring roughly the exciton energy of NaCl of order 8 eV [2]. Once primed with this (surface) exciton the alkali halide solid is

known to emit a halogen atom with creation of a surface F-center [3–7]. Recent experiments with STM tips on NaCl(100) atomically thin films [8] showed in addition that it is feasible to extract halogen atoms under a tip without prior excitation but in conditions of applied voltage.

For the extraction of neutral Na atoms the preliminary neutralization process is on the contrary exoenergetic, since an electron initially at the energy of vacuum zero can lower its energy by falling in the affinity level of the alkali halide surface, or of a defect, as will be discussed below.

Here we examine theoretically the emission of both neutral Cl and Na atoms upon subtraction or donation respectively of electrons to NaCl cubic nanoclusters. Experimentally, neutral NaCl nanoclusters may acquire negative charge through electron attachment, or positive charge via electron photoemission [9]. Early empirical estimates suggested the possible thermal emission of neutral Na atoms from NaCl nanoclusters with an activation energy as small as 0.4 eV. An even smaller energy of about 0.04 eV was estimated for the detachment of neutral Cl atoms [10–12]. Such low detachment energies are likeliest for the weakly bound atoms at the cluster corners.

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Interestingly, since as mentioned above electron attachment to the NaCl affinity level will itself liberate energy, this suggests the possibility of cheaply generating reactive alkali atoms whose availability might be of considerable importance for investigation of their principles as well as for practical applications.

In this paper we use first principles density functional theory (DFT) methods to calculate the energy necessary to detach a neutral corner alkali (halogen) atom after donation (subtraction) of an electron to an alkali halide crystalline nanocube. The calculated neutral Na extraction energy is 0.6–0.7 eV, somewhat larger than, but of similar magnitude of, the semi-empirical estimates. The extraction energy obtained for neutral Cl is about 0.8 eV, much larger than the empirical estimates. In the process, we independently clarify several aspects of NaCl(100) surface electronic structure.

Initially carrying out our calculations for an infinite flat, fully relaxed NaCl(100) surface, we first of all identify the surface electronic states, focusing on those that lie energetically inside the bulk energy gap. To a zero order approximation, these states foreshadow the wavefunctions which an added hole or an extra electron would occupy in a hypothetical fully delocalized, plane-wave like state when added to the infinite, perfect NaCl(100) surface. Thus, these filled and empty surfaces qualitatively describe respectively the ideal ionization and affinity levels of the infinite NaCl solid, when bounded by NaCl(100) surfaces.

Actually, however, a hole/electron initially created in such a surface state may not generally remain stable in such a plane-wave like, delocalized state. Even in the absence of defects and of extrinsic traps, electron–phonon coupling alone can lead to a spontaneous local deformation of the surface lattice structure, whereby the surface electron or hole may become localized, or ‘self-trapped’. A self-trapped hole near a Cl<sup>−</sup> surface ion, or a self-trapped electron near a Na<sup>+</sup> surface ion can lead to ion neutralization, canceling the electrostatic attraction which originally tied that ion to surface lattice. The surface atom thus neutralized will in that case remain bound to the surface only through weak induced-dipole and dispersion forces, now relatively easy to break. We will not actually pursue the existence of such ideal surface self-trapped states here. The reason for this is that in presence of such omnipresent surface defects as steps, kinks, or corners, the actual trapping of electrons and holes will take place right there, with great preference over possible self-trapping in the flat surface regions.

As a preliminary step, the physics and the energetics of electron/hole capture will be addressed in this paper by direct electronic structure calculations of initially neutral, then charged, NaCl(100) nanocubes. The cubes are chosen with ‘magic structures’ [10] of increasing size, namely (NaCl)<sub>4</sub> (NC4) and (NaCl)<sub>32</sub> (NC32). Following the charging of the nanocube, yielding NC4<sup>±</sup> and NC32<sup>±</sup>, one corner atom, Cl in the positive case, Na in the negative case, is gradually and adiabatically forced to detach, by moving along a (111) direction away from the cube corner. The detaching Cl and Na atoms have captured the added hole or electron and are spontaneously neutral, while the cluster left behind has an ion

vacancy and is charged. The increase of total energy upon detachment defines the energy barrier for neutral atom escape. We find that the results for the two cluster sizes, NC4 and NC32 essentially coincide, suggesting that size effects are negligible, so that the resulting calculated detachment energies can be trusted as a good approximation to the cost of neutral corner atom extraction for arbitrary sizes, and probably even from corners of more general geometries.

These results now permit a quantitative discussion of the overall energy balance of the neutral atom emission process and in particular the probability of direct thermal emission. In addition, we obtain as a byproduct a description of the atomic and electronic structure of the NaCl(100) surface, and of the nanocube corner vacancies with their ionization and affinity levels, all of potential spectroscopic interest.

We did not attempt to simulate the process of electron attachment or electron removal, since they are not relevant to our problem. Actually, calculations of electron attachment to a NaCl nanocluster already exist in the literature based on quantum path-integral molecular dynamics methods, using classical interatomic potentials, and by treating the quantum nature of the extra electron in an effective way [13, 14].

The paper is organized as follows. In section 2 we will describe the computational method and the geometrical aspects of the systems that are the subject of our calculations. In section 3 we will present and discuss the electronic structure for the neutral and charged NaCl(100) surface, and subsequently that of the neutral and charged nanoclusters. In section 4 we present the energetics of neutral atom emission processes, with an estimation of thermal emission rates. Finally, section 5 will present our conclusions.

## 2. Computational methods

We carried out *ab initio* electronic structure and total energy calculations based on the density functional theory (DFT) [15] in the generalized gradient approximation (GGA). We adopted the plane-wave pseudopotential approach [16], using norm-conserving pseudopotentials [17] and a plane-wave cutoff of 40 Ryd. The Na pseudopotential was generated from the ionized configuration (3s<sup>0.6</sup> 3p<sup>0.1</sup> 3d<sup>0.1</sup>) and non-linear core corrections [18] were included.

Charged systems were simulated by adding one electron to the cluster LUMO (conduction band in the infinite surface case) or subtracting one electron from the cluster HOMO (valence band in the infinite surface case) in presence of a uniform neutralizing background. Surfaces and isolated nanocubes were simulated by periodically repeated slabs and nanocubes, all replicas well separated by a sufficient amount of vacuum. All calculations were spin polarized, and made use of the gradient-corrected PW91 exchange–correlation functional [19].

We started by computing the electronic structure, the equilibrium lattice spacing (5.62 Å) and the bulk modulus (22 GPa) of bulk fcc NaCl, in good agreement with experimental values (5.54 Å and 28.6 GPa [20]) and with previous calculations. The calculated DFT energy gap is 5.42 eV, substantially smaller than the experimental gap

8.97 eV [21]. We should point out that this defect, which is standard in DFT calculations, does not cause errors or problems with the accuracy of the total energy, so long as the energetic ordering of levels is correct. Thus, for example, the total energy calculation would develop problems if, say, the Kohn Sham 3s electronic energy level of the neutral Na atom were to fall accidentally outside the NaCl cluster energy gap, for that would wrongly make the neutral atomic state unstable. We find no such occurrence in our calculations, which can therefore be relied upon to a state of the art DFT accuracy.

As the next step, we calculated the electronic structure, total energy and equilibrium atomic positions of the neutral infinite NaCl(100) surface. For that we used a slab consisting of 10 atomic layers, periodically repeated and separated by 8 Å of vacuum. Sampling of two-dimensional  $k$ -points was done by means of a Monkhorst–Pack mesh of  $4 \times 4$  in the 2d Brillouin zone (BZ). Surface electronic states were identified based on their energy location inside the surface projected bulk energy gap, and on their exponential decay from the surface towards the slab center. The zero of Kohn–Sham electronic eigenvalues is taken to be the vacuum level, initially extracted from the average value of the Hartree potential in the geometric center of the vacuum region between the slabs, after a careful extrapolation to the infinite distance limit.

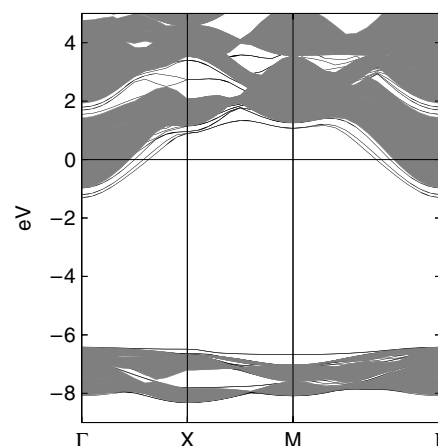
Cubic NaCl nanocluster geometries were subsequently created by cutting out cubelets from a perfect NaCl crystal, with an initial interatomic Na–Cl distance of 2.81 Å. We studied neutral nanocubes of two sizes, a small one  $\text{Na}_4\text{Cl}_4$  made up of 8 atoms or 4 molecules (NC4), and a larger one  $\text{Na}_{32}\text{Cl}_{32}$  of 64 atoms or 32 molecules (NC32). Calculations were carried in a cubic supercell of 10 Å lateral side for the smaller cube and 20 Å for the larger one. We sampled the supercell BZ at the  $\Gamma$  point only. For the neutral nanocubes, we verified that the residual interaction between periodic replicas is negligible. However, for the charged cubes, the residual interaction is not negligible and was removed by the technique described in [22].

### 3. Results

We will begin this section by describing the electronic states of the infinite ideal neutral NaCl(100) surface, followed by results for charged NaCl(100), where the extra electron and the extra hole are fully delocalized. Subsequently we will present results for the neutral and charged nanocubes, and the calculated extraction energy curves.

#### 3.1. Neutral NaCl(100)

Modeling the infinite flat NaCl(100) surface with a 10-layer slab, its geometric structure was fully relaxed so as to minimize the calculated DFT total energy. The largest relaxation occurred for the outer surface atoms, the  $\text{Na}^+$  surface ions relaxing inwards, the  $\text{Cl}^-$  surface ions outwards. As a result the electron charge distribution (carried almost entirely by  $\text{Cl}^-$  ions) spills out further into the vacuum. Overall, the zero temperature equilibrium neutral NaCl(100) geometry is thus predicted to be slightly buckled, with a



**Figure 1.** NaCl(100) surface band structure. The gray bands are the bulk projected band structure. The vacuum level is indicated by the horizontal line. The Cl 3s states (not shown) lie around  $-18$  eV.

difference in height between  $\text{Cl}^-$  surface ions and  $\text{Na}^+$  surface ions of 0.095 Å. The computed surface energy is  $13.17 \text{ meV } \text{Å}^{-2}$  ( $211 \text{ erg cm}^{-2}$ ), in line with experimental estimates and in striking agreement with Born–Mayer–Huggins–Fumi–Tosi classical potential calculations, which yield about  $200 \text{ erg cm}^{-2}$  at  $T = 0$  [23].

The electronic states of the slab were plotted in the 2d surface BZ, in superposition with the surface projected bulk bands. Possible NaCl(100) surface electronic states were then identified by their energetic location inside the surface projected bulk energy gap.

Our calculated surface electronic structure of the fully relaxed, neutral NaCl(100) is shown in figure 1. The edge of the conduction band lies 1.02 eV below the vacuum level. Below that, we find a pair of empty surface states, 1.35 eV and 1.46 eV below vacuum respectively. The wavefunction of these states mainly consists of surface Na 3s and 3p orbitals spilling out into vacuum—strikingly unlike the conduction states of bulk NaCl, which have instead a sizable Cl 3p character. Qualitatively, these neutral surface states suggests electron affinity levels of NaCl(100) of a very similar nature, namely surface Na 3s and 3p. Their significance however is obviously not quantitative, because these states are not occupied by an actual electron. The experimentally reported electron affinities of NaCl in fact range from 0.5 eV [24] and [25] to 1 eV [26], roughly 35%–70% of the calculated empty surface state energy value below vacuum zero.

By charging the slab with an extra electron, we attempted to compute the electron affinity as the total energy difference between the slab with an extra electron and the neutral slab  $A = E(N + 1) - E(N)$ . This should work in principle, so long as the sequence of the electronic levels is preserved. However we found that within DFT-PW91, the extra electron level rises above the conduction band edge. As a result, the SCF procedure does not converge. This, we believe, is an effect of the incomplete cancelation of self-interaction in DFT, and thus an artifact, reflecting the well known difficulty that approximate XC functionals have in binding extra electrons [27, 28]. Due to the fact that we do not have

a reliable calculation of the surface electron affinity levels of NaCl(100), and all we can state is that they should lie between the empty surface state levels at 1.35 and 1.46 eV below vacuum, and vacuum zero.

Coming to the filled states, the surface projected valence band edge lies  $\sim 6.4$  eV below vacuum. Due to the DFT underestimation of the energy gap, the true valence band edge actually lies  $\sim 9$ – $10$  eV below the vacuum level, as suggested by the experimental work function [26]. Just above the calculated valence band edge we find for neutral NaCl(100) a filled surface state, whose existence is restricted to the neighborhood of the  $M$  point in the 2d BZ. Like the valence band states, this surface state has a Cl 3p character. We repeated the calculation by removing one electron and we found that the hole state is delocalized over all surface Cl 3p<sub>z</sub> orbitals.

### 3.2. Neutral NaCl nanocubes

It is known from experiments [10, 9] that in equilibrium gas phase ionized NaCl clusters exhibit ‘magic sizes’ corresponding to small cubelets exposing (100) facets, whose general formula is  $[\text{Na}_n\text{Cl}_{n-1}]^+$  or  $[\text{Na}_n\text{Cl}_{n+1}]^-$ . Even if neutral clusters cannot be directly detected in mass-spectroscopy experiments because of the destabilizing nature of charging, they are nonetheless predicted [9] with cubic shape, and a different general formula  $\text{Na}_{2n}\text{Cl}_{2n}$ . Equilibrium charged clusters (which are observed) possess an odd number of ions on the cubic edges, as opposed to neutral clusters which have an even number of ions. Positively charged clusters, in this idealized picture, have only  $\text{Na}^+$  corner ions, no chlorine corners at all. Conversely, negatively charged clusters have  $\text{Cl}^-$  corner ions only, and no sodium corners at all. Neutral  $\text{Na}_{2n}\text{Cl}_{2n}$  clusters instead have four  $\text{Na}^+$  and four  $\text{Cl}^-$  corner ions. Our aim here is to predict electronic properties and energies valid for NaCl clusters up to macroscopic sizes, which are not destabilized by a single electron or a single hole. Thus we will restrict our calculations to  $\text{Na}_{2n}\text{Cl}_{2n}$  nanocubes, even in the charged case.

In order to get a first account of the energetics associated with the structural relaxation of the nanocubes, we carried out the structural relaxation of the two nanocubes  $\text{Na}_4\text{Cl}_4$  and  $\text{Na}_{32}\text{Cl}_{32}$ , starting from the perfect cubic structures, generated according to the prescription of section 2. The deviations of atomic coordinates from idealized bulk-like positions are largest for the corner atoms. The Na corner ions relax strongly inwards, towards the center of the cube, while the Cl corner ions relax weakly outwards. The corner atom displacements are shown in table 1, together with the energy difference between the relaxed structures and the ideal cubes. The pattern of displacements of the  $\text{Na}^+$  and  $\text{Cl}^-$  corner ions follows the same trends as for the NaCl(100) relaxation, namely  $\text{Na}^+$  corner atoms move toward higher electronic density regions, while the  $\text{Cl}^-$  corner atoms relax away from it.

The relaxation process lowers the symmetry of the nanocubes from  $O_h$  to  $T_d$ , the tetrahedral group. The HOMO is a three-fold degenerate linear combination of corner Cl 3p orbitals, their lobes pointing along the diagonals of the cube

**Table 1.** Structural relaxation of the neutral nanoclusters, starting from the ideal cubic structures. The final structure has  $T_d$  symmetry.  $\Delta E$  is the energy difference between the relaxed structures and the starting one.  $\Delta\mathcal{E}_{\text{LUMO}}$  and  $\Delta\mathcal{E}_{\text{HOMO}}$  are the energy difference of the HOMO and LUMO with respect to the initial ideal structure with bulk NaCl distances. The degeneracy of LUMO and HOMO nanocube levels is given in the last column.

	Small cube ( $\text{Na}_4\text{Cl}_4$ )	Large cube ( $\text{Na}_{32}\text{Cl}_{32}$ )	
Na corner displ. ( $\text{\AA}$ )	0.35	0.54	(inward)
Cl corner displ. ( $\text{\AA}$ )	0.02	0.21	(outward)
$\Delta E$ (eV)	-0.65	-1.59	
$\Delta\mathcal{E}_{\text{LUMO}}$ (eV)	+0.15	+0.10	( $\times 1$ )
$\Delta\mathcal{E}_{\text{HOMO}}$ (eV)	-0.71	-0.45	( $\times 3$ )

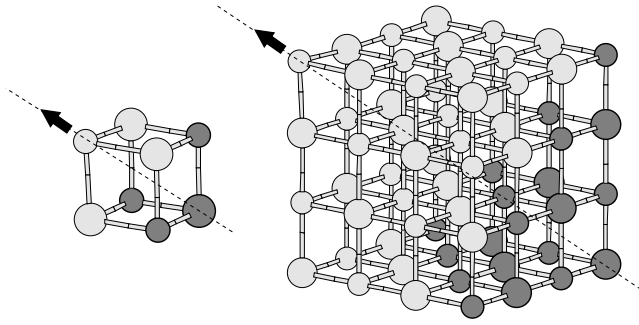
([111] directions). The LUMO is non-degenerate and consists of a linear combination of Na corner atoms 3s and 3p orbitals. The LUMO wavefunction is, as could be expected, very much diffuse outside the nanocluster than the HOMO.

The neutral nanocube HOMO and LUMO states might be hoped to provide, as the surface states of the previous section did, a qualitative indication of the ionization and affinity levels of the nanocube, after an electron is removed or added to the nanocube. However, after charging the nanocube, we will find that in this case levels actually fail to provide a good reference state for computing the extraction energies. The reason is twofold. First, removal of an electron from the HOMO is accompanied by a Jahn–Teller (JT) distortion and the symmetry of the nanocube is lowered. The energy gain associated with the JT distortion can be large in the smallest nanocubes. A precise calculation of this artificial JT energy gain within DFT is beyond the scope of this paper. On the contrary, addition of an electron to the LUMO is less problematic since on account of the lack of true degeneracy it only gives rise to a relaxation, or pseudo JT effect, where the energy gain is smaller with respect to the JT case. Second, these highly symmetrical HOMO and LUMO states, perfectly delocalized over opposite corners as they are because of symmetry, are unrealistic. In fact as soon as one corner atom is even slightly displaced outwards, the extended nature is removed and the extra electron (hole) wavefunction collapses to become strongly localized precisely on that atom. Based on these considerations, the effective initial state energy is calculated by assuming a very small outward displacement which breaks cubic symmetry in the initial state as well, and extrapolating the initial displacement to zero.

### 3.3. Electron addition: corner neutral Na atom detachment

We simulated the detachment of a corner neutral Na atom by donating an electron to the small cube  $\text{NC}_4^-$  and to the large one  $\text{NC}_{32}^-$ . As discussed in the previous sections, the  $\text{Na}^+$  corner ions constitute the affinity site for the extra electron, whose wavefunction collapses onto a single Na corner ion as this is even slightly pulled outwards. As a result, already at the earliest stage of detachment the  $\text{Na}^+$  corner ion becomes naturally neutralized (reduced) to its neutral state.

To calculate the energy cost of detachment we gradually displaced the Na atom outwards in the [111] direction away



**Figure 2.** Left: small cube  $[\text{Na}_4\text{Cl}_4]^-$ . Right: large cube  $[\text{Na}_{32}\text{Cl}_{32}]^-$ . Small circles: sodium; large circles: chlorine. Dark circles: fixed atoms (both Na and Cl). The arrow indicates the direction of extraction of the Na corner atom.

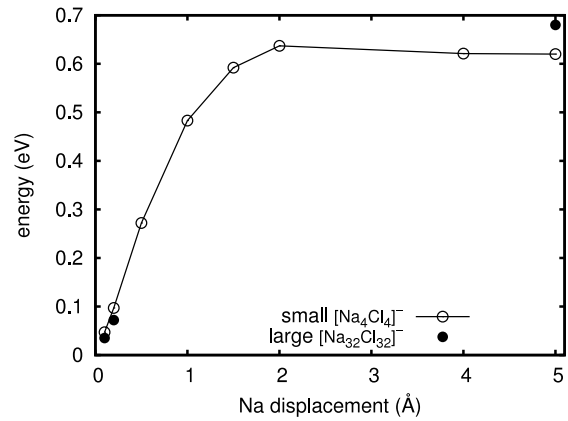
**Table 2.** Energy necessary to extract a neutral atom from the corner of a nanocube.

	Small cube	Large cube
Na extraction $\Delta E_{\text{Na}}$ (electron addition) (eV)	0.62	0.68
Cl extraction $\Delta E_{\text{Cl}}$ (electron removal) (eV)	0.80	0.78

from the corner of the nanocube. The displacement was measured from the ideal corner coordinates of the perfect cube, taken as the reference geometry. Relaxation of the other ions was allowed during detachment. Actually, in order to simulate the mechanical rigidity of a much bigger cube or corner, only the ions closest to the resulting corner vacancy were allowed to relax, whereas the remaining ions (roughly 1/3 of the total) were kept fixed as indicated by the different shading in figure 2. We relaxed the structure adiabatically after each outward displacement of the corner atom, increased in steps from 0.1 up to 5.0 Å.

The total energy change is followed by adiabatically relaxing the remaining atomic positions so as to minimize the energy as a function of the corner Na nucleus extraction coordinate. Extraction is complete when the total energy levels off at some large pull-off distance which we take to be 5 Å. The total energy is found to increase monotonically, leveling off for an outward displacement of  $\sim 4$  Å and higher (figure 3). The extraction energy is evaluated as a difference between the total energy for a displacement of 5 Å and the total energy for zero displacement. The results are summarized in table 2. The energy required to extract a neutral Na atom, by addition of an electron is calculated to be  $\sim 0.6$  eV, in fairly good (even if in our view somewhat fortuitous, given the approximations implied by the empirical estimates) agreement with the previous estimate of 0.4 eV [10–12].

The detachment energetics we just presented is in principle affected by nanocube finite-size effects. However, the near coincidence of results of the small and large cubes indicates that finite-size errors arising from various sources are relatively unimportant. This also agrees with the localized nature of distortions and of electronic states involved. Because of that we did not attempt to compute larger nanocubes, due to the much larger computational costs, but also comforted by the

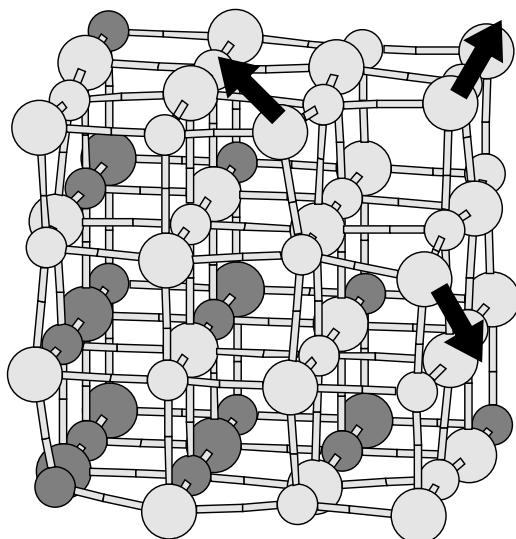


**Figure 3.** Na extraction energy profile (electron addition). The total energy of the relaxed nanocubes is plotted against the outwards displacement of one Na corner atom along the [111] direction.

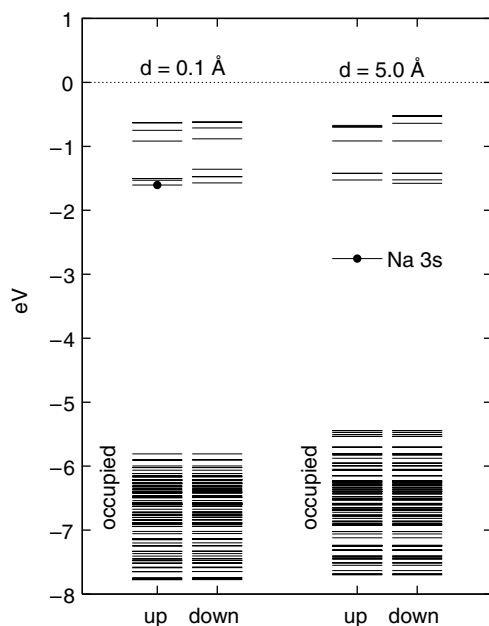
convergence observed. Our small-size results are we believe fully representative of the physics of even a macroscopic cubic corner.

More subtly, the incomplete cancellation of electron self-interaction in DFT might constitute another source of error. A different degree of localization of the extra electron in the initial and final state will introduce an error, due to a correspondingly different self-interaction of the two electron states: the initial one spread on the whole cluster and the final one in the neutral Na atom only. However, as explained earlier, we generate our effective initial state by introducing a very small displacement which breaks the ideal cubic symmetry in the initial state too. With that, the localization of the electronic state is no longer very different in the initial and final states, also implying that the self-interaction error is very much reduced. The effect is, in any case, not a large one to start with. For an appreciation of the magnitude, the total energy of the perfectly cubic  $\text{NC}_{32}^-$  is  $E_0 = -1687.173$  eV, that of the same nanocube after a slight corner Na extraction (extrapolated to zero) is  $E'_0 = -1687.211$  eV, and the final one after full Na atom extraction  $E'_5 = -1686.531$  eV. The difference  $E_0 - E'_0 = 38$  meV (which also contains the self-interaction), is negligible compared the Na extraction energy  $\Delta = E'_5 - E'_0 = 0.68$  eV.

Finally, we examined the atomic relaxation pattern and the electronic structure of the Na corner vacancy, after the neutral Na atom is fully extracted. All atomic relaxations (figure 4) are mostly localized in the vicinity of the vacancy. The three first neighbors  $\text{Cl}^-$  ions relax outwards in such a way as to minimize their electrostatic repulsion. We show in figure 5, the energy levels of the large cube  $[\text{Na}_{32}\text{Cl}_{32}]^-$  with an extra electron, in the initial and final state ( $[\text{Na}_{31}\text{Cl}_{32}]^- + \text{Na}$ ). Initially, the electron is trapped in a corner state  $\sim 1.6$  eV below vacuum. After Na extraction, the extra electron sits on the Na 3s atomic level which lies  $\sim 2.75$  eV below vacuum. We note that this level is too high in energy, for in reality the valence electron energy of a neutral Na atom in vacuum below vacuum zero should be about equal to the Na ionization potential (5.1 eV). As is well known, this is a standard DFT problem. However, as far as total energy differences are concerned, DFT



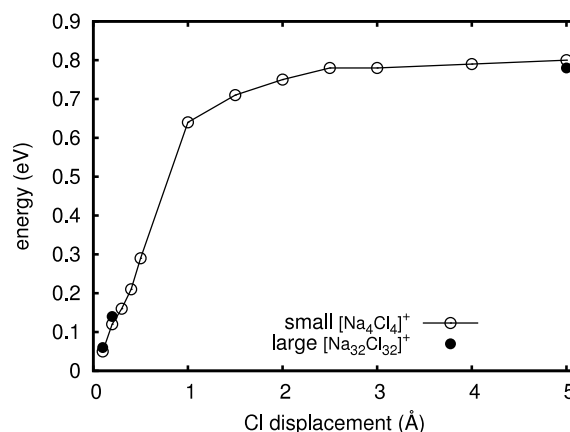
**Figure 4.** Relaxation pattern around the Na corner vacancy (top right) in the large cube when the neutral Na atom is fully extracted ( $[\text{Na}_{31}\text{Cl}_{32}]^-$ ). Small circles: sodium; large circles: chlorine. Dark circles: fixed atoms (both Na and Cl).



**Figure 5.** Na extraction (electron addition): energy levels (in eV) from the vacuum level (set to zero) for the large  $[\text{Na}_{32}\text{Cl}_{32}]^-$  nanocube. Left column: corner Na displacement 0.1 Å; right column: corner Na displacement 5.0 Å (fully extracted). The levels below  $-5.5$  eV are fully occupied. The solid circle indicates the level of the extra electron.

is generally accurate and reliable, at least so long as the self-consistent level configuration has the correct ordering, which it does in our case.

In the final state, negative nanocube plus detached neutral Na atom, there is also a second group of levels lying in the gap, around  $-5.5$  eV—that is about 0.3 eV above the bulk valence states. These are Cl based defect states associated with the relaxation of the three Cl ions neighboring the Na corner vacancy.



**Figure 6.** Cl extraction energy (electron removal).

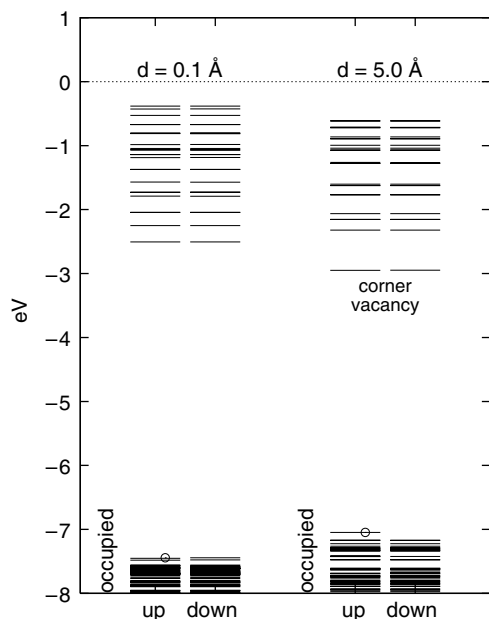
### 3.4. Electron removal: corner Cl detachment

We simulated the detachment of a corner Cl atom by removing an electron from the nanocube, generating both a small positive cluster  $\text{NC}_4^+$  and a large one  $\text{NC}_{32}^+$ . The overall mechanics is similar to the previous section. In the case of Cl, an electron is naturally removed from a  $\text{Cl}^-$  corner atom, neutralizing (oxidizing) it to its neutral state.

We followed a procedure similar to that described in the previous section, except now for the Cl corner atom. Similarly to the case of Na, the total energy upon Cl detachment was found to increase monotonically as a function of the Cl outward displacement along [111], leveling off for an outward displacement of  $\sim 4$  Å and higher (figure 6). The extraction energy is evaluated as a difference between the total energy for a displacement of 5 Å and the total energy for zero displacement. Like in the previous case, we considered the sources of errors, and found them to be equally tolerable.

Our resulting Cl extraction energy (table 2)  $\Delta E_{\text{Cl}} \sim 0.8$  eV is in contrast with the earlier semi-empirical estimate of 0.04 eV, 20 times smaller [10, 11]. That estimate however had been obtained attributing the binding energy of a neutral Cl atom entirely to dispersion forces, much smaller in Cl than in Na because their atomic polarizabilities differ roughly by a factor 3. Our result shows that, on the contrary, the energy cost to extract a neutral Cl or a neutral Na atom are close. This suggests that the main contribution could be the formation energy of the corner vacancy. This energy cost could be reduced if the Cl atom is adsorbed on top of another Cl atom, as shown recently in [29].

As in the case of the  $\text{Na}^+$  vacancy, atomic relaxations (not shown) are now mostly localized in the vicinity of the  $\text{Cl}^-$  vacancy. The first three neighboring  $\text{Na}^+$  ions relax inwards. We show in figure 7 the energy levels of the large cube ( $[\text{Na}_{32}\text{Cl}_{32}]^+$ ) with an extra hole, in the initial and final state. Initially, the hole is trapped in a corner state  $\sim 7.5$  eV below vacuum. In the final state, the hole sits in one of the Cl 3p atomic levels,  $\sim 7$  eV below vacuum. After the  $\text{Cl}^-$  is extracted, a corner vacancy empty electronic state  $\sim 3$  eV appears below the vacuum level. This level might act as a final state for optical transitions from the neighboring  $\text{Cl}^-$



**Figure 7.** Cl extraction (electron removal): energy levels (in eV) from the vacuum level (set to zero) for the large  $[\text{Na}_{32}\text{Cl}_{32}]^+$  nanocube. Left column: corner Cl displacement 0.1 Å; right column: corner Cl displacement 5.0 Å (fully extracted). The open circle indicates the position of the hole, otherwise the levels below  $-7$  eV are fully occupied.

ions, similar to optical transitions in bulk or surface F-centers. Experimentally a surface F-center empty level is known to lie  $\sim 2$  eV below vacuum [2].

#### 4. Discussion

We calculated the energetics of detachment of neutral atoms from NaCl nanocube corners after charging the nanocube with an electron or with a hole. The energies of detachment— $\sim 0.6$  eV for neutral Na,  $\sim 0.8$  eV for neutral Cl—are similar, and altogether relatively small.

From a practical point of view, among the two processes, the electron induced extraction of Na atoms from NaCl nanocubes is more important for two reasons. First, an extra electron coming from vacuum can gain energy by spontaneously attaching to the cluster and occupying the empty surface states which gives rise to a positive electron affinity of NaCl(100), of the order  $\sim 1$  eV, to be compensated by an energy cost of 0.6 eV to extract a Na corner atom. In contrast, electron removal requires an energy as large as the work function ( $\sim 9$  eV). Second, detachment of neutral Na atoms from charged NaCl nanocubes could provide a cheap abundant source of very reactive atoms. After detachment, a neutral alkali atom could react in the gas phase with a water molecule yielding sodium hydroxide and molecular hydrogen:



a reaction which is very exothermic, with an enthalpy of reaction of  $-247$  kJ mol $^{-1}$  or ( $-2.56$  eV per Na atom) [1]. Combined with our calculated Na extraction energy, the net

balance is still exothermic,  $\sim 190$  kJ mol $^{-1}$  ( $\sim 2$  eV per Na atom).

Even assuming the starting neutral NaCl nanoclusters, and an abundant ‘beam’ of (nearly) zero-energy electrons to be given, there are still two main limiting factors in this scheme. These are the uncertain yield of electron attachment, and the small escape rate of Na atoms. Electron attachment depends crucially on how the electron is donated to the cluster and on the microscopic mechanisms of excess energy disposal, a subject far beyond the scope of this paper. The Na atom thermal escape rate (average time between single atom emission events) can be estimated easily as

$$\tau = \Omega^{-1} \exp[\Delta E_{\text{Na}}/k_{\text{B}}T].$$

Assuming an attempt frequency  $\Omega$  of  $\sim 1$  THz, the neutral Na atom escape rate is very small, of the order of one atom every 1.8 s at room temperature. Of course, that could be substantially increased by heating.

#### 5. Conclusion

We calculated the extraction process of a neutral Na (Cl) atom from NaCl nanoclusters to which one electron has been donated (removed). For the neutral Na atoms, a relatively low extraction energy of the order of 0.6 eV, about 50% higher than previously suggested [10–12] is determined by our calculation. The extraction energy of a neutral Cl atom is of the order of 0.8 eV, about 20 times larger than earlier suggestions [10, 11]. It is suggested that neutral Na atoms that will to some extent be thermally emitted by corner sites of negatively charged NaCl nanocubes could provide a cheap source of very reactive halogen atoms.

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