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Theoretical study of the localization of excess electrons at the surface of ice

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Abstract

The localization of excess electrons at the basal plane surface of hexagonal ice Ih is investigated theoretically, combining density functional theory (DFT) with a partial self-interaction correction (SIC) scheme, to account for spurious self-interaction effects that artificially delocalize the excess electrons. Starting from energetically favored surface geometries, we find strong localization of excess electrons at surface dangling bonds, in particular for surface adsorbed water monomers and dimers.

(Some figures in this article are in colour only in the electronic version)

The properties of charged clusters and surfaces are of fundamental interest in cluster and surface science, atmospheric chemistry and astrophysics. Aqueous systems are especially intriguing due to the unique role of water in biological and many chemical or technological processes [1, 2]. Experiments on anionic aqueous systems range from first reports of the solvated electron in bulk water [3] and water clusters [4] to recent works on ultrafast solvated electron dynamics [5–8]. Water clusters have been studied thoroughly over the last decades, both experimentally and theoretically; anionic water clusters are of interest since the polar solvent should allow for self-trapping of the excess electrons within the clusters. Indeed, depending on cluster size and preparation conditions, possible electron localization sites have been found at both the surface and in the interior of water clusters [9–20]. For small water clusters the localization of excess electrons in a surface state seems well established, the minimum cluster size required for interior localization is controversially discussed [9, 16, 18–20]. Going further from clusters to extended systems, the localization of excess electrons at the ice surface was explored in several recent theoretical studies [21–23]. There, molecular dynamics techniques were most often applied; such techniques are suitable for following the dynamics of a localized electron state. However, a systematic approach directly comparing different possible localization sites that are likely to occur at real ice surfaces [24] is still missing. The present paper is one first step in this direction.

We investigate the localization of an excess electron at the basal plane surface of hexagonal ice Ih by performing gradient-corrected density functional theory calculations (DFT-GGA). In order to account for spurious self-interaction effects that artificially delocalize the excess electron, the DFT wavefunctions are used as input for a partial self-interaction correction (SIC) scheme [25]. Thereby the potential of the excess electron is corrected for self-interaction, whereas the remaining electrons are treated on the usual DFT basis. In a previous study we investigated the neutral ice Ih(0001) surface and found water monomer adsorption on several non-crystallographic surface sites to be favorable [24]. Starting from these geometries, we find localization of the excess electron at surface adsorbed water molecules that is significantly more pronounced than on the ideally terminated ice basal plane.

Describing localized excess charges within DFT poses an inherent problem: in contrast to Hartree–Fock (HF) calculations, the electron self-interaction in the Hartree and the exchange–correlation contributions to the total energy do not cancel each other. This leads to spurious delocalization of the electronic wavefunction. While it is possible to perform HF-type calculations, these are computationally very demanding and neglect electron correlation effects. SIC schemes [26] (almost) correct the error in the exchange correlation functional, but lead to an orbital-dependent Hamiltonian, and thus to a complicated variational principle problem that may be technically difficult to solve.

A partial SIC scheme that applies only to the excess electron appears as an affordable yet sufficiently accurate

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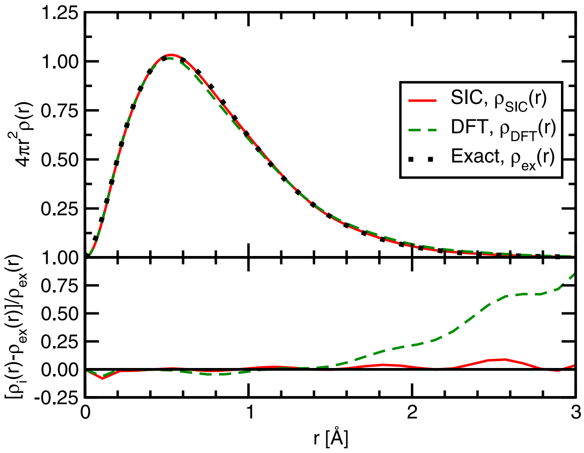

Figure 1. Upper panel: radial charge density $4\pi r^2\varrho(r)$ of a hydrogen atom, calculated in DFT and with a partial SIC scheme (see text), and compared to the exact solution. Lower panel: relative deviation of the DFT and SIC density from the exact result.

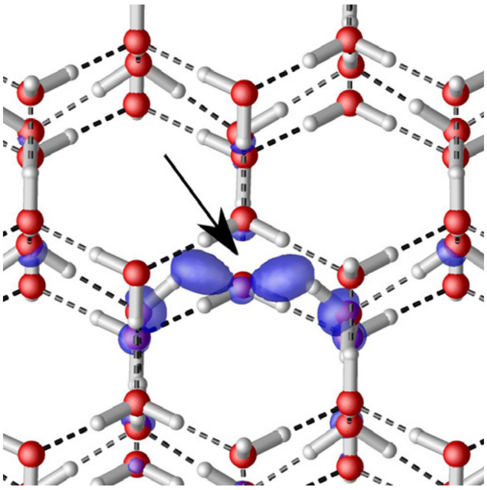

Figure 2. Excess electron density at bulk vacancy (arrow). $\varrho_{\mathrm{iso}} = 0.03\ e\ \text{Å}^{-3}$.

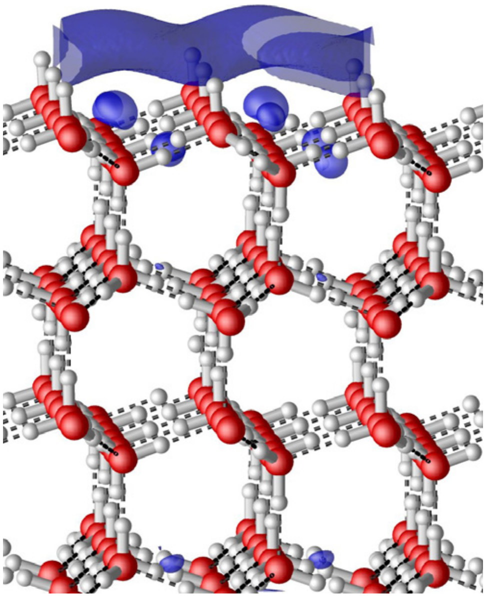

Figure 3. Excess electron density at an ideal bilayer-terminated surface. $\varrho_{\mathrm{iso}} = 0.03\ e\ \text{Å}^{-3}$.

alternative, since the neutral system of interest (hydrogen-bonded ice) is well described within DFT, while the self-interaction error is largest for the localized excess charge. In a system of $2N + 1$ electrons, we therefore solve

$$\left\{-\frac{\hbar^2}{2m}\triangle + V_{\mathrm{KS}}[n(\mathbf{r})]\right\}\psi_{i\sigma}(\mathbf{r}) = \varepsilon_i\psi_{i\sigma}(\mathbf{r}),\qquad i = 1,\ldots,N \tag{1}$$

$$\left\{-\frac{\hbar^2}{2m}\triangle + V_{\mathrm{KS}}[\tilde{n}(\mathbf{r})]\right\}\psi_{N+1,\sigma}(\mathbf{r}) = \varepsilon_{N+1}\psi_{N+1,\sigma}(\mathbf{r}), \tag{2}$$

where

$$n(\mathbf{r}) = \sum_{i,\sigma}^{\mathrm{occ}}|\psi_{i\sigma}(\mathbf{r})|^2, \qquad \tilde{n}(\mathbf{r}) = \sum_{i,\sigma}^{N}|\psi_{i\sigma}(\mathbf{r})|^2, \tag{3}$$

are the total and paired-electron densities, respectively, and V_{KS} is the total Kohn–Sham potential given as a functional of these densities. The above equations (1) and (2) can be derived from the modified energy functional

$$F[\{\psi_{i\sigma}\}] = F_0[\{\psi_{i\sigma}\}] - E_H[n_{N+1}] - \int n_{N+1}(\mathbf{r})(V_{\mathrm{xc}}(\mathbf{r}) - \tilde{V}_{\mathrm{xc}}(\mathbf{r}))\mathrm{d}\mathbf{r} + \int n_{N+1}(\mathbf{r})(V_{\mathrm{KS}}[n(\mathbf{r})] - V_{\mathrm{KS}}[\tilde{n}(\mathbf{r})])\mathrm{d}\mathbf{r} \tag{4}$$

by variation with respect to $\psi^*_{i\sigma}(\mathbf{r})$. There, $F_0[\{\psi_{i\sigma}\}]$ is the DFT total energy functional, evaluated using the eigenvalues and eigenfunctions from (1) and (2), and the remaining terms in (4) correct for self-interaction contributions in the various parts of $F_0[\{\psi_{i\sigma}\}]$. $V_{\mathrm{xc}}(\mathbf{r}) = \delta E_{\mathrm{xc}}/\delta n(\mathbf{r})$ and $\tilde{V}_{\mathrm{xc}}(\mathbf{r}) = \delta E_{\mathrm{xc}}/\delta\tilde{n}(\mathbf{r})$ denote the exchange–correlation potential of the total and paired-electron density, respectively. Recently, Mauri *et al* [25] used a similar approach, but their scheme calculates SIC based on the magnetization density, which is assumed to be equal to the density of the unpaired electron. The approach used here is closely related to an earlier work by Lundin *et al* [27] who applied this scheme to correct self-interaction of 4f electrons in atomic calculations.

The partial SIC scheme was implemented in the Vienna *Ab Initio* Simulation Package [28]. Due to the non-Hermiticity of the Hamiltonian, equations (1) and (2) are not solved self-consistently. Rather, starting from the optimized DFT wavefunctions, one SIC iteration is performed. A plane wave basis (kinetic energy cut-off of 30 Ryd) is employed in conjunction with ultrasoft pseudopotentials to model the electron–ion interaction. The electronic exchange and correlation effects are described by the PW91 functional [29]. Bulk ice defects are modeled in a 128-molecule supercell. Surface calculations of the ice Ih(0001) basal plane are performed using repeated slabs consisting of four ice bilayers that are separated by a vacuum equivalent of eight bilayers (about 28 Å). There, and in the bulk calculations, the zero wavevector term of the Ewald contribution to the total energy is neglected. That corresponds to the introduction of a spatially uniform positive background charge that neutralizes

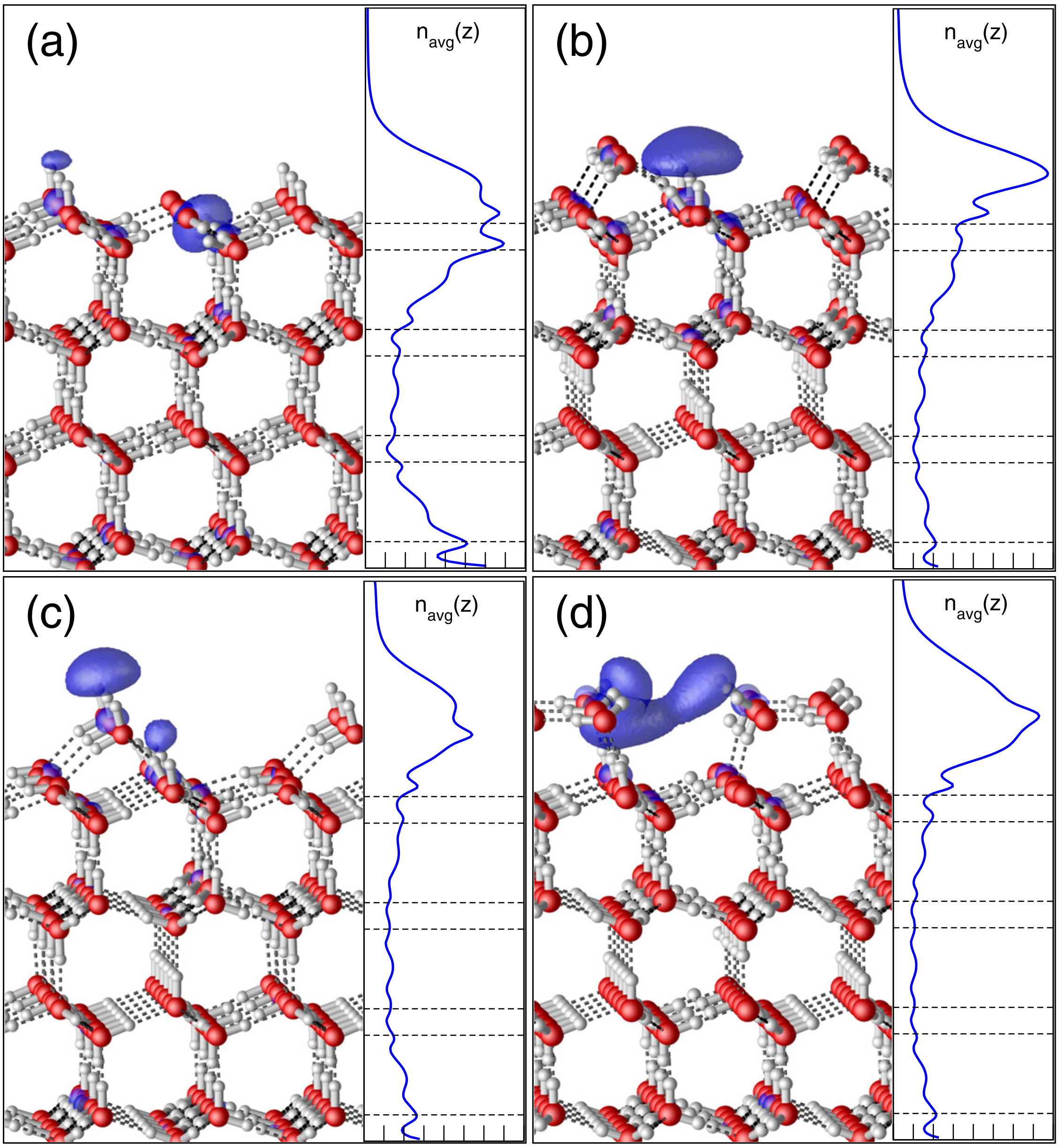

Figure 4. Excess electron density at various surface defect sites. $\varrho_{\rm iso} = 0.03\ e\ \text{Å}^{-3}$. (a) Surface vacancy, $E_b = 1.11$ eV, (b) and (c) water monomer adsorbed surfaces, $E_b = 0.08$ eV and -0.06 eV, and (d) water dimer adsorbed surface, $E_b = 0.04$ eV; all per 2×2 surface cell.

the cell. While this removes the divergence of the electrostatic energy of the system, a spurious interaction between the excess and the background charge is introduced that vanishes only in the limit of infinite supercells. Analytic correction formulae for this interaction energy have been proposed and implemented [30]; however, their applicability is currently under discussion [31, 32]. Their influence on the accuracy of the results could only be assessed by extrapolating from a series of calculations to infinite cell size, which currently exceeds our capabilities. A dipole correction scheme prevents long-range interaction between surface slabs arising from surface dipole moments. Surface periodicity is 2×2; reciprocal space integration is limited to the Γ point.

As a test the partial SIC scheme is applied to the hydrogen problem. For $N = 0$ paired electrons, the scheme completely removes the Hartree and exchange–correlation potentials from the Hamiltonian. Only the electron–ion interaction (modeled with a DFT pseudopotential) remains. The resulting radial charge density is plotted in figure 1 and compared to DFT-GGA and the exact result. The artificial delocalization of the DFT charge density is corrected for by the self-interaction correction. The remaining deviation from the exact solution is most probably due to the finite box and the use of an ultrasoft pseudopotential.

We start the calculations by considering bulk ice Ih with vacancy defects. As shown in figure 2, an excess electron can localize at bulk vacancy sites at dangling OH bonds, occupying $4a_1$-like LUMO states. It is to be expected that it could localize even better at a vacancy that has four inward pointing OH bonds. However, it is not possible to construct a crystal supercell that, aside from this defect, obeys the ice rules [33] everywhere else; a compensating second vacancy defect or a combination of Bjerrum defects [34] would have to be introduced. Calculations of such systems were not performed for reasons of computer resources and because it appears unlikely that fast electron solvation, on a timescale of 0.2 ps [6], facilitates the formation of such defect combinations, with defect migration times of tens of picoseconds [35]. However, the formation of Bjerrum defects was found to facilitate *ionic* charge localization: a recent theoretical study found that common L and D defects enhanced simultaneous solvation of anions and cations in ice [36].

At the ideal bilayer-terminated surface, a scenario similar to the bulk vacancy emerges: excess electrons occupy $4a_1$-like LUMO states of surface water molecules. However, contrary to the bulk vacancy site, no localization occurs laterally, i.e. in the surface plane between the upward pointing OH groups as shown in figure 3. The binding energy of the excess electron is 0.69 eV. However, it was recently found that the formation of rough ice surfaces terminated with single water monomers and dimers is energetically favored [24]. Other experimental studies found an abundance of dangling OH bonds at the ice surface [37] and increasing ice surface disorder with temperature, before the formation of a quasiliquid layer [38]. Therefore we also explore the localization of excess electrons at rough surfaces.

Figure 4 shows the excess electron densities along with the in-plane averaged density $n_{\mathrm{avg}}(z)$ plotted along the surface normal direction for some of these surface structures. In all investigated cases, the excess electron localizes at the surface. Furthermore, in agreement with the results above, it preferentially localizes at dangling OH bonds. Therefore the excess electron is also laterally confined on rough surfaces. The localization perpendicular to the surface plane is by and large independent of the detailed surface geometry; a slightly increased localization can be found on isolated dangling OH bonds (see figure 4(b)) and for larger adsorbate complexes, where the localization sites are farther away from the ideal bulk (see figure 4(d)). Binding energies range from a slightly non-binding scenario (localization at the LUMO of co-adsorbed water, cf figure 4(c)) to at most 1.11 eV (localization at the surface vacancy, cf figure 4(a)). Ionic relaxation of the surface region was not included in the present study. However, it should be expected that any atomic relaxation in response to the excess electron should enhance rather than weaken its localization and increase its binding energy. Moreover, since the local rearrangement of hydrogen bonds is easier at the surface than in the bulk crystal, we expect the self-trapping of excess electrons in unoccupied ice surface states to be more effective than in the bulk.

The results above show that excess charges in aqueous systems prefer to occupy LUMO-like states at dangling OH bonds of water molecules. The presence of these in ice bulk vacancy sites or in various ice surface terminations allows for electron localization even in these rigidly hydrogen-bonded systems. The application of SIC leads to an increased localization compared to DFT results in all cases studied. For some systems, SIC is necessary to achieve a physical solution (see figure 5, where we compare the in-plane averaged charge densities of the excess electron for one of the ice surface terminations, as arising from the DFT and the SIC calculations). In DFT, the excess electron is smeared out in the vacuum region between adjacent slabs; removing its self-interaction leads to localization near the surface. Rough surfaces allow for increased lateral electron localization. The degree of vertical localization is by and large independent of the detailed adsorbate geometry. However, we find the highest electron binding energy for a surface vacancy site that provides several OH dangling bonds; localization at an ad- or surface molecule's OH group is found to be energetically much less favorable. The general result that excess charges in ice preferentially localize at the surface confirms recent electron solvation experiments on ice clusters grown on a Cu substrate [6]. It also suggests that atmospheric reactions catalyzed or assisted by ice surfaces may often take place in a charged environment. Provided the underlying ice surface is ionized, e.g. by cosmic radiation, uptake and reaction mechanisms of atmospheric molecules may differ significantly from commonly studied neutral ice substrates [2, 23, 39]. Recent interpretations of atmospheric data see the role of charge-assisted heterogeneous reactions in ozone depletion differently [40–42]; however, our findings that realistic models of the ice surface provide various electron localization sites should justify further experimental and theoretical studies on these systems. It would be interesting to study the time evolution of such a localized electron, for example to answer the question for how long such an excess electron remains localized on the surface.

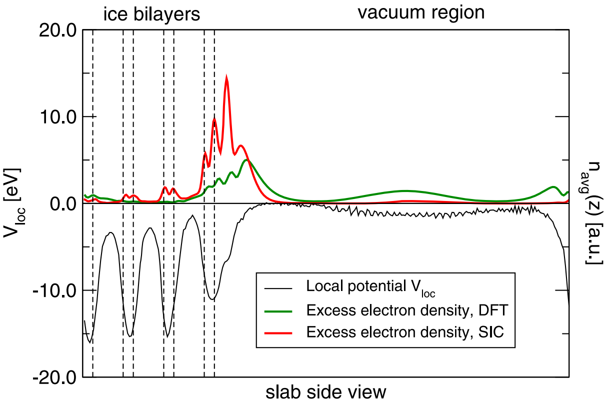

Figure 5. Comparison of excess electron density from DFT and SIC calculations. The local potential from DFT calculation is also given; dashed lines indicate positions of ice bilayers.

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