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Aqueous Solvation of the Chloride Ion Revisited with Density Functional Theory: Impact of Correlation and Exchange Approximations

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The specificity of aqueous halide solvation is fundamental to a wide range of bulk and interfacial phenomena spanning from biology to materials science. Halide polarizability is thought to drive the ion specificity, and if so, it is essential to have an accurate description of the electronic properties of halide ions in water. To this end, the solvation of the chloride anion, Cl^- has been reinvestigated with state-of-the-art density functional theory. Specifically, the PBE-D3, PBE0-D3, and SCAN functionals have been employed to probe the impact of correlation and exchange approximations. Anticipating the findings, adding exact exchange improves the electronic structure, but simultaneously significantly reduces the Cl^- polarizability, resulting in an over-structured Cl-O radial distribution function (RDF) and longer water H-bond lifetimes to Cl^- . SCAN does not yield as much improvement in the energetics of Cl^- relative to bulk water, but does result in a smaller reduction of the polarizability and thus a less structured Cl-O RDF, which agrees better with experiment. Special consideration is therefore warranted in assessing the impact of exchange on the energy, charge density, and the charge density response when designing and testing hybrid functionals for aqueous halide solvation.

1 Introduction

The nature of the solvation of ions in water is an important field of study with an enormous range of applications. The role of ions in biological systems has been recognized for well over a century, beginning with the discovery of the Hofmeister series¹ for proteins and extending to a wide variety of systems^{2–4}. Ion solvation also plays an important role in geoscience and environmental chemistry, where ions display specific adsorption at aqueous interfaces^{5,6}, driving dissolution behavior of oxide minerals^{7,8} as well as playing an important role in the structure of sea spray aerosols^{9,10}, which impact ice nucleation and radiative forcing^{11,12}. Solvated ions play an important role in batteries¹³ and catalysis in both biological¹⁴ and artificial systems^{15,16} as well. In all of these applications, it is essential to understand the specific nature of the ion and how it interacts with H_2O molecules, aqueous interfaces, and other molecules. It is therefore paramount that one has highly accurate models of ion-water interactions, which yield not only the correct structural, electronic, and optical properties of the hydrated ions, but the correct dynamical properties as well.

Halide ions display specific ion phenomena. The oldest and

most famous is the Hofmeister series, where it was found that the ability of halides to precipitate egg white protein follows the behavior¹: $\text{Cl}^- > \text{Br}^- > \text{I}^-$. Similar trends in the halides were found in their affinity for the air/water and hydrophobic interfaces, with larger, more polarizable halides displaying greater propensity for the surface^{5,17,18}. The opposite can be found at hydrophilic interfaces, where sum frequency generation experiments show that smaller, less polarizable ions like F^- have a greater impact on the intensity and therefore are inferred to have a greater surface affinity¹⁹. The Hofmeister series is also found in bulk solutions via the impact of halides on Raman spectra²⁰ and the viscosity²¹. Taken together, these data have led to the classification of ions as either “structure-makers” (cosmotropes) or “structure-breakers” (kaotropes), with smaller, less polarizable ions increasing the structure of nearby water molecules and larger, more polarizable ions decreasing the local structure. Simple classical models of halide solvation are inadequate to explain these observations, which require an accurate description of the electronic structure of halide ions in water, and in particular an accurate model of halide polarizabilities. Indeed, polarizable force fields generally yield significantly more accurate results for halides when compared to non-polarizable force fields^{22–24}, correctly predicting the affinity of Cl^- for “surface” structures in small water clusters^{24–27}.

The complex electronic structure of halide-water interactions presents significant challenges for modeling and simulation. While polarizable force fields generally yield accurate structures for halide ions, they have a limited range of accuracy and generally cannot be used to study electronic properties. Bulk sol-

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vation is typically studied with density functional theory (DFT) and a periodic system containing one ion plus at least 63 H₂O molecules^{28,29}, as the high level quantum chemistry methods appropriate for small halide-water clusters are prohibitively expensive. The use of DFT presents its own set of challenges, as LDA and GGA functionals generally do not yield accurate halide polarizabilities due to self-interaction errors. Thus, it is often necessary to use expensive hybrid functionals, which include a portion of exact exchange to yield accurate polarizabilities from DFT³⁰. However, although hybrid functionals include exact exchange, the percentage is an empirical parameter and can still fail for systems where electron correlation is important, e.g. strongly correlated systems. Meta-GGA functionals include a dependence of the energy of the kinetic energy density and thereby reduce the delocalization error, allowing meta-GGAs like SCAN³¹ to yield much more accurate results for a wide range of systems³². Recent energy decomposition analysis calculations of small halide-water clusters show that several popular GGA, hybrid, and meta-GGA functionals can differ strongly in the predicted energies, especially for the energy associated with Pauli repulsion and London dispersion, emphasizing the importance of many-body effects and the details of the chosen functional^{33,34}. In bulk solutions, these discrepancies can lead to significant differences in the solvation structure and electronic properties^{28,35}. Discrepancies between models can help drive controversy in the community over e.g. the extent to which halides modify the structure of the surrounding H₂O molecules^{36–38,38–42}. Thus, it is important to properly characterize the impact of different functionals on halide solvation. Specifically, the effects on the solvation structure and polarizability, and how the properties of the system correlate with the accuracy of the exchange and correlation energy approximations.

Ab Initio Molecular dynamics (AIMD) simulations have been performed on a periodically replicated system of one Cl⁻ solvated by 63 H₂O molecules in order to study the solvation structure, the H-bond dynamics, and the polarizability and charge distribution of the Cl⁻ ion. The PBE-D3, PBE0-D3, and SCAN functionals have been employed in order to compare different approximations of the exchange and correlation energies. The SCAN meta-GGA functional is known to yield excellent results for water⁴³, hydrophilic interfaces¹⁶, and the solvation of alkali ions⁴⁴. Recent benchmark calculations show that SCAN yields errors of ~ 2 kcal/mol for Cl⁻-(H₂O)₂ clusters, compared to errors of ~ 0 kcal/mol PBE, PBE0, and ω B97M-V functionals²⁵. Nevertheless, the SCAN functional has been employed here due to its excellent accuracy for water in a wide range of environments. Moreover, the accuracy of a functional for isolated clusters may not necessarily hold in bulk due to changes in structure and charge density upon complete solvation²⁶. We have chosen not to use SCAN-D3 or the hybrid functional SCAN0 as adding vdW corrections leads to large negative pressures in liquid water⁴⁵, while adding exact exchange to SCAN does not lead to an improvement in accuracy in all cases⁴⁶.

To address the above issues, here Cl⁻ solvation is investigated using state of the art density functional approximations, including a range of correlation approximations and exact exchange fractions. It is found that the choice of functional has a strong impact

on both the solvation structure of the Cl⁻ as well as the electronic properties of the system. While both the meta-GGA functional SCAN and hybrid GGA functional PBE0-D3 soften the Cl-O RDF with respect to PBE-D3, in agreement with experiment^{37,47}, SCAN yields a solvation structure that is closest to experimental values. The PBE0-D3 yields a slightly more structured Cl⁻ solvation shell compared to SCAN because the addition of exact exchange leads to a large reduction in the Cl⁻ polarizability, thereby leading to longer H-bond lifetimes and a more rigid solvation environment. By systematically varying the exact exchange fraction and density functional, it is found that the Cl⁻ polarizability strongly depends on the exact exchange fraction for hybrid PBE. It is also found that this dependence on the exact exchange fraction is reduced in hybrid SCAN, and that the reduction in the Cl⁻ polarizability when moving from PBE to SCAN is much less than when moving from PBE to PBE0. On the other hand, PBE0-D3 is the only functional to yield a Cl⁻ (3p) band above the VBM of water in the density of states in a manner that is qualitatively consistent with photoelectron spectroscopy experiments⁴⁸, though SCAN does improve the separation of the Cl⁻ (3p) and VBM of water compared to PBE. Thus, while the exact exchange term of hybrid GGAs can improve the accuracy of the functional by reducing the self-interaction error, it can also yield incorrect results for properties such as the polarizability due to the empirical nature of the exact exchange fraction.

2 Computational Methods

MD simulations were carried out on periodically replicated systems of a single Cl⁻ solvated by 63 H₂O molecules in either the NVT or NVE ensembles at a temperature of 330K. An elevated temperature was used in order to mimic the effects of nuclear quantum effects on the structure of the water solvent. A cubic simulation cell with box edge length 12.518 Å yielded a density of 0.998 g/cm³. The AIMD calculations were initialized with configurations taken from classical MD simulations that employed the SPC/E water intermolecular potential⁴⁹ plus a Cl⁻ ion-water potential⁴⁷ using the LAMMPS package⁵⁰. The MD simulations were run for 2 ns in the NVT ensemble to equilibrate the random initial configurations which were generated with PACKMOL⁵¹. All subsequent molecular dynamics calculations (MD) are run using CP2K v.5.1⁵². Three different simulations of Cl⁻ in water were run with three different functionals: PBE^{53,54} with the Grimme D3 vdW correction^{55–57} (PBE-D3), PBE0⁵⁸ with the D3 correction (PBE0-D3), and SCAN³¹. For all atoms the GTH pseudopotentials⁵⁹ are used with the MOLOPT⁶⁰ split valence triple zeta basis sets. A plane-wave cutoff of 500 Ry is used for the PBE-D3 and PBE0-D3 simulations, while for the SCAN simulations a cutoff of 1200 Ry is used in order to obtain accurate forces^{61,62}. The *Quickstep* module of CP2K is used to run the molecular dynamics simulations with a timestep of 0.5 fs. Wannier functions were computed every 5 timesteps (2.5 fs) and the Wannier centers and spreads were saved to file. In order to improve the efficiency of the hybrid simulations, the auxiliary density matrix method⁶³ with the cpFIT3 basis as the auxiliary basis, and a truncated Coulomb operator was used with a cutoff radius of 6.0 Å in order to prevent self-exchange interactions. For the density of states cal-

culations Quantum Espresso v.6.3^{64,65} was used with the HSCV pseudopotentials⁶⁶, a cutoff of 95 Ry for the PBE-D3 and PBE0-D3 calculations, and a cutoff of 130 Ry for the SCAN calculations. Quantum Espresso was also used for initial Born-Oppenheimer MD simulations of Cl^- solvated by 63 H_2O molecules using the SCAN functional with a cutoff of 85 Ry at 300K using the cp.x module in order to test the performance of SCAN for Cl^- solvation.

AIMD simulations were first initialized from the last frame of the classical MD simulations, and were then run in the NVT ensemble with the PBE-D3 functional for 1 ps. The last frame of this first AIMD simulation was then taken as the initial configuration for all subsequent AIMD simulations. Each different simulation for each functional was then run in the NVT ensemble using a Nose-Hoover thermostat at 330K until the total energy of the system appeared to stop changing (around 2-3 ps) followed by simulations run in the NVE ensemble. Each simulation was run for at least 16 ps in order to compute the structural and electronic properties of the solvated Cl^- ion. The density of states (DOS) of the system was sampled every 0.125 ps, and the Hirshfeld-I^{67,68} charges and the static polarizabilities of the Cl^- and H_2O were sampled every 0.5 ps. The Cl^- polarizability is computed by applying electric fields of intensity ± 0.0025 a.u. in the x, y, and z directions, computing the dipole of the ion/molecule at each point, and finally taking the gradient with respect to the electric field.

3 Results and Discussion

The structure of solvated Cl^- was characterized by the distribution of distances, angles, and coordination numbers. An AIMD simulation was run using Quantum Espresso (QE) at 300K for 50 ps in order to obtain well-converged Cl-O and Cl-H radial distribution functions (RDFs) shown in Figure 2, which is compared to AIMD simulations of the same system run at 330K using CP2K for 16 ps. While the RDFs from the 300K simulation closely match the experimental data, they are slightly overstructured, likely due to the absence of nuclear quantum effects (NQE). The 330K SCAN simulation on the other hand yields a second solvation shell of the Cl-O RDF which better matches experiment, while the first peak associated with the first solvation shell is slightly lower than experiment. One can see similar effects of the temperature on the Cl-H RDF, with an increase in the temperature improving the second solvation shell while reducing agreement with experiment for the first solvation shell. Running the simulations at 330K does therefore improve the solvation structure, but cannot completely correct for the absence of NQE, as evidenced by the obvious discrepancy in the Cl-H RDF.

In order to compare different functionals, MD simulations were performed with the the PBE-D3, PBE0-D3, and SCAN functionals using CP2K at 330K to roughly mimic the impact of NQE on the water structure⁶⁹, and CP2K is preferred because it allows us to efficiently compute Wannier functions during the MD simulation. Notably, the PBE-D3, PBE0-D3, and SCAN functionals all yield O-O RDFs which are in good agreement with experiment, with the PBE0-D3 functional yielding slightly less structured water compared to PBE-D3, and SCAN yielding slightly less structured wa-

Table 1 Peak and minimum positions in the Cl-O RDF (\AA) as shown in Figure 3

Functional	$r_{max}^{(1)}$	$r_{min}^{(1)}$	$r_{max}^{(2)}$	$r_{min}^{(2)}$
PBE-D3	3.14	3.78	4.85	6.10
PBE0-D3	3.17	3.85	5.15	5.90
SCAN	3.17	3.85	4.90	5.90
Expt. ³⁷	3.14	3.77	4.99	6.19

ter compared to PBE0-D3 (Figure 1). While the differences in the O-O RDF are slight, the differences in the O-O-O angular distribution function (ADF) are more pronounced, with SCAN yielding a broader distribution, especially at smaller angles, indicative of the shorter H-bond lifetimes and less structured nature of SCAN water⁴³. These results are mirrored in the Cl-O and Cl-H RDFs in Figure 3. Notably, while all functionals yield similar peak positions (Table 1), PBE0-D3 yields a less structured Cl-O RDF compared to PBE-D3, and SCAN yields a much less structured RDF, with a very broad peak at around 5 \AA which is difficult to distinguish. Moreover, the SCAN Cl-O RDF best reproduces experimental results, which show that Cl^- has an RDF with very little structure^{37,47}, with the elevated temperature improving the agreement beyond the first solvation shell. The experimentally measured Cl-O RDF is similar to that of Br^- and I^- having no second maximum at all, while it differs from the F-O RDF which is much more structured. These findings are consistent with the determination that Cl^- , Br^- , and I^- are structure-breaking ions while F^- is structure-making⁷⁰. While the Cl-H RDF does not show as much difference between the functionals as the Cl-O RDF, note that SCAN shows better agreement with experiment at the first minimum, and is indicative of a more disordered solvation shell.

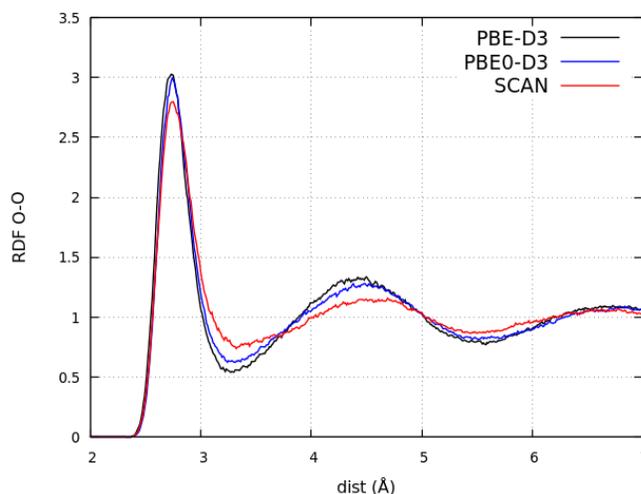


Fig. 1 The O-O radial distribution function for the simulations performed with CP2K at 330K.

Further evidence of the disordered nature of the Cl^- solvation shell in the SCAN simulation can be seen in the Cl^- coordination number (CN) and the O-Cl-O ADF. The distributions of Cl^- CNs for each functional are shown in Figure 4, which displays the

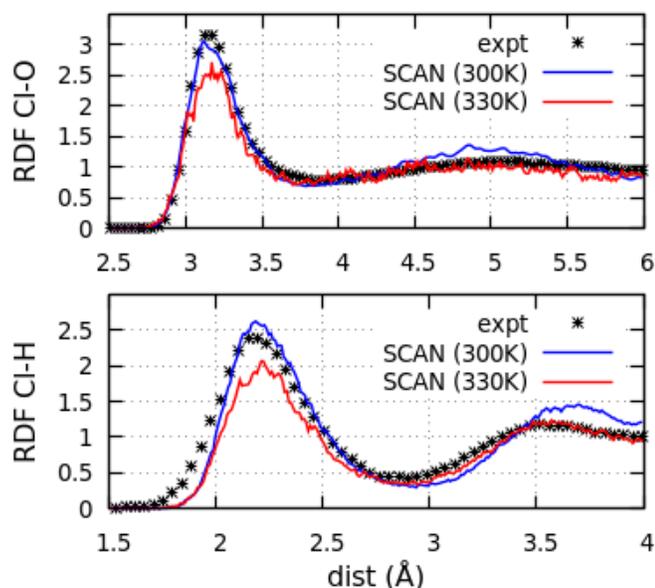


Fig. 2 The radial distribution function for Cl-O (top) and Cl-H (bottom). The SCAN (300K) simulations are performed with QE while the SCAN (330K) simulations are performed with CP2K, and the experimental RDF is inferred using empirical potential structure refinement from neutron diffraction data³⁷.

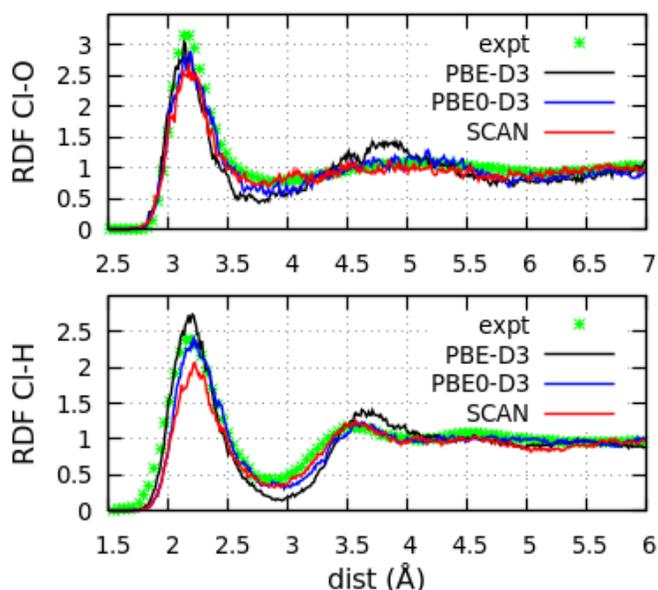


Fig. 3 The radial distribution function for Cl-O (top) and Cl-H (bottom). The simulations are performed with CP2K at 330K and the experimental RDF is inferred using empirical potential structure refinement from neutron diffraction data³⁷.

number of neighbors up to the first minimum in the Cl-O RDF. The SCAN functional has a much broader distribution compared to the GGA functionals and is shifted to larger CNs, with short-lived states with up to 12 neighbors that are likely due to exchange events. The PBE0-D3 functional on the other hand has a narrower distribution of coordination numbers compared to the PBE-D3 functional, despite the fact that the PBE0-D3 Cl-O RDF is less structured than that of PBE-D3. This suggests that PBE0-D3 predicts weaker H-bonds with shorter lifetimes compared to PBE-D3, but predicts a more rigid solvation shell with fewer exchange events. Meanwhile, the SCAN simulations suggest a much less structured solvation shell with a greater frequency of exchange events. Further evidence of a more disordered Cl⁻ solvation shell is revealed in the O-Cl-O ADF in Figure 5, which shows that the SCAN ADF is broader than the GGA functionals, with much greater amplitudes between 40 and 60°. This region of the ADF in the O-O-O distribution is associated with H₂O molecules with 0-1 H-bonds⁴³, and so the increase in the ADF in this region indicates that the water-Cl H-bonds are more likely to break and leave the Cl⁻ H-bond deficient. Finally, by comparing to the simulations of Cl⁻ run with SCAN using QE at 300K, one sees that the temperature of the simulation has a large impact on the solvation structure, particularly by increasing the incidence of configurations with few H-bonds to Cl⁻. This highlights the importance of nuclear quantum effects when modeling ion solvation, though such considerations are beyond the scope of this paper.

In order to gain a deeper understanding of the Cl⁻ solvation shell and its relation to the local H-bond network, the H-bond lifetime and number of H-bonds, defined as total number of H-bonds of each H₂O molecule or Cl⁻, was computed for each simulation.

The standard geometric definition of a H-bond was employed, where a H-bond exists if the distance between the donor O (Od) and the acceptor O (Oa) is within the first minimum of the O-O RDF (3.25 Å) and if the H-Od-Oa angle is within 30°. The H-bond from a H₂O molecule to Cl⁻ is defined to exist if the Od-Cl⁻ distance is within the first minimum of the Cl-O RDF (3.80 Å) and the H-Od-Cl angle is within 30°, as the H-Od-Cl angle within this cutoff has a very similar distribution to H-Od-Oa angles Figure 6.

The average H-bond lifetime and average number of H-bonds of each molecule and Cl⁻ are given in table 2. As expected from the O-O-O ADF⁴³, as one goes from PBE-D3 to PBE0-D3 to SCAN, the H₂O H-bond lifetime and number decrease, as SCAN yields a greater incidence of H₂O molecules with 0-1 H-bonds. While adding exact exchange to the PBE-D3 functional does yield shorter H-bond lifetimes, they are still significantly longer than the SCAN lifetimes. These results help explain the differences between the functionals in the Cl-O RDF, Cl-O CN, and O-Cl-O ADF. When exact exchange is added to the PBE-D3 functional to get PBE0-D3, there is a decrease in the overall water structure and a decrease in the H-bond lifetimes, leading to a slight softening of the O-O RDF. The change in H-bond lifetime is much less pronounced for the Cl⁻ however, which is why the distribution of CNs is so sharply peaked for PBE0-D3 and why the O-Cl-O ADF for PBE-D3 and PBE0-D3 are so similar. On the other hand, the SCAN functional leads to a large reduction of H-bond lifetimes for both H₂O and Cl⁻, leading to a softening of both the O-O and Cl-O RDFs as well as a broader distribution of Cl⁻ coordination numbers.

The electronic properties of the chloride simulations were investigated in order to understand how the differences in solvation structure and dynamics are related to the differences in the func-

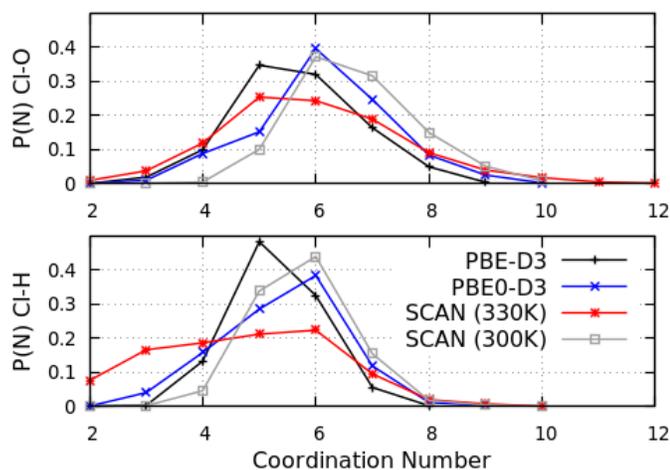


Fig. 4 The distribution of the Cl-O (top) and Cl-H (bottom) coordination numbers computed by counting the number of neighbors up to the first minimum in the Cl-O and Cl-H RDF, respectively. The SCAN (300K) simulations are performed with QE, while all others are performed with CP2K at 330K.

Table 2 H-bond lifetime and average H-bond number computed from AIMD trajectories with various functional approximations

H-bond Lifetimes (fs)		
Functional	O	Cl
PBE-D3	393	264
PBE0-D3	285	188
SCAN	210	141
Number of H-bonds		
Functional	O	Cl
PBE-D3	3.60	4.89
PBE0-D3	3.59	4.88
SCAN	3.41	4.61

tionals. The density of states (DOS) and projected DOS for Cl^- are sampled every 0.125 ps for each simulation, using the same functional that is used for the AIMD simulation, and is shown in Figure 7 with the CBM placed at the origin. Each DOS shows four main peaks due to H_2O , the lowest is associated with the 2s orbital of O while the three peaks in the upper valence region are associated with the 1b₂, 3a₁, and 1b₁ orbitals⁷¹. The 3s band of Cl^- is situated between the 2s and 1b₂ bands of H_2O , while the 3p band of Cl^- is close to the VBM of H_2O . Both PBE0-D3 and SCAN lead to a shift in the VBM to lower energies and a relative shift of the 3p band of Cl^- to higher energies. While PBE0-D3 shows the 3p band above the VBM of water as expected⁷², the 3p band in the SCAN simulation is not completely above the VBM, although its position is improved with respect to PBE-D3. This analysis is made more concrete by listing the positions of the O(1b₁) and Cl⁻(3p) peaks and their difference compared with experiment⁴⁸ in Table 3. Once again, PBE0-D3 yields the results closest to experiment, shifting the difference between the O(1b₁) and Cl⁻(3p) peaks (δE) to greater values. Meanwhile, SCAN improves the value of δE relative to PBE-D3, but does not yield as accurate results as PBE0-D3. Previous results have shown that the

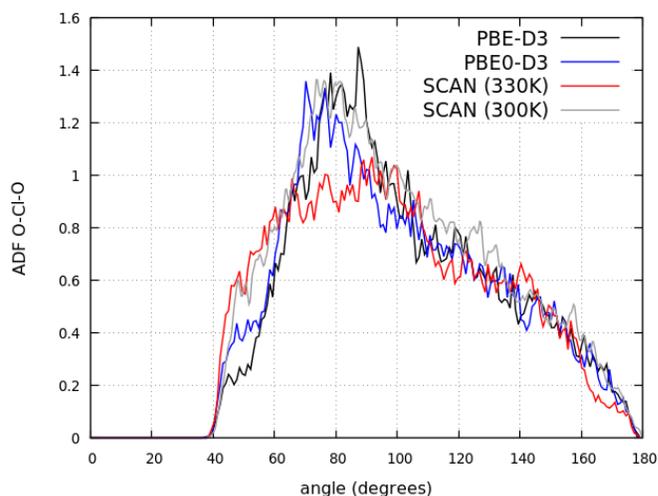


Fig. 5 The angular distribution function of the O-Cl-O angles (Cl pivot point) for all O atoms within the first minimum of the Cl-O RDF (3.85 Å). The SCAN (300K) simulations are performed with QE, while all others are performed with CP2K at 330K.

Table 3 The energy difference δE between the peaks of the 1b₁ peak of bulk water and the 3p state of the solvated Cl⁻ ion

	O 1b ₁ (eV)	Cl 3p (eV)	δE (eV)
Expt. ⁴⁸	-11.31	-9.6	1.71
PBE-D3	-6.13	-5.49	0.64
PBE0-D3	-8.90	-7.67	1.23
SCAN	-6.68	-5.69	0.99

DOS depends both upon the density functional approximation as well as the Cl^- solvation structure²⁸, with shifts in the Cl-O and Cl-H RDFs to slightly larger distances resulting in less favorable hybridisation between the Cl(3p) and O(2p) orbitals. The improvement in the δE yielded by SCAN is therefore likely due to improvements in the self-interaction error³² which impacts Cl-O hybridization directly^{28,35} and due to improvements in the accuracy of the Cl^- solvation structure.

When it comes to solvation however, often the more important quantities are the local charge and response of the halide ion, as the Hofmeister series appears to imply that the size and polarizability of halide ions is what drives ion specificity². With this in mind, the polarizability of the Cl^- ion was computed in each simulation. There are two approaches one can take to computing the polarizability: the first is to compute a static polarizability by applying an electric field and measuring the response of the charge density via the shift in the Wannier center positions. Note that this method slightly underestimates the polarizability by disregarding the shape of the Wannier functions, but should provide a good comparison between functionals⁷³. Alternatively, one can instead measure the fluctuation of the wannier centers over time and extract a frequency dependent response:

$$\alpha(\omega) = \frac{2\pi\omega^2\beta}{3cV\eta(\omega)} \int_{-\infty}^{\infty} \langle \mu(t)\mu(0) \rangle e^{i\omega t} dt \quad (1)$$

where β is the inverse temperature, c is the speed of light, and

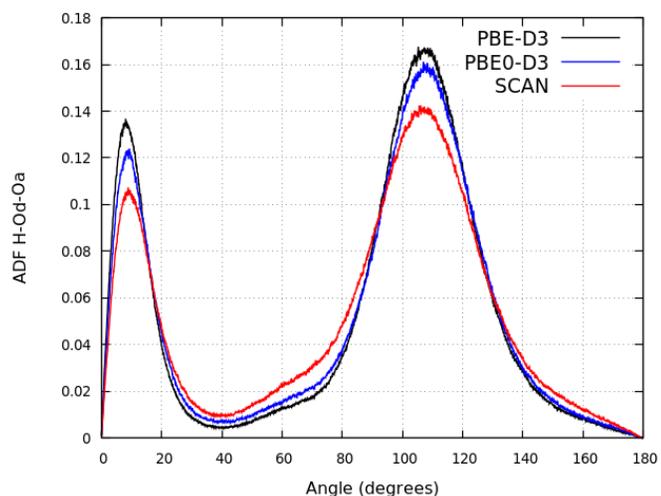


Fig. 6 The angular distribution function of the H-Od-Oa angles (Od pivot point) where we use a cutoff of 3.35 Å for the O-O distance and a cutoff of 1.2 Å for the O-H distance.

$\eta(\omega)$ is the index of refraction, which is multiplied out in order to get a quantity which is directly proportional to the polarizability⁷⁴. This quantity, if computed using the dipole moment of the Cl^- only, will not yield the intrinsic polarizability of Cl^- as the adsorption coefficient must go to zero as the frequency goes to zero. Nevertheless, $\alpha(\omega)$ does give us the response of the dipole moment of Cl^- to perturbations due to solvent fluctuations as a function of frequency, which should depend sensitively on the underlying electronic structure of the solvated ion.

The quantity $\alpha(\omega)$ is plotted in Figure 9 where significant differences are revealed between the adsorption coefficients of different functionals. The difference in the positions of the peaks in $\alpha(\omega)$ between each functional is easily explained by the differences in the vibrational density of states between each functional (Figure 8). Adding exact exchange to PBE significantly blue-shifts the O-H stretching peak at ~ 100 THz while switching from PBE to SCAN yields a lesser blue-shift. The different intensities meanwhile correspond to the response of charge density of the Cl^- ion to perturbations due to H-bonding and the local potentials of nearest neighbor H_2O molecules. As one moves from PBE-D3 to PBE0-D3 to SCAN, the response of the Cl^- is significantly reduced, especially in the OH-stretching region. This indicates that the polarizability of the Cl^- is reduced in the PBE0-D3 simulation, as equation 1 shows that the intensity of $\alpha(\omega)$ is proportional to the magnitude of the fluctuations of the Cl^- dipole moment.

In addition to computing $\alpha(\omega)$, the static polarizability and charge state of the Cl^- were evaluated every 0.5 ps in order to better understand how they differ with the choice of functional. Specifically, trajectories were sampled every 0.5 ps and the polarizability and Hirshfeld-I charge of Cl^- were computed using the Perdew-Zunger⁷⁶ (PZ), PBE, and SCAN functionals with exact exchange fractions of {0.00, 0.05, 0.10, 0.15, 0.20, 0.25}. Trajectories are sampled from the SCAN simulation at 330K only, computing the polarizability with each functional and exact exchange fraction for each frame, in order to provide a more direct compari-

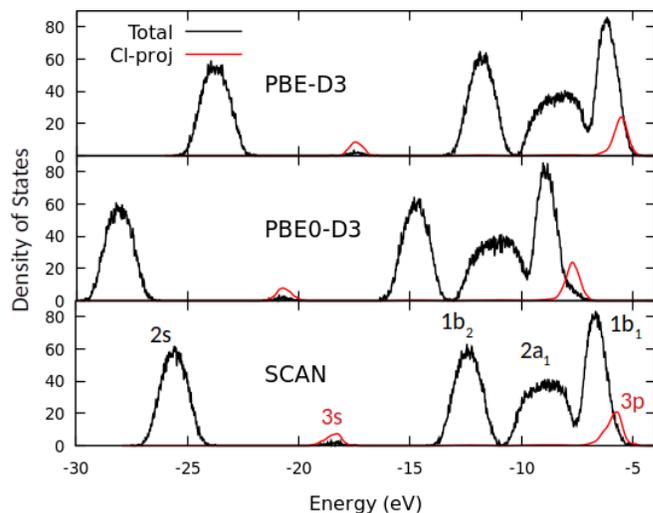


Fig. 7 The electronic density of states (black) and Cl^- projected density of states (red) sampled every 0.125 fs from each simulation and smoothed with a Gaussian with a width of 0.15 eV. The Cl^- projected density of states has been multiplied by 5 to make it more visible.

son. This procedure allows one to fully understand how the polarizability and charge are determined by the exchange and correlation approximations employed. At each frame one can freely change the fraction of exact exchange for each functional, and one can move from LDA to GGA to meta-GGA approximations of the exchange correlation potential as one goes from PZ to PBE to SCAN. This then gives a rough approximation of the polarizability as a function of the accuracy of the correlation and exchange energies without making use of more complex energy decomposition analyses. The average polarizability and Hirshfeld-I charge of the Cl^- as a function of the functional is listed in Table 4. As expected, going from PZ to PBE one sees a large change in the polarizability and charge, while when going from PBE to SCAN the change is much smaller. In addition, although the charge does not change much as a function of exact exchange fraction, the polarizability decreases by a large percentage as one goes from 0.00 to 0.25 fraction of exact exchange. This observation is consistent with the fact that local and semi-local DFT functionals generally over-estimate the delocalization of electrons due to self-interaction errors.

The choice of density functional approximation has a large impact on the Cl^- polarizability, and thereby a large impact on its solvation environment. Unfortunately, it is difficult to know what the “correct” value of the polarizability should be, as these calculations are impacted by finite size effects, which reduce the value of the polarizability compared to infinite dilution⁷³. However, larger scale calculations have shown that the polarizability of solvated Cl^- in the limit of infinite dilution is nearly equal to its gas phase value⁷³. Thus, one should not expect large reductions of the Cl^- polarizability upon solvation. Even though moving from PBE to SCAN results in a reduction in the Cl^- polarizability, one sees a much greater reduction when adding 0.25 exact exchange to PBE. Thus, it appears that the inability of PBE0-D3 to significantly improve the structure of solvated Cl^- stems from the er-

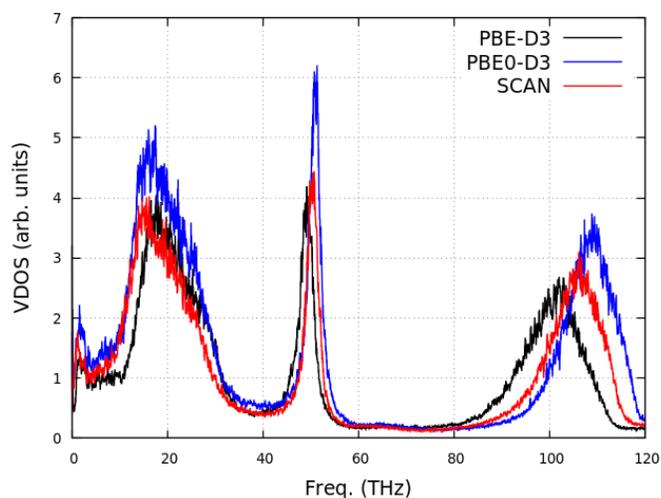


Fig. 8 The vibrational density of states (VDOS) of the H atoms for each simulation. The VDOS has been windowed using a Blackman-Harris function⁷⁵ and smoothed with a Gaussian with a width of 15 fs.

Table 4 Cl^- Polarizability and Hirshfeld-I Charge

Cl^- Polarizability (\AA^3)			
Fraction of Exact Exchange	PZ	PBE	SCAN
0.00	7.27	4.31	4.13
0.05	6.93	4.21	4.05
0.10	6.47	4.15	3.99
0.15	6.03	4.07	3.93
0.20	5.63	3.99	3.85
0.25	5.34	3.92	3.79
Cl^- Hirshfeld-I Charge (e)			
Fraction of Exact Exchange	PZ	PBE	SCAN
0.00	0.06	-0.38	-0.41
0.05	0.03	-0.39	-0.41
0.10	0.00	-0.40	-0.41
0.15	-0.03	-0.40	-0.42
0.20	-0.06	-0.41	-0.42
0.25	-0.08	-0.41	-0.42

ronously large reduction of the polarizability of the Cl^- and its solvation shell.

In the PBE0-D3 simulations, there is a decrease in the average Cl^- polarizability (table 4), thereby decreasing the response of the Cl^- charge density to perturbations induced by neighboring H_2O molecules (Figure 9). While one would expect the Cl^- H-bond lifetime to decrease upon adding a fraction of exact exchange, the reduction in the Cl^- polarizability leads to only a modest decrease in the lifetime (Table 2). This leads to a stiff Cl^- solvation shell and thus a more structured Cl-O RDF and a narrower distribution of Cl-O CNs compared to more accurate approximations (e.g. SCAN). Finally, it is thus interesting to note that, as one goes from PZ to PBE to SCAN, there is a reduction in the change in the polarizability and, to a lesser extent, the Hirshfeld-I charge as a function of the exact exchange fraction. This is important as the fundamental inability of DFT approximations to describe many electron systems means that the “best” functional for any application will likely include some fraction of

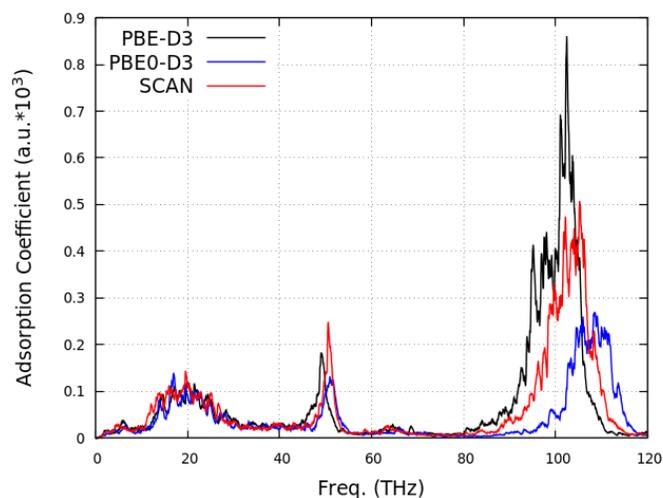


Fig. 9 The infrared adsorption coefficient per unit length computed from the dipole moment of the Cl^- ion. The spectrum has been windowed using the Blackmann-Harris function⁷⁵ and smoothed with a Gaussian with a width of 15 fs.

exact exchange. However, when adding exact exchange to SCAN and likely other meta-GGA functionals, one is likely to see less of a reduction in polarizability compared to GGA functionals. Indeed, it has been shown that simply adding 0.25 exact exchange to SCAN does not necessarily improve its accuracy, and can even yield poorer performance than PBE-based hybrid functionals⁴⁶. The exact exchange fraction of hybrid functionals therefore deserves careful consideration; while adding exact exchange causes modest changes in the energy and charge density, it also results in dramatic and at times erroneous changes in the response of the charge density.

4 Conclusion

AIMD simulations on a periodically replicated system of a single Cl^- solvated by 63 H_2O molecules have been carried out using the PBE-D3, PBE0-D3, and SCAN functionals to determine how different approximations of the exchange-correlation function impact the electronic properties and halide solvation structure. While the PBE0-D3 functional resulted in better agreement with experiment by reducing the structure of the O-O RDF, it still yielded slightly over-structured Cl-O and Cl-H RDFs, whereas the SCAN functional led to a significant reduction in the structure of the RDFs and superior agreement with experiment. The discrepancy between PBE0-D3 and SCAN is explained by the large reduction in the Cl^- polarizability on the addition of exact exchange. This decrease in polarizability reduces the response of the Cl^- charge density to external perturbation, increasing the lifetime of Cl^- H-bond lifetimes, and thereby leading to a more rigid and structured solvation shell.

The present results emphasize the importance of careful consideration of appropriate functionals, as generally applicable and accurate hybrid functionals like PBE0-D3 can yield greater errors than their GGA counterparts in describing certain aspects of the system. In particular, the polarizability and charge of the LDA and GGA functionals tested, demonstrate a greater dependence

on the fraction of exact exchange than the meta-GGA functional SCAN (Table 4). That said, the hybrid PBE0-D3 functional does yield more accurate results for the DOS, yielding a more accurate energy difference δE between the Cl^- (3p) band and H_2O ($1b_1$ band). While SCAN improved δE , it did not yield as large a δE as PBE0-D3, and a large portion of the Cl^- projected DOS is still within the VBM. Thus, while the addition of exact exchange helps to overcome fundamental limitations of DFT and generally improves the electronic structure, the fraction of exact exchange should be finely tuned and analyzed in order to prevent erroneous localization of the charge density and excessive reduction of the polarizability.

Conflicts of interest

There are no conflicts to declare.

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