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Interaction of halide ions with copper: the DFT approach

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Abstract

The applicability of density functional theory to the adsorbate–adsorbent interaction has been tested with the final goal of defining an appropriate combination of the DFT method with basis sets for metal cluster–halide ions studies. The Cu–X^- (X = F, Cl, Br, I) systems have been taken as tests cases to probe the different DFT methods (SVWN, BP86 and B3LYP) together with different combinations of basis sets for systems of this type. For comparison, the standard HF and its MP2 and MP4 corrections have also been calculated. Additionally, the results of a test for the Cu_5–I^- cluster are presented. The good quality of the DFT methods is recorded as they give results comparable to the MP2 and, for some cases, even to the MP4 level of standard calculations. The B3LYP method combined with a fairly inexpensive description of the metal atoms is proposed as an appropriate option for studies of the adsorption of halide ions at noble metal surfaces.

1. Introduction

A detailed understanding of the interaction of halide ions with metallic atoms, clusters and surfaces is of wide interest. Especially important is the interaction of halide ions with the metallic surface of an electrode as it determines many electrochemical processes. The difficulty of interpreting the experimental results renders the theoretical approach crucial for the understanding of these phenomena. In computational chemical treatments of this problem, the metallic surface is usually modeled by an atomic cluster. A wide variety of computational methods has been used in the past, mostly of semi-empirical type as large clusters are required to represent the surface. The results reported for EHT [1–6] and CNDO [7–9] calculations do not contradict the meager experimental information that is known. However, recent ab initio calculations at the Hartree–Fock level [10–12] give results that do not agree with earlier semi-empirical ones. The most recent results of Kuznetsov [12] predict the interaction energies of $Cu_7(111)$ with F^-, Cl^-, Br^- and I^-, which disagree with their relative magnitudes as calculated earlier for mercury and silver clusters by EHT [4–6] and CNDO [8] semi-empirical methods; more important, the top position is predicted to be the one preferred for adsorption (in vacuum) while experimental data [13–18] indicates otherwise. This Letter will contribute to the elucidation of this problem and, especially, include electron correlation effects in the calculated interaction energies as these are deemed to be important. The standard methods of accounting for electron correlation become computationally too expensive for the relatively large systems needed to evaluate the ion to surface interaction. The DFT (density

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functional theory) methods have found a widening domain of application in quantum chemistry as a good cost/quality compromise. However, as these methods are not bound by a minimization principle, extensive tests are necessary to evaluate their performance for each particular type of problem and to decide which of the proposed functionals and basis sets should be preferred.

In this Letter, DFT calculations with several functionals that have been proposed in the literature, combined with various basis sets, are presented for the Cu–X$^-$ (X = F, Cl, Br, I) systems as test cases. The results and, especially, the energetics as obtained from DFT calculations are compared with analogous quantities obtained from the standard Hartree–Fock method with and without correlation effects, these being estimated by a perturbation approach. The same comparative tests are presented for Cu$_5$–I$^-$ as a preliminary example of application towards problems of chemisorption.

2. Methods and results

The system Cu–X$^-$ (X = I, Br, Cl, F) has been selected to test and compare the quality of the DFT methods. The final goal of this exercise is to select a method of estimation of the interaction of the halide ions with metal clusters that model the electrode surface. The inner shell 18 electrons of copper have been represented by the effective core potentials (ECPs) of Hay and Wadt [19]. For the description of the 3d104s1 valence electrons two different basis sets have been tested – a single-exponent minimal basis set (MB) and a double-zeta quality (DZ) one. A more extended description of the copper atom has also been used for comparison when just 10 electrons are represented by ECPs and the remaining 19 electrons are given a double-zeta basis set (DZ2) [20]. The inner shells of the chloride, bromide and iodide ions are also represented by ECPs, as proposed by Wadt and Hay [21], while their *nsnp* valence electrons are given a double-zeta quality basis set of Dunning and Huzinaga [22]. In the discussion below, the notation MB–DZ, DZ–DZ and DZ2–DZ is used to refer to the combined description of the Cu and X$^-$ particles following the notation introduced above for each of them. All the calculations have been performed using the GAUSSIAN 92 package [23]. Several different density functional exchange and correlation formalisms may be combined. In the calculations reported here, three alternatives have been tested. Two of these are pure DFT techniques using (i) the exchange functional proposed by Slater [24] combined with the correlation functional of Vosko, Wilk and Nusair [25] (notation SVWN) and (ii) Becke's exchange functional [24] used together with a gradient-corrected correlation functional of Perdew [26] (notation BP86). Additionally, (iii) the hybrid method (denoted B3LYP) has been tested, which includes a mixture of HF and DFT exchange terms and the gradient-corrected correlation functional of Lee, Yang and Parr [27], proposed and parametrized by Becke [28].

For comparison the standard HF as well as Møller–Plesset (MP2 and MP4) calculations have been performed; the MP4 calculations include single, double, triple and quadruple substitutions (SDTQ). In all cases (except MP2 and MP4) the atom–ion distance has been optimized and the equilibrium

Table 1
Interaction energies ΔE (kJ/mol), optimal distances $r_{\min}$ (Å) and charges on the ions $q(X^-)$ for the Cu–X$^-$ systems described by the DZ–DZ and DZ2–DZ combination of basis sets, using the UHF method. The MP2 and MP4SDTQ interaction energies as calculated at the UHF equilibrium distances are also given

Ion	DZ–DZ					DZ2–DZ				
	UHF			MP2	MP4	UHF			MP2	MP4
	$r_{\min}$	ΔE	$q(X^-)$	ΔE	ΔE	$r_{\min}$	ΔE	$q(X^-)$	ΔE	ΔE
F$^-$	1.96	−192.6	−0.80	−239.7	−265.3	1.94	−198.8	−0.79	−247.6	−271.4
Cl$^-$	2.40	−129.5	−0.69	−165.9	−184.0	2.38	−134.9	−0.67	−173.1	−189.2
Br$^-$	2.57	−103.4	−0.68	−139.6	−157.1	2.55	−107.7	−0.66	−145.4	−160.3
I$^-$	2.79	−74.9	−0.68	−104.6	−123.0	2.77	−78.4	−0.66	−111.0	−124.3

interaction energy has been computed. The MP2 and MP4 corrections to the interaction energies have always been calculated for the HF optimal distances.

In Table 1 a comparison is made between the DZ–DZ and the DZ2–DZ basis sets; the results show the limited improvement that is obtained by the use of the larger basis set with the explicit description of another eight copper core electrons. This justifies the selection of the DZ–DZ basis sets as the standard for the calculations reported in this Letter. For both basis sets, including or not the Møller–Plesset corrections, the interaction energies reported in Table 1 show a consistent monotonic decrease as one goes from fluoride up to iodide. The DZ2–DZ/MP4 results must be considered to be the best estimate available for these properties as no experi-

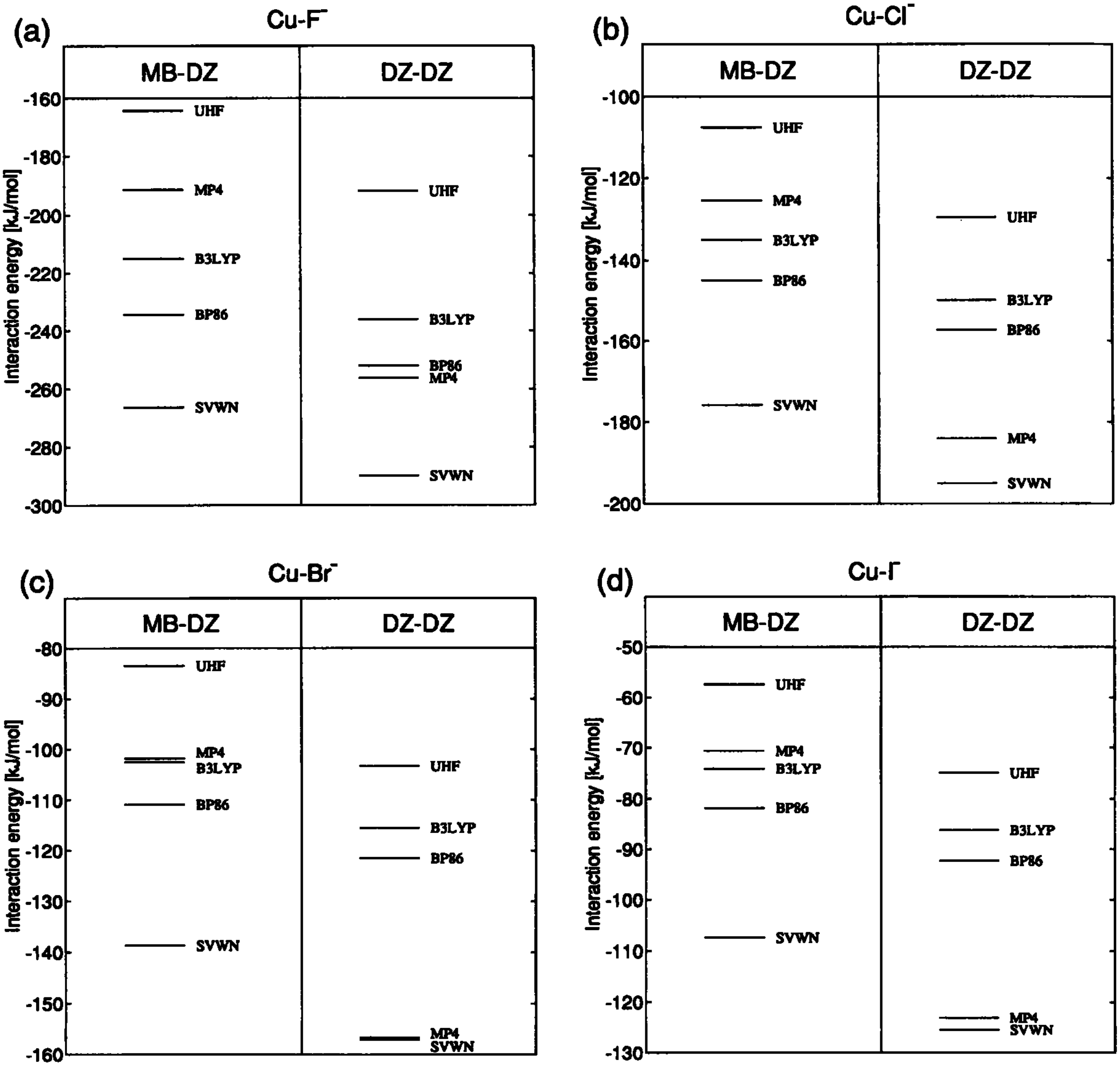

Fig. 1. Interaction energies for the Cu–X$^-$ systems as calculated by the UHF, MP4, SVWN, BP86 and B3LYP methods with two different basis sets used for the copper atom (MB and DZ) combined with DZ basis sets on the halide ions. (a) Cu–F$^-$, (b) Cu–Cl$^-$, (c) Cu–Br$^-$, (d) Cu–I$^-$.

Table 2
The equilibrium interaction energies ΔE (kJ/mol) and (in parentheses) the corresponding distances $z_{\min}$ (Å) from I^- to the plane defined by four Cu atoms in the square pyramidal Cu_5 system as calculated using the DZ basis set for the iodide combined with the MB and the DZ basis set for the copper

Basis set	UHF	MP2	B3LYP	BP86	SVWN
MB–DZ	−124.4 (2.9)	−153.5 (2.9) [a]	−157.2 (2.7)	−180.5 (2.7)	−240.1 (2.6)
DZ–DZ	−105.0 (3.0)	−140.7 (3.0) [a]	−123.5 (2.7)	−148.5 (2.7)	−196.0 (2.6)

[a] The MP2 and MP4SDTQ interaction energies have been calculated at the $r_{\min}$(UHF) distances.

mental data exist to our knowledge. These values, varying from −271.4 kJ/mol for Cu–F^- to −124.3 kJ/mol for Cu–I^-, will be used for comparison and evaluation of the quality of the results obtained with other methods.

To facilitate comparisons, most results are presented in a pictorial way. The interaction energies of the copper atom with the halide ions are shown in Fig. 1, as computed by the different methods mentioned above and using two alternative basis sets for the metal atom. It may be seen that the electron correlation energy, as estimated by the MP4 correction to UHF, is about 60 kJ/mol for Cu–F^- and about 40 kJ/mol for the other cases, when the DZ–DZ basis sets are used, while the alternative MB–DZ basis sets give much smaller estimates. DFT results do appear to include an estimate of the correlation energy comparable to that of MP4 when DZ–DZ bases are used; with the smaller basis MB–DZ the DFT values are much larger than those of MP4, comparable to those of the larger bases DZ–DZ. See, however, an extension of this discussion in the final section below.

Basis set superposition errors (BSSE) are known to be important in calculations of interaction energies of this type. The BSSE corrections were found to be larger for the DFT results reported here than for the Hartree–Fock results. For both methods, the corrections are the largest for fluoride and, at the other end, the smallest for iodide. However, the order of the interaction energies of copper with the different halide ions does not change.

Due to the well-known cluster size dependence of the interaction energy, the conclusions drawn from the atom–ion tests may not be valid for the relatively large cluster used to model electrode surfaces. To test the validity of the methods proposed here to calculate the interaction of halide ions with clusters, a five-atom copper cluster has been constructed. This has a pyramidal shape reproducing the fcc crystallographic structure of copper. The nearest neighbours Cu–Cu distance has been fixed at the experimental value of 2.55 Å and the iodide is placed at the hollow position above the four Cu atoms that represent the (100) plane, as there is some experimental evidence [13–18] that this site is favored for the

Table 3
Interaction energies ΔE (kJ/mol), optimal distances $r_{\min}$ (Å) and charges on the ions $q(X^-)$ for the Cu–X^- systems described by the MB–DZ combination of basis sets, using the UHF, MP2, MP4 and B3LYP methods. The MP2 and MP4SDTQ interaction energies as calculated at the $r_{\min}$ (HF) distances are also given

Ion	UHF			MP2	MP4	B3LYP		
	$r_{\min}$	ΔE	$q(X^-)$	ΔE	ΔE	$r_{\min}$	ΔE	$q(X^-)$
F^-	2.03	−164.3	−0.86	−185.6	−191.4	2.03	−215.0	−0.71
Cl^-	2.53	−107.6	−0.78	−122.1	−125.4	2.51	−135.1	−0.66
Br^-	2.77	−83.5	−0.77	−97.7	−101.8	2.74	−102.5	−0.68
I^-	3.07	−57.4	−0.78	−67.9	−70.6	3.01	−74.1	−0.69

adsorption of halides in the low-index metal surfaces. In Table 2, interaction energies and equilibrium distances as calculated by different methods and with the MB–DZ and DZ–DZ basis sets are compared. It should be noted that the ion to cluster distance is measured from the iodide to the four copper atoms plane. The interaction energies were calculated as $\Delta E = E(Cu_5I^-) - E(Cu_5) - E(I^-)$. The equilibrium distance appears fairly insensible to the method or the basis set used, while the interaction energies show important variations. By inspection of Fig. 1, the DFT method denoted SVWN with the DZ–DZ basis set gives results in closest agreement with our best estimate of the interaction energies, the UHF–MP4 results. However, for the cluster calculations in Table 2, the smaller basis set MB–DZ gives a lower interaction energy than the DZ–DZ basis set, suggesting that this may be overestimated. To avoid this risk, one may prefer to stay closer to the MP2 level of approximation by using the methods denoted by B3LYP and BP86. In a global evaluation, the B3LYP is proposed for adoption for cluster calculations; this, being a HF/DFT hybrid, has much less convergence difficulties than those commonly found for pure DFT methods such as BP86.

In Table 3, B3LYP results for the equilibrium distance, the remanent charge at the ion as well as the interaction energy for the Cu–X^- systems are compared with the corresponding results for the UHF up to the MP4 level. From the results just presented, the hybrid method B3LYP appears to be acceptable for the cluster calculations and compare well with our best estimates of the properties of the copper–ion systems.

3. Discussion and conclusions

Calculations of the interaction of a copper atom and of a copper cluster with halide ions by several density functional formalisms are presented with the final goal of selecting a method for calculating such interactions for the relatively large clusters needed to model a metal surface.

As mentioned before, earlier theoretical studies on the adsorption of halide ions on metal clusters do not yield clear conclusions about a sequence of the ion–metal interactions. Most of the semi-empirical works suggest an ordering of their magnitudes that agrees with the electrochemical predictions, where the iodide has been found to be the strongest adsorbed on the metal. The more recent ab initio studies undertaken for the Hg_7–X^- [11] and Cu_7–X^- [12] systems suggest an opposite order: in vacuum, the largest metal–ion binding energy is found for fluoride. Although some uncertainties appear in two of those works for a bromide ion, a clearly defined order has been found in the work of Blanco et al. [11] where the adsorption of halides on the Hg_7 cluster modeling the (111) surface have been studied by means of HF SCF calculations. As there is no experimental data about the strength of such an interaction for the metal atom–halide ion systems and theoretical considerations are, for such systems, limited, the Cu–X^- results, obtained from our calculations, must be related to the cluster–ion studies mentioned above. The comparison of values should be made with a caution as the size of the systems differs greatly in those cases.

From the results shown in all the tables, the dissociation energies of the copper–halide ion systems are always in the order:

$$|\Delta E_{Cu-F^-}| > |\Delta E_{Cu-Cl^-}| > |\Delta E_{Cu-Br^-}| > |\Delta E_{Cu-I^-}|,$$

independently of the method or basis set used. The ordering of the calculated interaction energies may appear surprising when compared with the opposite sequence that is found experimentally for the adsorption of halide ions onto metal electrodes where iodide is found electrochemically to be the strongest chemisorbed [29,30]. However, the contradiction may be only apparent. Indeed, the chemisorption of an ion at the metal surface in a real system is a complex phenomenon that is influenced by several processes occurring concurrently in the electrode/electrolyte interface region: the solvation of the ion and of the metal, the formation of complexes, the decomposition of the metal surface and the interaction of the ion with the metal.

It should be noted that the basis sets used have no polarization or diffuse functions which have been suggested to have a relevant effect on the properties of ions. Tests have been performed on the reliability of the basis sets used to calculate the electron affinities and the polarizabilities of the halide ions. For the electron affinities, calculated as $EA = E_{tot}(X) - E_{tot}(X^-)$, the UHF method gives poor estimates and especially so for the fluoride ion (a calculated value of 0.52 eV in comparison with the experimental estimate of 3.40 eV). When B3LYP is used with the same DZ basis sets, a great improvement is observed ($EA = 2.11$ eV for the same fluoride), but errors of up to 40% are still found. Good estimates (error of less than ≈ 5%) are obtained only after extending the basis sets to include polarization and diffuse functions. For the polarizability, with the standard basis sets, B3LYP and UHF give extremely low estimates, that for bromide being the smallest. Extending the basis sets with polarization and diffuse functions produces much larger values that grow monotonically from fluoride to iodide. The use of these polarization and diffuse functions on the halide ions does not give a comparable improvement on the calculated charge transfer between the ion and the copper atom. Indeed, this charge transfer is shown in Tables 1 and 3 to be insensitive to the choice of basis set on the metal atom and tests done with the extended basis sets on the ion produce similar results: the charge on the chloride, bromide and iodide ions is always the same to within 0.03 of an electronic charge and smaller than that for fluoride. Experimentally, it is normally assumed that the ion loses almost all its charge upon adsorption. The calculations reported here are not sufficient to clarify this point as the atom/ion behaviour may not model correctly the cluster/ion and, especially, the surface/ion behaviour. This same improvement of the basis sets on the halide ions has a marked effect upon the interaction energies, weakening them without changing their order. Thus, the qualitative picture is not changed by this change of basis set. BSSEs should also be taken into account; however, it has been checked that this latter correction is much smaller when these extended basis sets are used than before.

Detailed tests of the basis sets have shown that the MB–DZ combination always gives a weaker interaction energy for the copper–halide ion than the DZ–DZ combination, while the reverse order is found for the Cu_5I^- interaction. From the results in Fig. 1 it should be clear that all DFT methods that were tested improve the interaction energy in relation to the UHF value. The SVWN results are always below the UHF–MP4 estimates and close to them in the iodide and chloride cases when the DZ–DZ basis sets are used. As stressed earlier, however, this method does not behave well for the interaction with copper clusters. Inspection of Tables 1–3 shows that the BP86 and B3LYP results give reasonable estimates of the UHF–MP2 values. It may be seen in Fig. 1 that the DFT results are less sensitive than the UHF results to the choice of basis set and the BP86 and B3LYP estimates are reasonably close to the UHF–MP2 values when the DZ–DZ basis set is used.

As a compromise between the performance of the different methods for the atom–ion and cluster–ion interactions, the method denoted B3LYP is selected. This is a hybrid of Hartree–Fock and density functional exchange with a correlation functional term and gradient corrections, that has already been shown to perform well in the description of copper compounds [31,32]. Our results show the following features of the B3LYP results.

(a) B3LYP geometrical parameters, i.e. equilibrium distances, are close, but slightly smaller than those predicted at the UHF level. This is also true for copper cluster–ion distances as shown in Tables 2 and 3.

(b) The charge transfer from the ion is correctly predicted to be the smallest for fluoride both in UHF and in B3LYP calculations. No well-defined pattern is found among the values calculated for the other ions. This may be associated with the insufficient description of the polarizabilities and electron affinities of the ions.

(c) The charge transfer predicted by B3LYP is larger than that calculated at the UHF level, both with the MB–DZ basis set. An improvement of the basis sets on the metal is shown to produce a modest decrease in the charge transfer.

(d) B3LYP is shown to be a relatively inexpensive method of calculating metal–ion interactions, including some contribution from electron correlation. The results reproduce well, at least in a semi-quantitative way, those obtained by more expensive methods and thus suggested for calculations with larger clusters.

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