JCTC Journal of Chemical Theory and Computation

Describing Anions by Density Functional Theory: Fractional Electron Affinity

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Abstract: It is shown that the majority of commonly used exchange-correlation potentials in Kohn−Sham density functional theory describe anions as having only a fraction of the extra electron bound, while the remaining fraction drifts off to infinity when sufficiently flexible basis sets are employed. For systems with both cationic and anionic sites, this leads to fractional electron transfer, even when standard basis sets are used, and thus a qualitative incorrect description of the electronic structure. Exchange functionals without Hartree−Fock exchange display the largest effects, but hybrid functionals also show the phenomenon, except for strongly bound anions. The source of the error is the incorrect long-range behavior of the exchange potential and can be avoided by employing the long-range correction method. The results have consequences for density functional descriptions of systems with localized anionic or strong electron donor sites for almost all of the commonly employed exchange-correlation functionals.

I. Introduction

Density functional theory (DFT) in the Kohn−Sham version is firmly established as a useful tool for calculating a variety of properties for both molecular and extended systems.[1] The Hohenberg−Kohn theorem establishes that DFT is capable of providing an exact description of the electronic structure using only the electron density as a variable,[2] but at present only approximations to the elusive exchange-correlation (XC) potential exist. Different XC functionals are counted by the hundreds, and calibration of these functionals with various basis sets is a popular topic in the literature. For routine applications in molecular systems, the ubiquitous B3LYP functional[3] is often the method of choice in combination with a medium sized Pople type basis set, like 6-31G*.[4] In many cases such calculations provide useful results at a low computational cost, which has led to their widespread popularity.

One of the challenging properties to calculate accurately is the electron affinity (EA), corresponding to the energy difference between an atom or molecule and its corresponding anion. Sophisticated wave function methods are capable of achieving accuracies of a few milli-eV (few kJ/mol),[5] but

such methods are computationally expensive. In the dawn of the DFT era in computational chemistry, concerns were raised that approximate DFT might not be suitable for describing anions, as the highest occupied molecular orbital (HOMO) energy often was calculated to be positive.[6−8] A positive orbital energy describes an unbound electron, although the use of a finite basis set prevents this from happening in normal calculations. Systems with a formally unbound electron were nevertheless often found to have a positive EA when calculated as a difference between total energies of the anion and neutral species. Galbraith and Schaefer addressed these concerns by showing that the calculated EA for the fluorine atom does not change substantially by addition of multiple diffuse p-functions (smallest exponent used was $2 \cdot 10^{-5}$) with a selection of different XC functionals.[9,10] The calculated EA with the B3LYP functional was 340 kJ/mol, and the HOMO energy for the fluorine anion converged to a value of essentially zero. The calculated EA with the BLYP functional was even larger, 355 kJ/mol, despite the fact that the HOMO energy for the anion was positive with a value of 0.053 au. Jarecki and Davidson later reinvestigated the fluorine anion with the BLYP functional[11] and showed that by adding further diffuse functions (smallest exponent used was $7 \cdot 10^{-9}$) the EA increases further by ∼15 kJ/mol and resulted in the

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Table 1. Calculated Electron Affinities in kJ/mol with Four Different Methods[c]

anion	HF apc-2	HF limit	BHHLYP apc-2	BHHLYP limit	B3LYP apc-2	B3LYP limit	BLYP apc-2	BLYP limit	exp[b]
H⁻	−27.4	0	64.3	68.8	88.2	105.1	82.2	116.4	72.8
Li⁻	−10.8	0	41.9	44.2	53.6	62.3	43.7	63.1	59.6
Be⁻	−88.3	0	−68.5	6.5	−51.8	27.8	−58.8	36.0	0
B⁻	−26.2	0	18.8	34.9	46.9	74.7	45.6	89.4	27.0
C⁻	53.6	53.3	104.1	104.1	136.7	150.7	135.2	168.2	121.9
N⁻	−160.1	0	−28.4	21.4	21.1	77.0	35.2	108.2	0
O⁻	−52.6	0	109.0	108.5	164.9	180.5	179.6	216.4	141.0
F⁻	127.6	126.3	288.6	287.6	347.9	347.3	362.5	373.0	320.2
MAD[a]	**113.1**	**93.8**	**19.3**	**18.4**	**18.0**	**29.7**	**23.0**	**47.3**	

[a] Mean absolute deviation relative to experimental values for the six nonzero EAs. [b] Reference 13. [c] apc-2 indicates results obtained with the aug-pc-2 basis set; limit indicates the basis set limiting results.

HOMO energy stabilizing to a value of −0.065 au, indicating that the extra electron is bound when sufficiently diffuse functions are included in the basis set. We encountered the problem of formally unbound electrons when designing diffuse augmentation functions for the polarization consistent basis sets,[12] which are optimized for DFT calculations. Attempts of determining the optimum diffuse exponents by minimizing the BLYP energy for anions in most cases lead to the exponent diverging toward zero, and we suggested that only systems with a large EA may have well-defined EA values.

The early reservations regarding the ability of DFT to describe anions seem largely to have been overlooked or ignored by the practitioners in the field, and well over 1000 publications have appeared using DFT methods to calculate EA.[13,14] In a few cases, the papers by Galbraith and Schaefer,[9] and by Jarecki and Davidson,[11] are taken as evidence that DFT is capable of describing anions as stable species when sufficiently diffuse functions are included, although this is almost never done in actual calculations. The fluorine atom is one of the species with the largest known EA, and the above finding may thus not be generally applicable, but very few detailed investigations of other systems have been reported. It has been argued that atomic systems having strongly localized electrons will be the most problematic cases, and molecular anion where the extra electron can be delocalized over a larger volume of space will be better behaved,[10] but again no detailed investigation has been reported. Even for the fluorine atom with a large EA, the puzzle remains how an anion with a positive HOMO energy and a formally unbound electron nevertheless can have a positive EA when calculated as a difference in total energies.

We will in the present paper show that most commonly employed XC functionals lead to DFT descriptions of anions as having only a fraction of the extra electron bound and that this is the rule rather than the exception for anions in general. We will use the term "fractional electron affinity" to describe this situation and show that this has consequences also for intermolecular ion complexes, zwitterionic and electron donor−acceptor systems in general.

II. Computational Details

Performing calculations with very diffuse basis functions faces a number of numerical issues that standard settings of many commonly used program packages have not been designed for. All integral thresholds have been tightened to essentially machine precision, and density matrices have been converged to at least 10^{-8}. The XC contribution has been calculated using an Euler-Maclaurin radial grid[15] with 5000 points in combination with a Lebedev angular grid with 434 points.[16] A large radial grid is necessary for integrating electron density corresponding to basis functions with very small exponents, and the Davidson radial norm criterion[11] has in all cases been fulfilled to within 10^{-6}. It was checked that the results did not change upon further enlargement of the grid size. Threshold screenings for discarding integration points with low density for determining the XC energy have been disabled. Linear dependency of the basis sets is not a problem, as only a single expansion center is employed for the very diffuse basis functions. Standard methods for converging the SCF equations are often found to display divergence when multiple diffuse functions are present, and combinations of steepest descent and second order optimization methods are required. It is furthermore important that the SCF solutions are verified to be genuine minima in the parameter space, as convergence to saddle points is very common when near-degenerate orbitals are present.

In order to check the coherency of the results and detect numerical problems, we have performed parallel calculations with locally modified versions of the Gaussian-09,[17] Gamess-US,[18] and Dalton[19] programs and verified that the results are internally consistent.

Atomic populations have been done using the natural population analysis method.[20] The amount of unbound density can be obtained by numerical integration or, more conveniently, by placing the very diffuse basis functions on a dummy atom, in which case the unbound density is simply the electron population for this atom.

III. Results and Discussion

Table 1 shows electron affinities (EA) for first row atoms calculated with four different methods using the aug-pc-2 basis set,[12] which is of triple-ζ quality augmented with diffuse functions, as well as the basis set limiting results obtained as described in more detail in the next section. The pc-*n* basis sets have been optimized for DFT calculations,[21] but results similar to those with aug-pc-2 can be obtained using other basis sets of similar quality, as for example the 6-311+G basis set. The four methods are Hartree−Fock (HF)

and three density functional, BHHLYP,[22] B3LYP[3], and BLYP, where the exchange energy is modeled by the Becke gradient corrected functional,[23] and the LYP functional[24] is used for calculating the correlation energy. These three functionals can be considered as successively replacing the HF exchange energy by the corresponding DFT analogue. The HF method thus contains 100% HF exchange (and no correlation), BHHLYP contains 50% HF and 50% Becke exchange, B3LYP is 20% HF and 80% Becke exchange, while BLYP is 100% Becke exchange.

The results in Table 1 show that the HF method systematically underestimates the EAs due to the lack of electron correlation and only predicts positive EAs for the carbon and fluorine atoms. The DFT methods in general perform much better, and the combination of the B3LYP method and the aug-pc-2 basis set reproduces the six experimentally nonzero EAs (H, Li, B, C, O, F) with an average deviation of only 18 kJ/mol (0.19 eV, 1 eV = 96.5 kJ/mol), and such calibration studies lie at the root of promoting DFT methods with medium basis sets for calculating electron affinities.[25]

A closer inspection of the results in Table 1, however, reveals a systematic trend. For the HF and BHHLYP methods, there are only small changes by extending the size of the basis set beyond aug-pc-2 for atoms predicted to have positive EAs (BHHLYP MAD value changes from 19.3 to 18.4 kJ/mol); however, as the amount of HF exchange is reduced, the effect of basis set extension increases to a mean value of 24 kJ/mol for the BLYP method.

The beryllium and nitrogen atoms do not have stable anions and consequently have EAs of zero. In finite basis sets, like aug-pc-2, the extra electron relative to the neutral atom is confined by the basis set to remain close to the nucleus, and the EA calculated as a difference between total energies is often found to be negative. This is a well-known limitation, and calculated negative EAs are therefore usually associated with *de facto* zero EAs. With the aug-pc-2 basis set, all four methods predict a negative EA for the beryllium atom, but the three DFT methods predict a small positive EA at the basis set limit. Somewhat more troublesome is the behavior for the nitrogen atom, where the B3LYP and BLYP methods predict a positive EA even with the aug-pc-2 basis set, and the BLYP value at the basis set limit is a sizable 108 kJ/mol.

The following sections show that these behaviors are due to DFT methods describing anions as having only part of the extra electron bound, while the remaining part drifts off to infinity when a sufficiently flexible basis set is used, where the fraction of the electron bound depends on the magnitude of the EA.

III. a. Atomic Systems. The starting point for establishing the basis set limiting EA values in Table 1 is the aug-pc-*n* basis sets.[12] Only s- and p-functions are required to describe the electron density for the atoms in Table 1, and we have used the aug-pc-*n* (*n* = 0,1,2,3,4) basis sets in their uncontracted forms to avoid possible contraction errors. The aug-pc-4 basis set was systematically extended by adding diffuse s- and p-functions by scaling the outer exponent with a factor of $\sqrt{10}$ until the exponent of the most diffuse function dropped below 10^{-10}. An s- or p-type Gaussian

basis function with an exponent of 10^{-10} has a maximum in the corresponding integrated density corresponding to $\sim 10^5$ au. While basis functions with exponents $\sim 10^{-4}$ are sufficient to describe electrons that are essentially unbound relative to the atom, diffuse functions with exponents $\sim 10^{-8}$ are required to allow the unbound electron density to spread sufficiently to converge the total energy to micro-Hartree accuracy and thus establish the basis set limiting EA.

The hydrogen anion is the simplest system, having only two electrons, and provides a framework for describing the general behavior. In a conventional description, the two electrons are placed in one doubly occupied orbital, which at the HF/aug-pc-2 level of theory leads to an EA of −31.8 kJ/mol. This value changes by only 0.1 kJ/mol when the basis set is extended as described above, i.e. at the basis set limit the HF EA value is −31.7 kJ/mol. The negative value indicates that the total energy of the anion is higher than that of the neutral atom, which is due to the restriction that both electrons are described by the same spatial orbital. When the α and β spin−orbitals are allowed to become different, the energy can be lowered by allowing the β spin−orbital to become as diffuse as the basis set allows. This symmetry breaking leads to an energy lowering of 4.4 kJ/mol with the aug-pc-2 basis set, producing the calculated EA value of −27.4 kJ/mol shown in Table 1. When the basis set is made sufficiently flexible, the β electron drifts off to infinity, and the energy of the anion converges to that of the neutral atom and thus a calculated EA of zero at the basis set limit. These results are shown in Table 2, where the values in parentheses are for the symmetric wave function corresponding to restricting the two electrons to the same spatial orbital. The symmetry breaking is also displayed by the HOMO energies shown in Table 3. In a symmetric description, the HOMO energy is negative (−0.046 au), but in the symmetry-broken solution, the HOMO (β spin−orbital) is positive with the aug-pc-2 basis set and converges to zero from above as the basis set is made sufficiently flexible. The positive HOMO energy and negative EA are thus clear indications that the extra electron is unbound at the HF level, but the use of a limited basis set like aug-pc-2 cannot describe this situation.

With the BLYP functional, the calculated EA with the aug-pc-2 basis set is 82.2 kJ/mol (Table 1), and for this basis set only a symmetric solution corresponding to one doubly occupied orbital can be found, but when a sufficient number of diffuse basis functions are added, both symmetric and symmetry-broken solutions can be found. At the basis set limit, the calculated EAs are 109.1 and 116.4 kJ/mol (Table 1) for the two solutions, respectively, and basis set extensions beyond aug-pc-2 thus changes the EA by 26.9 and 34.1 kJ/mol (Table 2), respectively. The HOMO energy, however, is positive with the aug-pc-2 basis set and converges toward zero for both solutions as the basis set limit is approached (Table 3). The BLYP functional thus predicts a formally unbound electron, despite giving a lower total energy for the anion than for the neutral atom.

This contradiction is resolved by inspecting the HOMO of the symmetric solution, where both the HF and BLYP occupied orbitals display the expected maximum at a distance of ∼1.2 au from the nucleus which then decays toward zero.

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Table 2. Calculated Atomic Properties[a]

anion	HF		BHHLYP		B3LYP		BLYP	
	$\Delta EA_{2\text{-}\infty}$	$D_{unbound}$	$\Delta EA_{2\text{-}\infty}$	$D_{unbound}$	$\Delta EA_{2\text{-}\infty}$	$D_{unbound}$	$\Delta EA_{2\text{-}\infty}$	$D_{unbound}$
H$^-$	27.4	1.00	4.1	0.25	16.9	0.31	34.1	0.37
	(0.1)	(0)	(0.5)	(0.01)	(9.3)	(0.18)	(26.9)	(0.30)
Li$^-$	10.8	1.00	2.4	0.21	8.7	0.29	19.4	0.38
	(0.1)	(0)	(0.9)	(0.08)	(6.5)	(0.22)	(17.9)	(0.35)
Be$^-$	88.3	1.00	75.0	0.72	79.6	0.59	94.8	0.60
B$^-$	26.2	1.00	16.1	0.43	27.8	0.41	43.7	0.45
	(−0.1)	(0)	(5.6)	(0.17)				
C$^-$	−0.3	0	0.0	0	13.9	0.25	33.0	0.33
					(10.2)	(0.18)		
N$^-$	160.1	1.00	49.8	0.61	55.8	0.48	73.0	0.48
O$^-$	52.6	1.00	−0.5	0	15.7	0.25	36.8	0.25
					(11.7)	(0.19)		
F$^-$	−1.3	0	−1.0	0	−0.6	0	10.5	0.15
							(9.6)	(0.14)

[a] Values correspond to lowest energy solution, which may be symmetry-broken. Values in parentheses are for symmetric solutions, if both types of solutions exist. $\Delta EA_{2\text{-}\infty}$ is the change in the calculated electron affinity between the aug-pc-2 basis set and the basis set limit (kJ/mol). $D_{unbound}$ is the amount of unbound electron density in units of one electron when the basis set is made sufficiently flexible.

Table 3. Calculated HOMO Energies (au)[a]

anion	HF		BHHLYP		B3LYP		BLYP	
	apc-2	limit	apc-2	limit	apc-2	limit	apc-2	limit
H$^-$	+0.026	0	+0.004	0	+0.036	0	+0.065	0
	(−0.046)	(−0.046)						
Li$^-$	+0.001	0	+0.007	0	+0.022	0	+0.037	0
	(−0.014)	(−0.015)						
Be$^-$	+0.033	0	+0.065	0	+0.077	0	+0.087	0
B$^-$	−0.026	0	+0.023	0	+0.047	0	+0.067	0
		(−0.027)						
C$^-$	−0.078	−0.078	+0.0004	−0.0005	+0.041	0	+0.073	0
N$^-$	+0.056	0	+0.055	0	+0.084	0	+0.110	0
O$^-$	−0.074	0	−0.005	−0.005	+0.048	0	+0.088	0
		(−0.074)						
F$^-$	−0.181	−0.181	−0.073	−0.073	−0.0006	−0.002	+0.053	0

[a] apc-2 indicates results obtained with the aug-pc-2 basis set; limit indicates the basis set limiting results. Values correspond to the lowest energy solution, which may be symmetry-broken. Values in parentheses are for symmetric solutions, if both types of solution exist.

At long distances, however, the BLYP HOMO displays a wavelike behavior with significantly nonzero MO coefficients for the most diffuse basis functions. Figure 1 shows the integrated HF and BLYP HOMO densities normalized to one as a function of the distance from the nucleus, and it is clear that the BLYP method leads to a description where 15% of the density (0.30 electrons) has been expelled from the atom. In a sufficiently flexible basis set, the BLYP method thus describes the H$^-$ system as a hydrogen atom with 0.70 extra electrons attached, while the remaining density corresponding to 0.30 electrons behave as free electrons. The BLYP predicted positive EA in a limited basis set like aug-pc-2 is therefore a combination of an energy lowering due to addition of density corresponding to 0.70 electrons, which is partly compensated by an energy increase from constraining a density of 0.30 electrons to occupy the same physical space. In a sufficiently flexible basis set, the latter effect is removed, which accounts for the 26.9 kJ/mol increase in the calculated EA upon enlarging the basis set (Table 2). The symmetry-broken solution provides the same qualitative picture, where a density corresponding to 0.37 (β) electrons becomes unbound, which leads to a change in the EA of 34.1 kJ/mol (Table 2).

The detachment of electrons from the anion can be understood by considering the HOMO and LUMO energies
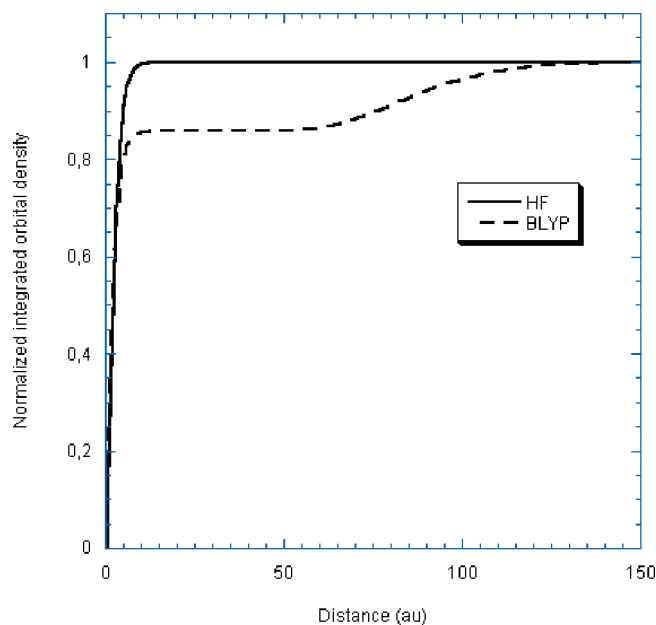
Figure 1. Normalized integrated orbital density for the H$^-$ ion as a function of distance from the nucleus using the HF and BLYP methods.

from a SCF calculation with integer electron occupancy. As basis functions with successive smaller exponents are added,

the LUMO energy will converge to zero from above. If the HOMO energy is positive, the LUMO energy will at some stage become lower than the HOMO energy, at which point a lower energy solution can be obtained by transferring electron density from the HOMO to LUMO. The formation of unbound electron density will therefore always occur when a HOMO with positive energy is obtained in a limited basis set and a sufficient number of diffuse basis functions are added. Furthermore, the amount of unbound density will be related to the magnitude of the positive HOMO energy. As electron density is removed from the HOMO, its energy decreases until it becomes degenerate with the formal LUMO. In the limit of a sufficient number of very diffuse basis functions, the LUMO energy will be zero regardless of the amount of electron density it contains, and the unbound electron density is thus the amount required to reduce the HOMO energy to zero.

The B3LYP and BHHLYP methods with 20% and 50% HF exchange behave intermediate between the BLYP and HF results, as shown in Tables 2 and 3. Both these hybrid functionals produce positive HOMO energies that converge toward zero as the basis set is augmented with multiple diffuse functions and thus describe partly unbound electron density. With the B3LYP functional, the unbound fraction is 0.31 electrons for the lowest energy symmetry-broken solution, while it is reduced to 0.25 electrons with the BHHLYP method. The changes in the calculated EA between the aug-pc-2 and basis set limit are correspondingly smaller than for the BLYP functional. The unbound density using the LSDA functional (not shown) is 0.11 and 0.27 for the symmetric and symmetry-broken solutions, respectively, which is in agreement with the study of Shore et al.[6]

The lithium anion behaves very similar to the hydrogen anion, with slightly larger fractions of electrons being unbound, while the more diffuse character of the 2s-orbital leads to slightly smaller changes in the calculated EA upon improving the aug-pc-2 basis set to the basis set limit, as shown in Table 2.

The carbon atom has a positive EA at the HF level and the anion a negative HOMO energy. With the BHHLYP functional the HOMO energy is slightly positive (+0.0004 au) with the aug-pc-2 basis set but becomes negative with the aug-pc-3 basis set and converges to a value of −0.0005 au at the basis set limit (Table 3), while the B3LYP and BLYP functionals produce positive HOMO energies for all basis sets. In a symmetric description, the three singly occupied p-orbtials are equivalent, but when two sets of diffuse functions have been added to the aug-pc-4 basis set, a symmetry-broken description can also be found. In the symmetric solution, the energy of the three degenerate p-orbitals converges toward zero as the basis set limit is approached, while the symmetry-broken solution allows two of the p-orbitals to acquire negative energies, and the third p-orbital has a positive energy that converges toward zero as the basis set limit is attained. With the B3LYP functional, the symmetric solution corresponds to ejecting 0.18 electrons, while the symmetry-broken solution corresponds to having 0.25 electrons unbound. When the BLYP functional is used, only symmetry-broken solutions can be found when more

than three diffuse functions are added to the aug-pc-4 basis set, and this leads to 0.33 electrons being unbound at the basis set limit.

The boron and oxygen anions behave very similar to the carbon anion, with the results shown in Tables 2 and 3.

The fluorine anion has, as mentioned in the Introduction, been used as a test system for probing whether the BLYP functional predicts a bound system. Galbraith and Schaefer calculated a positive HOMO energy of 0.053 au when basis functions with exponents down to $2 \cdot 10^{-5}$ were used,[9] while Jarecki and Davidson found that extension of the aug-cc-pV5Z basis set with diffuse p-exponents down to $7 \cdot 10^{-9}$ gave a negative HOMO energy of −0.065 au.[11] Using the same basis set and grid, we were initially unable to reproduce the latter result, until it was discovered that the behavior could be reproduced by one of the employed programs when the two-electron integrals accuracy was lowered to $\sim 10^{-11}$, which is a typically default setting in many programs. Using our prescription for approaching the basis set limit and employing full integral accuracy, the HOMO energy converges to a value of zero, and the shape of the HOMO leads to a density plot analogous to Figure 1, where the amount of unbound density is 0.14 electrons in a fully symmetric description. It is again possible to generate a symmetry-broken solution when a sufficient number of diffuse functions have been added, and this leads to a marginal increase of the EA by 0.9 kJ/mol and to 0.15 electrons being unbound. The BHHLYP and B3LYP functionals have negative HOMO energies when basis sets of aug-pc-2 quality or better is used and thus predicts a completely bound electron (Tables 2 and 3).

The beryllium and nitrogen anions are experimentally found not to be stable (EA = 0 kJ/mol) and are calculated to have positive HOMO energies with all four methods. At the HF level, the extra electron becomes unbound and the EA converges toward zero as the basis set is enlarged. For the beryllium anion, the three DFT methods lead to negative EAs with the aug-pc-2 basis set but positive values at the basis set limit. For the nitrogen anion, the BHHLYP calculated EA is negative with the aug-pc-2 basis set, while both the B3LYP and BLYP functionals predict positive EAs. As the basis set is increased toward the limit, all three DFT methods predict positive EAs, and the BLYP value is a sizable 108 kJ/mol (Table 1). In analogy with the other anions, the DFT description is in terms of a fractional EA with binding of 0.28−0.52 electrons (Table 2).

For the atoms with experimentally nonzero EAs, the amount of unbound density in general increases as the amount of HF exchange is reduced. Note that for these systems, the HF-LYP method (100% HF exchange + LYP correlation) predicts a completely bound electron. For the two atoms with zero EA (beryllium and nitrogen), the HF-LYP method predicts a completely unbound electron, and the trend is reversed, such that the amount of unbound density decreases as the amount of HF exchange is reduced (within numerical accuracy).

III. b. Molecular Systems. It has been argued that the problem with positive HOMO energies will be most severe for atoms, where the extra electron is strongly localized, and

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Table 4. Calculated Molecular Properties with Four Different Methods[a]

anion	HF			BHHLYP			B3LYP			BLYP			EA$_{Exp}$
	ε_{HOMO}	EA	$D_{unbound}$	ε_{HOMO}	EA	$D_{unbound}$	ε_{HOMO}	EA	$D_{unbound}$	ε_{HOMO}	EA	$D_{unbound}$	
CN^-	−0.192	280.8	0	−0.106	389.7	0	−0.046	389.8	0	+0.001	361.6 (361.6)	0.003	372.6 ± 0.4
OF^-	−0.167	130.2	0	−0.055	233.4	0	+0.019	254.2 (252.7)	0.06	+0.072	256.3 (235.1)	0.22	219.2 ± 0.6
$C_5O_2^-$	−0.068	60.1	0	+0.003	84.2 (84.1)	0.04	+0.048	92.9 (72.5)	0.32	+0.085	88.3 (40.4)	0.43	116 ± 19
NS^-	−0.086	142.8	0	−0.013	152.8	0	+0.037	156.9 (146.3)	0.21	+0.076	153.5 (119.5)	0.33	115.2 ± 1.1
NO^-	−0.087	49.5	0	+0.020	84.8 (78.7)	0.23	+0.081	118.9 (75.6)	0.39	+0.121	130.3 (53.5)	0.45	2.5 ± 0.5

[a] ε_{HOMO} is in au using the aug-pc-2 basis set, EA is in kJ/mol at basis set limit with the aug-pc-2 value in parentheses, and $D_{unbound}$ is in units of one electron.

molecular systems which allow the electron to spread out will be less prone to having unbound electrons.[10] Table 4 shows HF, BHHLYP, B3LYP, and BLYP calculated properties for a selection of small molecular systems arranged according to their experimental EA. The HOMO energy is the value obtained with the aug-pc-2 basis set, and for cases where this is positive, calculations have in analogy with the atomic case been performed where multiple diffuse s- and p-functions are added to the aug-pc-2 basis set using a single expansion center. The EAs shown in Table 4 are the values converged with respect to addition of very diffuse functions, with the results for the regular aug-pc-2 basis set shown in parentheses. It was checked that inclusion of very diffuse d-functions had only a marginal influence (less than 0.1 kJ/mol) on the resulting EAs.

The strongly bound CN^- anion has a negative HOMO energy with the HF, BHHLYP, and B3LYP methods, while the value is slightly positive with the BLYP functional. The amount of unbound electron density in the latter case, however, is only 0.003 electrons, and this has an insignificant effect on the calculated EA, and all three DFT methods provide good estimates of the experimental EA.

The OF^- anion represents an intermediate case, where the HF and BHHLYP methods give negative HOMO energies, while the B3LYP and BLYP functionals produce positive HOMO energies. The amount of unbound density in the two latter cases is 0.06 and 0.22 electrons, respectively, and for the BLYP functional, the EA changes by 21 kJ/mol when the unbound density is allowed to escape. The values in Table 4 correspond to a symmetric solution where the α and β spin−orbitals are constrained to be identical, but in analogy with the atomic systems, it is possible to generate symmetry-broken solutions where the α and β spin−orbitals are inequivalent. The symmetry-broken solution further increases the EA by 2 kJ/mol and corresponds to 0.24 electrons being unbound.

The NS^- and NO^- anions are triplet ground states and have smaller EAs, with the latter being near-zero experimentally. The HF method predicts negative HOMO energies for both species, while the B3LYP and BLYP methods have positive HOMO energies, and the BHHLYP method predicts a positive HOMO energy for NO^- and a negative HOMO energy for NS^-. For the cases where the HOMO energy is positive only symmetry-broken solutions, where the π_x- and π_y-orbitals are inequivalent, could be found when a sufficient

number of diffuse functions were added. The NS^- and NO^- results follow the trend that the amount of unbound density increases as the EA becomes lower and increases as the amount of HF exchange is decreased. With the BLYP functional, the NS^- and NO^- systems have 0.33 and 0.45 electrons unbound, respectively, and the changes in the calculated EA upon addition of multiple diffuse functions are 34 and 77 kJ/mol. The B3LYP and BHHLYP results are again intermediate between the BLYP and HF results.

The $C_5O_2^-$ anion, which has an experimental EA very similar to NS^-, albeit with a rather large uncertainty, also displays the phenomenon of fractional EA with all three DFT methods (Table 4). The $C_5O_2^-$ system has slightly more positive HOMO energies and slightly more unbound density than NS^-, and the calculated EAs are actually closer to that of NO. The similarity of the $C_5O_2^-$ results with those of NS^- and NO^- suggest that delocalization of the extra electron over a few atoms is not enough to overcome the inherent tendency for a given XC functional to predict unbound electron density. As the system size increases, the delocalization effect will of course at some point become important, and for example the C_{60}^- anion is calculated to have a negative HOMO energy with the BLYP functional. Note, however, that the delocalization effect results in the HF method predicting positive EAs for all five systems. The results in Table 4 indicate that many commonly encountered anions will display the phenomenon of fractional EA when using standard DFT methods.

III. c. Intermolecular Complexes, Zwitterions, and Donor−Acceptor Systems. The DFT description of anions as having fractional unbound electron density has consequences for systems where (localized) anions are part of a larger system that also have moieties that can accept electron density, even when using regular basis sets and grids. To illustrate this point, we have performed BLYP/6-31+G* calculations[4] for the intermolecular complex of a formate anion (HCO_2^-) and an ammonium cation (NH_4^+) as a function of the distance between the carbon and nitrogen atoms, as shown in Figure 2. At the HF and MP2 levels of theory using the restriction of doubly occupied orbitals, the complex separates into two ions having a full negative and positive charge, and this charge separation is essentially complete for distances longer than 6 Å, as shown in Figure 3. At large separations, a similar solution can be found also with the BLYP functional; however, this is a saddle point
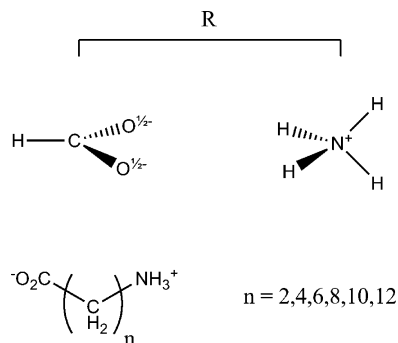
Figure 2. Molecular complex and zwitterions used for the results in Figures 3 and 4.
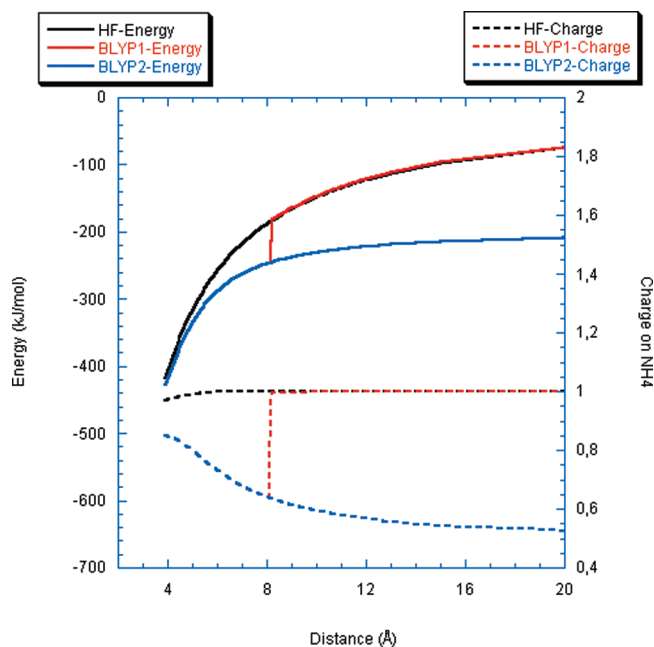
Figure 3. Energies relative to the ion separated limit and charge on the NH_4 group for the HCO_2^- - NH_4 complex in Figure 2 as a function of separation distance. BLYP1 and BLYP2 indicate two different SCF solutions, see text for details.

in the parameter space. The lowest energy solution corresponds to the formate ion having transferred 0.53 electrons to the ammonium group, and at the dissociation limit this is 189 kJ/mol lower in energy than the complete charge-separated solution. For distances smaller than 8.2 Å, only a single SCF solution can be found, and from the continuity of the energy and charge curves in Figure 3, the solution at shorter distances is of the fractionally transferred electron type. It should be noted that several other solutions corresponding to intermediate fractional electron transfer can be found in the medium distance range of 9−13 Å, but these have been omitted in Figure 3 for clarity.

The two other XC functionals display a behavior intermediate between the BLYP and HF results. The popular B3LYP method thus dissociates into a formate ion having transferred 0.45 electrons to the ammonium group, leading to an energy lowering of 115 kJ/mol relative to the completely ion-separated description, while the corresponding values for the BHHLYP method are 0.27 electrons and 35 kJ/mol. The collapse of the ionic solution occurs at a

distance of 7.0 Å with the B3LYP method and 9.0 Å with the BHHLYP functional.

At large separation distances, the employed programs converge to the pure ionic solution when using automated start guesses for the SCF procedure, and manual procedures must be employed to locate the fractional electron transfer solution. At intermediate distances, the convergence using the automated start guesses is erratic, and which SCF solution that is obtained depends on numerical details.

When using an unrestricted wave function, the HF solution corresponding to dissociation into neutral formate and ammonium radicals is 13 kJ/mol higher in energy than the ion-pair dissociation, while the MP2 level favors the neutral dissociation by 19 kJ/mol, and the energy difference can be taken as the difference in EA between the formate radical and the ammonium cation. The three DFT methods also predict a neutral dissociation channel to be lowest, by 9, 51, and 88 kJ/mol for the BHHLYP, B3LYP, and BLYP methods, respectively. It may be argued that the DFT results with fractional electron transfer are trying to mimic this radical dissociation within a restricted framework using doubly occupied orbitals. The fact that the fraction of density transferred dependent on the XC functional, that the BLYP energy difference between the two solutions is 189 kJ/mol, compared to the near zero values at the HF and MP2 levels, and the similarity with the ejection of density from the isolated anions, suggest that fractional electron transfer is an artifact of the DFT methods, rather than an attempt of describing the actual physical system.

The formate ammonium complex in Figure 2 can be taken as a model for negatively and positively charged side chains in peptides and proteins. If these are in close contact and form a salt bridge, Figure 3 suggests that DFT methods will predict too little charge separation between the two moieties due to fractional electron transfer. Furthermore, they will display an incorrect behavior for how the atomic charges change as a function of separation distance, i.e. Figure 3 shows that the charge separation becomes smaller as the distance is increased instead of becoming larger. If a number of anionic and cationic sites are separated by more than a few Ångstrøms, there may be multiple SCF solutions corresponding to combinations of fractional electron transfer, and which solution a given program finds may depend on numerical details.

The DFT description of fractional electron transfer is not limited to intermolecular ion complexes but is also present in zwitterionic systems, where the anionic and cationic sites are part of the same molecule. For the ammonium-alkyl-carboxylates shown in Figure 2, the charges on the NH_3 and CO_2 groups are shown in Figure 4 as a function of chain length ($n = 2,4,6,8,10,12$) at the HF and BLYP levels of theory with the 6-31+G* basis set. For the two longest chains, there are two BLYP solutions, where the one with the lowest energy is of the fractional electron transfer type. For $n = 12$, corresponding to a distance between the terminal carbon and nitrogen atoms of 16.6 Å, the energy difference is 86 kJ/mol and has ~0.31 electrons transferred from the carboxylate to the ammonium group. For the systems with eight or less methylene groups, only a single BLYP solution
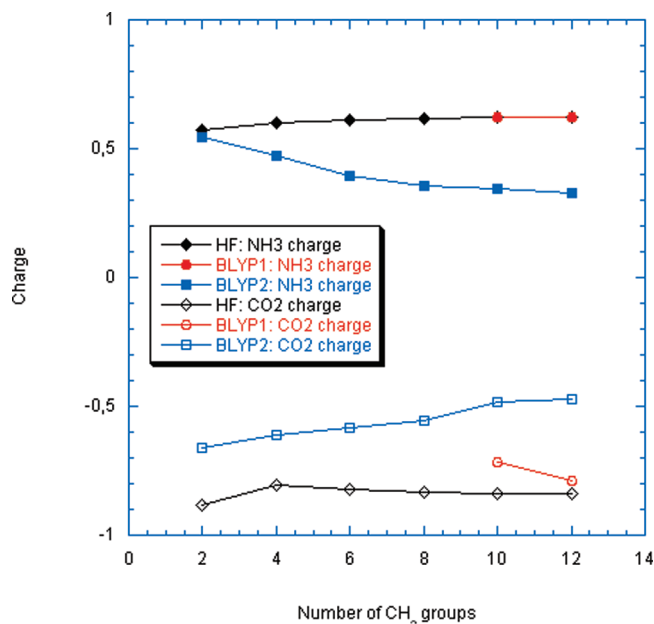
Figure 4. Charge on the CO_2 and NH_3 groups for the zwitterionic systems in Figure 2 as a function of number of methylene units. BLYP1 and BLYP2 indicate two different SCF solutions, see text for details.

can be found, and from the continuity of the curves in Figure 4, this is of the fractional electron transfer type. The B3LYP method produces results intermediate between the HF and BLYP, with two different solutions for the two longest chains, where ~0.22 electrons have been transferred in the lowest energy solution.

The fractional electron transfer displayed by large distance separated ionic system, being either inter- or intramolecular, is a direct consequence of the fractional unbound electron density for isolated anions discussed in the previous sections. In the general case, however, it is likely that the phenomenon will be present when a sufficiently electron-rich donor is present together with a sufficiently electron-poor acceptor, where neither of these needs to carry a full negative or positive charge. To illustrate this point, we have carried out calculations of two systems derived from the formate and ammonium ions in Figure 2. If the formate anion is protonated to give a formic acid-ammonium complex, the system still display fractional electron transfer with the BLYP functional, although only 0.02 electrons are transferred to the ammonium group. Similarly, the formate anion complexed with neutral ammonia leads to transfer of 0.02 electrons in the large separation limit. The energy differences between the pure ionic and fractional electron transfer solutions are only a few tenths of a kJ/mol. With the B3LYP functional, both of these systems have completely localized charges, again confirming that pure density functional methods are most prone to fractional electron transfer. The small amounts of electron transfer with the BLYP functional will only have notable effects for intermolecular complexes separated by a large distance and will most likely only have small consequences for intramolecular systems. It is likely, however, that there is a continuous range of fractional electron transfer, when the amount of density transferred depends on the strengths of the electron donor and acceptor,

with isolated anions and cations representing the limiting case, and the XC functional. How severe this problem is will have to be settled by more detailed investigations for a larger variety of systems.

The results in Figures 3 and 4 suggest that standard DFT methods will be problematic for describing the electronic structure of anions and cations embedded in a large macromolecular system, like a protein. Assuming that the employed program is capable of locating the lowest energy SCF solution, the corresponding description will have too little charge separation and leads to incorrect descriptions of the electrostatic potential.

III. d. Dependence on XC Functional. We have in the above analysis shown results for the BHHLYP, B3LYP, and BLYP functionals, as these represent some of the most widely used methods. As shown by the results in Tables 2−4, the presence of a positive HOMO energy indicates that the method will display the phenomenon of fractional EA, and this may have significant consequences when HOMO energies calculated with a diffuse augmented basis set of double or triple-ζ quality are larger than ~0.01 au. There is a clear, although not quantitative, correlation between the magnitude of the EA and the HOMO energy, i.e. species with large EAs have negative or small positive HOMO energies, while species with low EAs have positive HOMO energies with all three XC functionals. Fractional electron transfer in inter- or intramolecular complexes can occur even in the absence of positive HOMO energies but can be detected by the presence of at least one virtual orbital with lower energy than the HOMO. Allowing these orbitals to mix will produce degenerate HOMO and LUMO orbitals with fractional occupation.

We have scanned a large part of the XC functionals available in the employed computational packages[17,18] for the B^-, C^-, O^-, F^-, CN^-, OF^-, NS^-, and NO^- anions using the aug-pc-2 basis set and find that the results are representative for all of the commonly employed functionals, including meta-functionals like TPSS and TPSSh.[26] Pure XC functional that do not contain HF exchange resembles the BLYP results in having the largest positive HOMO energies, while hybrid methods like B3LYP and BHHLYP have negative HOMO energies for the systems with large EAs but positive energies for systems with small EAs. The larger the amount of HF exchange in the functional, the lower HOMO energies are obtained, and functionals that employ 100% HF exchange display negative HOMO energies for all the tested species.

The dependence on the amount of HF exchange present in the XC functional clearly suggest that it is the incorrect distance dependence of the exchange functional[27] that is the reason for the fractional electron affinity phenomenon. In order to test this hypothesis, we have performed calculations with the long-range corrected version of the BLYP functional (LC-BLYP), where the amount of HF exchange increases continuously as a function of electron−electron separation distance,[28] and this indeed solves the problem. All the species with positive EAs are calculated to have negative HOMO energies for the corresponding anion with this functional, and no fractional electron transfer for the intermolecular complex or zwitterionic systems shown in Figure 2 is

observed. The LC-BLYP method correctly predicts a zero EA for the beryllium atom, predicts a small nonzero EA for the nitrogen atom (6 kJ/mol), and significantly overestimates that EA for NO by 91 kJ/mol but at least provides a qualitative correct description as having either zero or one electron bound.

IV. Summary

It is shown that the most commonly used DFT methods describe anions as having only a fraction of the extra electron bound, where the amount of bound electron density depends on the magnitude of the EA and the XC functional. Pure functionals without HF exchange display the largest effect, while hybrid methods with increasingly larger amounts of HF exchange behave intermediate between the pure functional and the pure HF methods. For species with large EAs, the fraction of electron bound is close to or equal to one, even for pure functionals like BLYP, and DFT methods provide estimates of the experimental EA within the expected DFT accuracy. For species with small EAs, however, most commonly employed functionals predict a significant overbinding when very large basis sets are used. When using standard basis sets, the unbound density is constrained to remain close to the nucleus, and the resulting Coulomb repulsion compensates partly for the inherent overbinding, which explains the observed reasonable correlation between DFT calculated and experimental EAs.

For inter- and intramolecular systems having both anionic and cationic sites, the phenomenon of fractional electron affinity results in fractional electron transfer SCF solutions even for regular basis sets. At large separation these solutions have a much lower energy than the ionic separation, and only the fractional electron transfer solution is present at short separation distances. This phenomenon is likely to be present in any system containing sufficiently electron-rich donors and electron-poor acceptors, at least for pure XC functionals. Clearly the existence of such fractional electron transfer descriptions will have consequences for the use of DFT methods to model ionic and polar systems.

Establishing the amount of unbound density for an isolated anion is technically somewhat difficult, as few programs are set up to handle very diffuse basis functions. Fortunately, the presence of a positive HOMO energy with a medium sized basis set is a clear indicator of this situation[29,30] and can be used as a diagnostics for whether a given XC functional can describe a given anion. Similarly, if a virtual orbital is lower in energy than the HOMO energy, this indicates that a lower energy SCF solution exists, and if the two orbitals are spatially well separated, this will be of the fractionally electron transfer type.

The origin of the phenomenon of fractional electron affinity is the incorrect long-range behavior of the exchange functional, and a possible solution is to apply the long-range correction method to the exchange functional. Using such long-range corrected functionals is strongly recommended when using density functional methods to describe the electronic structure of systems with localized anionic or strongly electron donating sites.

After submission of the present paper, Lee et al. published a paper with a detailed analysis of the XC potential for the lithium anion and arrived at conclusions in agreement with those in the present paper.[30]

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