A Systematic Failing of Current Density Functionals: Overestimation of Two-Center Three-Electron Bonding Energies

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Several density functional theories, chosen among the most popular, are shown to systematically overestimate three-electron bond dissociation energies in a series of model systems covering the full range of homonuclear three-electron $X\therefore X$ bonds (X = He, N, O, F, Ne, P, S, Cl, Ar) that can be found in organic cation radicals. The errors range from 15 to 54 kcal/mol with the SVWN local spin density method, from 6 to 45 kcal/mol with the gradient-corrected BLYP, BP86, and BPW91 functionals, and from 3 to 31 kcal/mol with the B3LYP, B3P86, and B3PW91 three-parameter hybrid functionals. The errors follow some regular tendencies according to the place of the X atom in the periodic table. The geometries and frequencies are also in error, the bond lengths being systematically too long and the frequencies too low. The errors are tentatively interpreted as consequences of electron self-interaction, leading to overstabilization of the Coulombic terms relative to the exchange-correlation terms in this type of bonds. At variance with these systematic errors, the BH&HLYP functional displays overall better results but still severely fails in some particular cases. Some lines of thought for devising modified DFT functionals are proposed.

1. Introduction

Density functional theory (DFT) is an increasingly popular technique which has proved successful, especially in its most recent options, in a wide variety of applications, including molecular heats of formation,[1] gas-phase acidities,[2] and structures and properties of various systems ranging from small closed-shell molecules[3] to transition metal complexes, bulk solids, surfaces, and interfaces.[4] Strongly bonded systems as well as weakly bonded ones, like hydrogen-bonded systems[5] or charge-transfer complexes,[6] are also described with reasonable accuracy. As the method is particularly cost-effective, it is now widely used as a standard alternative to conventional post-Hartree−Fock methods.

The exchange correlation density functional models that are most currently used may be broadly divided into three categories (see, e.g., ref 7). The simplest, and historically the oldest among modern DFT methods, is the *local spin density* functional (LSD), which is faithful to the uniform electron gas model. As the latter functional was rapidly seen to overestimate binding energies, the *gradient-corrected* or *nonlocal* functionals were later introduced, with the aim of correcting the LSD deficiencies by better describing regions in which the density changes rapidly. Lastly, it was suggested that adding some exact Hartree−Fock exchange to the DFT exchange-correlation functional would further improve results, leading to the hybrid functionals, among which is the popular B3LYP, a three-parameter hybrid functional which was fitted so as to best reproduce G2 results.

It is generally recognized that hybrid methods perform the best to reproduce experimental enthalpies of formation, as recently shown in a computational test involving 148 molecules of various categories, for which the B3LYP method has an average deviation of only 3 kcal/mol.[1] However, despite many systematic studies aimed at assessing its reliability, DFT still lacks the long history of calibration which exists for more conventional methods, and there remains some domains of application for which the accuracy of the DFT approximations has not been established. It is therefore important to extend the systematic evaluation to domains that have been unexplored so far, for the DFT method to be established as a widely applicable tool of chemical investigation. In that spirit, the present study is aimed at evaluating the abilities of DFT to deal with two-center three-electron (2c,3e) bonding.

Organic cation radicals form a fundamental class of systems that pose a challenge to computational chemistry. They may exhibit different isomeric forms, some displaying (2c,3e) bonds and some being stabilized by, e.g., hydrogen bonds.[8,9] While the latter type of interaction is rather well described at any theoretical level, the former, on the contrary, requires dynamic electron correlation to be properly taken into account. It is therefore of crucial importance for the theoretical study of such systems to dispose of a computational method that describes both types of interaction equally well. While the DFT method is indeed able to deal with hydrogen-bonded systems,[5] there are some indications that it might be much less successful for (2e,3c) bonds. In a theoretical study of the $HOOH^-$ radical anion, the three-electron-bonded form $(HO\therefore OH)^-$ was found, at various DFT levels, to be nearly as stable as the hydrogen-bonded $(O^-{\cdots}HOH)$ form, or even to be the absolute minimum,[10] while accurate studies[11] show on the contrary that the former isomer should lie some 10 kcal/mol above the second. More

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recently, the dissociation energy of the F_2^- anion was found to be 11 kcal/mol too large at the B3LYP level.[12] Turning to radical cations, the three-electron-bonded form $H_2O\therefore OH_2^+$ was found to be lower than the $(OH)(H_3O^+)$ form on the $(H_2O)_2^+$ potential surface in a DFT study[13] using both LSD and gradient-corrected functionals, in sharp contrast to the common belief based on experimental and accurate theoretical studies.[9] Lastly, a very recent DFT calculation of the He_2^+ radical yielded some dissociation energies some 12−27 kcal/mol too large.[14] At variance with these questionable results or established failings, a surprisingly good bonding energy was found for the Ar_2^+ radical cation[15] at the "BH&HLYP" level, though this latter functional is less generally used than B3LYP or other three-parameter hybrid functionals. All these contrasting results prompted us to evaluate the abilities of nine DFT functionals, chosen among the most popular, to reproduce three-electron-bonding energies in a systematic series of symmetric cation radicals.

2. Theoretical Methods

The various exchange correlation density functionals are designated according to their keywords in the GAUSSIAN 94 series of programs,[16] which has been used throughout this work. The local spin density approximation includes the Slater functional and the correlation functionals of Vosko, Wilk, and Nusair[17] and has been used in two versions, VWN and VWN5. The three *gradient-corrected* or *nonlocal* functionals that are investigated in this study use Becke's 1988 exchange functional,[18] associated with various correlation functionals: that of Lee, Yang, and Parr[19] in BLYP, Perdew's functional[20] in BP86, and the Perdew−Wang 1991 functional[21] in BPW91. Lastly, B3LYP, B3P86, and B3PW91 are three-parameter hybrid functionals which incorporate a mixture of the latter gradient-corrected correlation functionals with Becke exchange and exact Hartree−Fock exchange.[22]

The "BH&HLYP" functional includes 50% Hartree−Fock exchange, 50% Slater exchange, and the additional correlation effects of the LYP functional.[23] Although less popular than the three-parameter hybrids, it has been included in this study for completeness, and because it has been reported to perform well in the particular case of Ar_2^+.

As we are interested in three-electron-bonding energies rather than absolute minima on the potential surfaces, the present study is limited to three-electron-bonded conformations, i.e., those displaying left-right symmetry, even in cases where some conformations of different types (e.g., hydrogen-bonded) happen to lie lower on the potential surface. The symmetry of the wave functions was imposed in all cases, to avoid possible symmetry-breaking artifacts. It should be noted that some species may also display two three-electron-bonded minima of different symmetries (e.g. D_{3h} or D_{3d} for $H_3N\therefore NH_3^+$); in such case, the conformation that was found lowest in the early theoretical study of Gill and Radom[9] was adopted.

All geometries were optimized by using a gradient technique. For the DFT calculations, the geometry optimizations were performed with the standard 6-31G** basis. The use of this relatively small basis set is justified by the number of geometry optimizations that had to be performed, and by the fact that DFT methods are known to be little basis set dependent, a property that will be further tested in this study. Using these geometries for the three-electron-bonded species and the separate fragments, the DFT bonding energies were calculated in three different basis sets: the standard 6-31G**, 6-311G**, and 6-311G(2d1f). This latter basis set is of valence triple-ζ quality and displays two sets of polarization functions (one of them being split) on the heavy atoms, but not on the light atoms (H, He). Accordingly, it was replaced by the 6-311G(2d1f,2p1d) basis set for He_2^+, for the sake of describing this latter species with the same accuracy as the others.

As there are very few experimental references for the geometries and bonding energies of radical cations (except for the rare gas cation dimers), some reference values were computed at the MP4 level in 6-311G(2d1f,2p1d) basis set, using geometries optimized at the MP2 level in 6-311G** basis set. It is indeed known[9,24] that the Møller−Plesset perturbation theory converges well for three-electron-bonded species and gives bonding energies in good agreement with higher levels, because the differential electron correlation associated to dissociation is entirely dynamical in nature, and made of a large number of small terms. To further ascertain this hypothesis, the bonding energies of the rare gas cation dimers were recalculated at the very accurate CCSD(T) level of theory.

The vibrational frequencies were calculated for the rare gas at the MP2 level and at the various DFT levels, using the same basis sets as for the geometry optimizations, i.e., 6-31G** for the DFT calculations, and 6-311G** for the MP2 calculations.

All calculations, of DFT or Møller−Plesset types, were performed within the spin-unrestricted formalism.

3. Results

A three-electron-bonded system is one in which a bonding σ molecular orbital between two atoms in a molecule is doubly occupied while the complementary σ^* antibonding orbital is singly occupied. For this to be possible, the fragments that are linked together in such a bond—one cation and one neutral molecule—must each bear a lone pair, which is singly occupied in the cation and doubly occupied in the neutral fragment. All molecules of the generic type XR_n ($X = Ne, F, O, N$; $n = 0-3$) and their second-row analogues are therefore candidates for forming three-electron bonds with cations taken from the same set, the strongest bonds being generally those that associate two identical fragments.[8] To modelize this infinite series of three-electron-bonded organic radicals, we have limited ourselves to homonuclear bonds and to fragments bearing hydrogen atoms as substituents (R=H). Accordingly, the systematic $H_nX\therefore XH_n^+$ series ($X = Ne, F, O, N, Ar, Cl, S, P$; $n = 0-3$) will be investigated, in addition to the helium dimer cation $He\therefore He^+$. The DFT functionals will be tested on these typical three-electron-bonded species as regards the three classical spectroscopic parameters: the dissociation energy, the equilibrium bond length and the vibrational frequency of the three-electron bond.

Geometries. The results of the geometry optimizations, using the various DFT functionals in 6-31G** basis set, are shown in Table 1, along with the reference geometries arising from MP2 optimizations in large basis set (see Theoretical Methods section). For the sake of compactness, only the X−X bond length, which is the geometrical parameter of interest to characterize the three-electron bond, is indicated in the table. The results of MP2 optimizations[9] in the 6-31G* basis set are also recalled in the table, showing some significant basis set dependence, however much smaller than the errors found at the DFT level, as will be seen below. On the other hand, the basis set dependence of DFT-optimized geometries was tested by comparing optimizations made in 6-31G** and 6-311G(2d1f) basis set in the $(H_2O)_2^+$ case. The basis set dependence was found to be very small for all functionals, with deviations being always inferior to 0.01 Å for bond lengths and 1° for angles, from one basis set to the other.

TABLE 1: X−X Bond Lengths (Å) of $H_nX\therefore XH_n^+$ Three-Electron-Bonded Radicals, Arising from Full Geometry Optimization by Means of Various Types of DFT Functionals or MP2 Calculations

method	He_2^+	Ne_2^+	$(FH)_2^+$	$(OH_2)_2^+$	$(NH_3)_2^+$	Ar_2^+	$(ClH)_2^+$	$(SH_2)_2^+$	$(PH_3)_2^+$
LSD[a]									
SVWN	1.151	1.790	1.913	2.066	2.192	2.567	2.655	2.826	2.569
SVWN5	1.161	1.802	1.917	2.070	2.198	2.573	2.663	2.835	2.583
gradient-corrected[a]									
BLYP	1.184	1.874	2.016	2.173	2.303	2.675	2.822	3.020	2.884
BP86	1.176	1.870	2.004	2.151	2.273	2.653	2.771	2.951	2.731
BPW91	1.178	1.906	2.020	2.163	2.281	2.716	2.783	2.956	2.733
hybrid[a]									
B3LYP	1.147	1.808	1.939	2.103	2.242	2.622	2.740	2.932	2.790
B3P86	1.137	1.808	1.926	2.084	2.217	2.600	2.697	2.875	2.684
B3PW91	1.141	1.820	1.939	2.096	2.228	2.619	2.712	2.889	2.569
BH&HLYP	1.108	1.743	1.867	2.035	2.188	2.548	2.669	2.860	2.734
MP2 (6-31G*)[b]	1.082	1.717	1.843	2.023	2.151	2.519	2.642	2.835	2.700
MP2 (6-311G**)	1.086	1.760	1.881	2.037	2.161	2.484	2.655	2.817	2.695
experiment[c] or accurate theory[d]	1.081[c]	1.75[c]				2.42[d]			

[a] Optimization in 6-31G** basis set. [b] 6-31G** for He_2^+. [c] Reference 25. [d] Reference 26.

TABLE 2: Dissociation Energies (kcal/mol) of Some Representative Three-Electron Bonded Radicals As Calculated by Means of Standard ab Initio Methods

method[a]	He_2^+	Ne_2^+	$(FH)_2^+$	$(OH_2)_2^+$	$(NH_3)_2^+$	Ar_2^+	$(ClH)_2^+$	$(SH_2)_2^+$	$(PH_3)_2^+$
UHF[b]	45.3	4.3	10.9	20.2	21.3	14.3	17.9	19.4	20.8
MP2[c]	52.4	34.5	39.0	44.2	38.3	29.5	32.2	31.8	29.4
MP4[c]	55.3	33.1	37.4	43.1	37.9	28.7	31.3	31.3	29.4
CCSD(T)[c]	56.0	32.7				28.8			
experiment[d]	56.9[e]	31.4[f]				29.3[f]			

[a] All dissociation energies are calculated in 6-311G(2d1f,2p1d). The geometries are optimized in 6-311G** basis set. [b] Geometries optimized at the UHF level. [c] Geometries optimized at the MP2 level. [d] Derived from D_0 values + ZPE. [e] Reference 25. [f] Reference 28.

It is seen that the performances of the various functionals are very different and depend on which categories they belong to. The gradient-corrected methods (BLYP, BP86, and BPW91) all yield much too long a bonding distance for all compounds, with errors ranging from 0.10 to 0.20 Å, relative to the MP2 level. The three-parameter hybrid methods (B3LYP, B3P86, and B3PW91) perform a little better, but still overestimate the bond lengths by quantities as large as 0.05−0.13 Å. Perhaps surprisingly, the old LSD methods which are generally considered as less accurate than the two first categories, provide better bond lengths, with the exception of Ar_2^+ which is found 0.09 Å too long. Finally, the simple BH&HLYP hybrid method yield results which are consistently much better than the other functionals.

In general, all the functionals belonging to a given category behave the same way, yielding errors of comparable magnitudes, as logically expected. As an exception, some very variable errors are found with the $H_3P\therefore PH_3^+$ cation radical, whose very erroneous bond lengths do not seem to follow any simple logic. Apart from this particular case, the results of the geometry optimizations can be summarized as follows: all DFT methods overestimate the bond lengths of three-electron-bonded compounds. The worse methods in that respect are the gradient-corrected functionals, followed by the three-parameter hybrid functionals. The LSD methods are in general better, with some exceptions, and the BH&HLYP hybrid functional is close to correct.

Dissociation Energies. The three-electron bond dissociation energies D_e were calculated by means of eq 1.

$$D_e(H_nX\therefore XH_n^+) = E(H_nX) + E(XH_n^+) - E(H_nX\therefore XH_n^+) \quad (1)$$

No attempt was made to generate dissociation energy profiles, as DFT methods are already known to be unable to yield meaningful energies for the dimer cations at large interatomic distances.[14,27]

The dissociation energies, calculated with the various theoretical methods after geometry optimizations of both the neutral and cationic fragments and their dimers, are reported in Tables 2−5. Table 2 reports the results of UHF and Møller−Plesset calculations in 6-311G(2d1f,2p1d) basis set, which can be compared to bonding energies calculated at the accurate CCSD(T) level in the same basis set and to experimental bonding energies for rare gas. It first appears that the UHF bonding energies are all exceedingly low, showing the absolute necessity of taking electron correlation into account to describe three-electron bonding, as has been discussed in a previous paper.[24] On the other hand, the MP2 and MP4 results are remarkably close to each other, showing a good convergence in the Møller−Plesset series, and are in good agreement with CCSD(T) and experimental bonding energies when available. This indicates that our MP4 bonding energies can be taken as reference bonding energies with confidence, even though the geometries have been optimized in a smaller basis set.

The bonding energies and their errors (italicized in the tables) relative to the MP4 values are shown in Table 3 for the functionals of LSD type (SVWN and SVWN5), using different basis sets of increasing quality. It is first seen that the three basis sets that have been used, ranging from 6-31G** to 6-311G(2d1f), yield rather similar results, showing little basis set dependence, except for the particular case of Ne_2^+ and, to a lesser extent, Ar_2^+. This nice feature, which is customary with DFT methods, is, however, made worthless by the unusually large errors that are found on the calculated bonding energies (even knowing that LSD functionals are prone to overestimate these quantities), the latter being sometimes 2−3 times too large! Interestingly, the errors follow some regular tendencies, gradually increasing as the X atoms that are three-electron-bonded are taken from left to right of the periodic table (N∴N to Ne∴Ne or P∴P to Ar∴Ar), or from second row to first row.

The performances of the gradient-corrected functionals (BLYP, BP86, and BPW91) are displayed in Table 4. Once

TABLE 3: Dissociation Energies (kcal/mol) As Calculated by Means of LSD Functionals

method	He_2^+	Ne_2^+	$(FH)_2^+$	$(OH_2)_2^+$	$(NH_3)_2^+$	Ar_2^+	$(ClH)_2^+$	$(SH_2)_2^+$	$(PH_3)_2^+$
SVWN									
6-31G**	84.8	94.1	81.6	75.8	63.5	57.4	55.3	51.8	46.1
6-311G**	84.6	88.9	77.7	74.3	62.1	55.8	52.5	49.3	43.6
6-311G(2d,1f)[a]	85.0	87.2	78.3	74.8	61.4	60.5	55.2	50.9	45.1
error[b]	*29.7*	*54.2*	*40.9*	*31.7*	*23.5*	*31.8*	*23.9*	*19.6*	*15.7*
SVWN5									
6-31G**	86.1	93.3	81.1	75.1	62.9	56.8	54.7	51.2	45.4
6-311G**	85.8	86.0	77.2	73.7	61.4	55.6	51.9	48.6	42.8
6-311G(2d1f)[a]	86.2	86.9	77.7	74.2	60.7	60.7	54.5	50.2	44.2
error[b]	*30.9*	*53.8*	*40.3*	*31.1*	*22.9*	*32.0*	*23.2*	*18.8*	*14.8*

[a] 6-311G(2d1f,2p1d) for He_2^+. [b] The error is the difference between the DFT and MP4 values (see Table 1) in the biggest basis set.

TABLE 4: Dissociation Energies (kcal/mol) As Calculated by Means of Gradient-Corrected Functionals

method	He_2^+	Ne_2^+	$(FH)_2^+$	$(OH_2)_2^+$	$(NH_3)_2^+$	Ar_2^+	$(ClH)_2^+$	$(SH_2)_2^+$	$(PH_3)_2^+$
BLYP									
6-31G**	84.1	84.1	71.5	65.2	52.4	49.1	47.0	43.0	35.3
6-311G**	83.1	77.8	68.7	63.9	51.3	47.1	44.3	40.6	33.1
6-311G(2d1f)[a]	83.5	78.5	68.7	63.8	50.4	48.7	45.5	41.4	33.5
error[b]	*28.2*	*45.5*	*31.4*	*20.7*	*12.5*	*19.9*	*14.2*	*10.1*	*4.2*
BP86									
6-31G**	82.3	81.6	70.8	64.7	52.5	48.3	47.0	43.5	36.6
6-311G**	82.1	75.9	67.3	63.3	51.2	46.8	44.5	41.5	34.7
6-311G(2d1f)[a]	82.5	76.4	67.5	63.5	50.4	48.7	46.1	42.5	35.6
error[b]	*27.2*	*43.3*	*30.1*	*20.3*	*12.5*	*20.0*	*14.8*	*11.2*	*6.2*
BPW91									
6-31G**	78.2	80.8	69.4	63.2	51.2	47.0	45.7	42.4	35.6
6-311G**	78.1	75.5	66.0	61.9	49.8	46.2	43.4	40.6	34.0
6-311G(2d1f)[a]	78.4	75.6	66.1	61.9	49.0	47.9	44.9	41.5	34.8
error[b]	*23.1*	*42.5*	*28.7*	*18.8*	*11.2*	*19.1*	*13.6*	*10.2*	*5.5*

[a] 6-311G(2d1f,2p1d) for He_2^+. [b] The error is the difference between the DFT and MP4 values (see Table 1) in the biggest basis set.

TABLE 5: Dissociation Energies (kcal/mol) As Calculated by Means of Hybrid Functionals

method	He_2^+	Ne_2^+	$(FH)_2^+$	$(OH_2)_2^+$	$(NH_3)_2^+$	Ar_2^+	$(ClH)_2^+$	$(SH_2)_2^+$	$(PH_3)_2^+$
B3LYP									
6-31G**	77.4	69.0	60.7	57.4	48.1	42.2	42.0	39.4	33.8
6-311G**	77.1	63.4	57.3	56.1	46.8	40.7	39.5	37.3	31.9
6-311G(2d1f)[a]	77.5	64.0	57.5	56.2	46.0	42.8	41.3	38.3	32.7
error[b]	*22.2*	*30.9*	*20.1*	*13.1*	*8.2*	*14.0*	*9.9*	*7.0*	*3.4*
B3P86									
6-31G**	76.0	67.5	59.8	57.3	48.6	41.6	43.3	40.2	35.4
6-311G**	76.3	61.9	56.4	56.0	47.1	41.0	40.1	38.4	33.8
6-311G(2d1f)[a]	76.7	62.4	56.7	56.3	46.5	43.5	42.2	39.7	35.1
error[b]	*21.4*	*29.3*	*19.3*	*13.2*	*8.6*	*14.7*	*10.9*	*8.4*	*5.7*
B3PW91									
6-31G**	72.9	64.3	58.4	55.8	47.1	40.4	41.0	39.0	34.1
6-311G**	73.1	60.7	55.0	54.4	45.6	39.8	38.8	37.3	32.7
6-311G(2d1f)[a]	73.5	61.1	55.2	54.7	44.9	42.1	40.9	38.5	33.9
error[b]	*18.2*	*28.0*	*17.8*	*11.6*	*7.1*	*13.4*	*9.5*	*7.2*	*4.5*
BH&HLYP									
6-31G**	68.5	47.8	44.5	46.1	41.2	32.1	34.5	33.9	30.9
6-311G**	68.6	41.9	41.3	44.9	39.8	31.4	32.2	31.9	29.3
6-311G(2d1f)[a]	69.4	42.8	41.7	45.2	39.3	33.9	34.6	33.3	30.8
error[b]	*14.1*	*9.7*	*4.3*	*2.1*	*1.4*	*5.2*	*3.3*	*2.0*	*1.4*

[a] 6-311G(2d1f,2p1d) for He_2^+. [b] The error is the difference between the DFT and MP4 values (see Table 1) in the biggest basis set.

again the calculated bonding energies show little basis set dependence, with the exception of Ne_2^+, and the three functionals yield remarkably similar results. The calculated bonding energies are consistently better than those calculated with the LSD functional, but remain exceedingly overestimated in general, with an error as large as 35 kcal/mol for Ne_2^+. As in the preceding case, the errors follow some regular tendencies according to the rank of the X atom in the periodic table.

The results of the three-parameter hybrid functionals (B3LYP, B3P86, and B3PW91), displayed in Table 5, are comparable to those of the gradient-corrected functional, albeit slightly better, with a maximum error of about 30 kcal/mol for Ne_2^+. The smallest error, about 3 kcal/mol, is found with the B3LYP functional for the $H_3P \therefore PH_3^+$ radical.

The results for the three above categories of functionals can be summarized as follows: (i) all functionals display little basis set dependence; (ii) all bonding energies are systematically overestimated; (iii) the three-parameter hybrid functionals are better than the gradient-corrected ones, themselves better than LSD functionals; (iv) in all categories, the errors gradually increase as the X atom is taken from left to right or from bottom to top of the periodic table. In accord, the smallest errors are always found for $H_3P \therefore PH_3^+$, leading to nearly acceptable values in some cases, while the largest errors are found for Ne_2^+,

TABLE 6: Vibrational Frequencies (cm^{-1}) of Rare Gas Dimer Cations Radicals

method[a]	He_2^+	Ne_2^+	Ar_2^+
LSD			
SVWN	1305	444	213
SVWN5	1299	442	211
gradient-corrected			
BLYP	1198	346	157
BP86	1219	344	165
BPW91	1206	321	153
hybrid			
B3LYP	1367	441	197
B3P86	1393	445	206
B3PW91	1377	431	197
BH&HLYP	1561	552	240
MP2	1724	565	266
experiment[b] or accurate theory[c,d]	1698.5[b]	598.5[c]	304[d]

[a] The basis sets are the same as those used in the geometry optimizations displayed in Table 1: 6-31G** for the DFT calculations, 6-311G** for MP2 calculations. [b] Reference 25. [c] Reference 29. [d] Reference 26.

leading to exceedingly overestimated bonding energies with all functionals. It is to be noted that exactly the same tendency across the periodic table is observed for the magnitude of the Hartree−Fock error (difference between UHF and MP4 results in Table 2), with the difference that the Hartree−Fock level underestimates the bonding energy while the DFT level overestimates it.

Quite atypical is the behavior of the last functional that we have examined, BH&HLYP, whose bonding energies are displayed in Table 5. While this functional displays some very satisfying bonding energies, irrespective of the basis set that is used, in the series $(FH)_2^+$ to $(PH_3)_2^+$, it fails with the Ne_2^+ and He_2^+ rare gas dimers, overestimating the bonding energies by 10 and 14 kcal/mol, respectively. Still, while such errors are clearly unacceptable by modern standards, it remains that the BH&HLYP functional is the best—albeit not the most popular—among the nine functionals that have been examined here, for the purpose of estimating three-electron-bonding energies.

Frequencies. Another useful index to evaluate the adequacy of a method to describe a chemical bond is the vibrational frequency corresponding to the dissociating mode. Experimental or accurate values for this spectroscopic parameter, which characterizes the local shape of the dissociation curve in the vicinity of the equilibrium geometry, is available for rare gas. We have therefore calculated the vibrational frequencies for He_2^+, Ne_2^+, and Ar_2^+, using the nine DFT functionals above as well as MP2 perturbation theory, with the same basis sets as those used for the geometry optimizations.

The results, displayed in Table 6, show a good agreement between MP2-calculated frequencies and accurate values for He_2^+ and Ne_2^+. On the other hand, the MP2 value is found 12.5% too low for Ar_2^+, most likely for lack of high-rank polarization functions in the basis set. As for the DFT results, *all* DFT functionals undestimate the frequencies with respect to accurate values and to MP2 values.

As was found for the dissociation energies, the various functionals of a given category display very similar performances. The worst errors are found within the gradient-corrected functionals, followed by the LSD and three-parameter hybrid functionals which perform a little better but still underestimate the frequencies to a large extent, indicating a dissociation curve that is much too flat in the bonding region. At variance with these poor results, the BH&HLYP functional provides acceptable frequencies for all rare gas, not far from MP2 values, but still 7−10% lower.

4. Discussion

Apart from the BH&HLYP functional that exhibits somewhat erratic performances and will be discussed separately, the three categories of functionals that have been evaluated here all exhibit the same systematic errors for three-electron-bonded systems: (i) the bonding energies are overestimated; (ii) in apparent contradiction with the former error, the bond lengths are found too long and the vibrational frequencies too low, two features that are normally associated with bond weakening rather than strengthening.

A possible explanation for the unusually large errors that have been found in the above three-electron bond dissociation energies might be related to the known incorrect behavior of ionized dimers at large interatomic distances.[27] Instead of the expected localization of the electronic charge on one of the fragments, the charge is erroneously found to be equally shared between both fragments with most current DFT functionals, leading to an artifactual stabilization that shows up as the calculated energy of the supersystem (with an interatomic distance of, e.g., 20 Å) is found 1−4 eV lower than the summed energies of the separate fragments. Interestingly, the error rises with the compactness of the atoms along one row of the periodic table, precisely the tendency that has been found in the above calculations. Starting from this well-established fact, our hypothesis is that the error that is found at large interatomic distance persists, although to a lesser extent, at bonding distances. Such an artifact would overstabilize the bonded species relative to the separate fragments (as computed separately) and would explain the overestimation of bonding energies. It would also deform the dissociation curve by lowering the stretched conformations more than the tight ones, thus shifting the equilibrium geometries toward large distances and leading to lowered vibrational frequencies, thus explaining at once all the seemingly contradictory errors that are attached to the above series of DFT functionals.

If the latter interpretation is correct, then the problem would lie in an overstabilization of the Coulombic term relative to the exchange correlation term. As this error is expected to be significantly reduced in methods that are free from self-interaction, we made some exploratory calculations for the noble gas dimer cations. We treated the exchange exactly (in the Hartree−Fock fashion) and the electron correlation via the Lee−Yang−Parr functional (which yields no correlation energy for one-electron sytems). The resulting dissociation energies, obtained in self-consistent calculations, are 58, 13, and 23 kcal/mol for He_2^+, Ne_2^+, and Ar_2^+, respectively. The absolute deviations from the MP4 results (3, 20, and 6 kcal/mol) are smaller than those obtained from the best three-parameter exchange functionals (18, 28, and 13 kcal/mol). Moreover, such errors are not atypical of methods using a density functional for correlation only:[30] we remind that the larger magnitude of the errors usually found with correlation-only functionals relative to exchange-correlation functionals is one of the reasons that makes the latter methods more popular. Besides, it appears that the errors in the dissociation energies of X_2^+ parallel the errors in the ionization potentials of X: very small (1−2 kcal/mol) for He and Ar, but larger for Ne (14 kcal/mol). Correcting for this effect, one would get similar deviations for the dissociation energies of all three rare gas dimer cations.

Another way to understand the DFT errors in three-electron-bonding energies is to view the exchange density functional as a way to provide nondynamical correlation energy. It is often claimed[31] that such functionals, by describing the exchange hole as more localized than at the Hartree−Fock level, are able to account for the left−right electron correlation that is necessary for a proper description of chemical bonds−i.e., two electron bonds most of the time. Now an important difference between two-electron and three-electron bonds should be noted: while the one-determinant description of the former is indeed qualitatively incorrect and needs be corrected by proper account of left−right correlation, three-electron bonds are on the contrary qualitatively well described at the one-determinant level[24] and only necessitate dynamical correlation energy and orbital relaxation. As a consequence, the exchange density functional might well introduce an artifactual stabilizing term, in three-electron-bonded systems, that corresponds to some spurious left-right correlation effect that has no actual physical counterpart.

Lastly, the particular behavior of the BH&HLYP functional that displays some excellent results for some of the three-electron-bonded radicals (apart from the He_2^+ and Ne_2^+ cases) can be understood as a cancellation of systematic errors. Remembering that the Hartree−Fock method systematically underestimates three-electron-bonding energies (see Table 2) and that nonhybrid DFT methods overestimate them by the same amount or more, it is logical that one hybrid functional such as BH&HLYP which contains 50% Hartree−Fock exchange perform better than the three-parameter hybrid functionals which contain much less. It is unfortunate that this fortuitous cancellation of errors is not general and leaves som unacceptable errors in some cases.

5. Conclusion

We have identified a serious weakness of the most popular DFT methods that reveal themselves inapplicable to the description of three-electron-bonding situations. The error consists of a systematic overestimation of the dissociation energies, sometimes by a factor of 2 or 3, accompanied with erroneous geometries and frequencies. As a rule, the length of the three-electron bond is found too long, and the frequency is found too low. The errors are more or less severe, according to the categories that the functionals belong to. As regards dissociation energies, the three-parameter hybrid functionals (B3LYP, B3P86, and B3PW91) perform the best, followed by the gradient-corrected functionals (BLYP, BP86, and BPW91), and lastly by functionals of LSD types (SVWN and SVWN5). The errors follow some very regular tendencies according to the rank of the X atom in the periodic table, being minimal for the $P\therefore P$ bond and peaking to huge values for the $Ne\therefore Ne$ bond. On the other hand, LSD and three-parameter hybrid methods are grossly equivalent as far as frequencies and bond lengths are considered, while the gradient-corrected functionals remain worse in that respect.

The BH&HLYP functional, although not being the most popular functional, exhibits some excellent results for some of the three-electron-bonded species that have been considered in this study. Unfortunately, this good behavior is not general, and some species (He_2^+, Ne_2^+) are found to display unacceptable errors in their calculated bonding energies. It follows from the above study that the DFT methods prove quite inappropriate not only for the calculations of three-electron-bonding energies, but also for structural analyses or investigations of potential surfaces of radicals that may isomerize from three-electron-bonded forms to other bonding types.

The fact that the errors are systematic and follow some regular tendencies across the periodic table raises hopes that a general remedy may be found, probably along the general lines that have been suggested above. It is clear that more work needs be done to better understand the nature of the error before a remedy can be proposed. In that spirit, we intend to analyze more carefully the effect of using density functionals that are free from self-interaction, by using functionals of the types Hartree−Fock + correlation or Krieger−Lee−Iafrate + correlation.[32] We also intend to analyze a method which explicitly uses the short-range correlation, and treat the nondynamical part with a multideterminant wave function, such as that recently proposed (see, e.g., ref 33) by Flad and one of us (A.S.).

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