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The Failure of Generalized Gradient Approximations (GGAs) and Meta-GGAs for the Two-Center Three-Electron Bonds in He_2^+, $(H_2O)_2^+$, and $(NH_3)_2^+$

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The radical cations He_2^+, $(H_2O)_2^+$, and $(NH_3)_2^+$ with two-center three-electron A−A bonds are investigated at the configuration interaction (CI), accurate Kohn−Sham (KS), generalized gradient approximation (GGA), and meta-GGA levels. Assessment of seven different GGA and six meta-GGA methods shows that the A_2^+ systems remain a difficult case for density functional theory (DFT). All methods tested consistently overestimate the stability of A_2^+: the corresponding D_e errors decrease for more diffuse valence densities in the series $He_2^+ > (H_2O)_2^+ > (NH_3)_2^+$. Upon comparison to the energy terms of the accurate Kohn−Sham solutions, the approximate exchange functionals are found to be responsible for the errors of GGA-type methods, which characteristically overestimate the exchange in A_2^+. These so-called exchange functionals implicitly use localized holes. Such localized holes do occur if there is left−right correlation, i.e., the exchange functionals then also describe nondynamical correlation. However, in the hemibonded A_2^+ systems the typical molecular (left−right, nondynamical) correlation of the two-electron pair bond is absent. The nondynamical correlation built into the exchange functionals is then spurious and yields too low energies.

I. Introduction

The most comprehensive way to analyze the performance of the local-density (LDA) and generalized gradient approximations (GGA and meta-GGA) of density functional theory (DFT)[1] in molecular calculations is to compare the approximate exchange and correlation energies and energy densities with those calculated for the essentially accurate Kohn−Sham (KS) solution. The latter can be obtained from an accurate ab initio electron density $\rho(\mathbf{r})$. Benchmark KS solutions have been obtained previously for a number of atoms,[2−5] molecules,[6−11] prototype hydrogen abstraction and hydrogen exchange reactions,[12] and the bimolecular nucleophilic substitution (S_N2) reaction.[13] The comparison with the accurate KS quantities is of special importance in problematic cases, where standard DFT generalized gradient approximations (GGAs)[14−17] produce relatively large errors. Such cases have been reported and discussed in the literature,[12,18−28,29−31] and recently a qualitative rule has been put forward[13] to predict success or failure of GGAs.

A prototype difficult case are bifragmental radical cations A_2^+ with a two-center three-electron bond A−A, the stability of which is substantially overestimated by GGAs. This has been established in[18−20] by comparison of the GGA results with those of the ab initio Møller−Plesset perturbation (MP2 and MP4) and coupled-cluster CCSD(T) methods. Still, to our knowledge, no accurate KS solution has been reported for A_2^+. Furthermore, it is also desirable to assess the performance for A_2^+ of the recently developed meta-GGAs[32−35] in which, in addition to the density gradient $\nabla\rho(\mathbf{r})$, the KS kinetic energy density $\tau(\mathbf{r})$ and/or the density Laplacian $\nabla^2\rho(\mathbf{r})$ have been employed.

In this paper the Kohn−Sham solutions are constructed for the hemibonded systems He_2^+, $(H_2O)_2^+$, and $(NH_3)_2^+$ from ab initio densities obtained with configuration interaction (CI) calculations. In section II of this paper the results of CI calculations are discussed. The correlation contribution to the A−A hemibond is analyzed. It is stressed that the typical left−right (nondynamical, molecular) correlation of a bonding electron pair is absent in the hemibonded systems. This shows up in the structure of the CI wave functions. High quality of the CI solution has been achieved for the lightest system, He_2^+, while for the heavier $(H_2O)_2^+$ and $(NH_3)_2^+$ a size-consistency correction is required. In section III the KS solutions are constructed from the correlated CI densities and the components of the total energy E^{KS} of the KS determinant are compared with those of the total energy E^{HF} of the Hartree−Fock (HF) determinant. The total energies E^{KS} and E^{HF} appear to be close to each other for A_2^+, and therefore also the correlation energies with respect to HF, $E_c^{HF} = E - E^{HF}$, and with respect to the KS determinantal energy, $E_c^s = E - E^{KS}$. The KS quantities are denoted with sub- or superscript s, except for the expectation value of the KS determinantal wave function which is denoted E^{KS} to distinguish it from the energy of the KS system of noninteracting electrons, $E_s = \sum_i^N \epsilon_i^s$. The various components of the energy will be discussed in section III.

In section IV a comparative assessment of seven different GGA and six meta-GGA methods is made. GGA-type methods overestimate the stability of A_2^+. On average, GGAs and meta-GGAs show a similar quality of the results and even the best methods yield relatively large errors (in the range 25−40%) of the dissociation energy in the difficult case of A_2^+. Comparison to the accurate KS quantites shows that this is due to overestimation of the molecular exchange energy by the approximate exchange energy functionals. Following the analysis given in refs 12, 13, and 36, this is interpreted as inclusion of left−right correlation by the approximate exchange functionals, which is spurious in these systems where it is absent. In section V the conclusions are drawn.

II. CI Calculations of A_2^+

The ab initio ground-state calculations of the radical cations A_2^+ (A = He, H_2O, NH_3) and the corresponding fragments A

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and A^+ have been performed in this paper with the configuration interaction (CI) method with inclusion of all single and double excitations (CISD) of the reference Hartree−Fock (HF) configuration Ψ^{HF} by means of the ATMOL package.[37] The effect of size extensivity on the CI energy has been estimated with the correction of ref 38. The restricted HF and the subsequent CI calculations have been performed in the large correlation-consistent polarized valence quintuple-ζ (cc-pV5Z) basis for He[39] and in the smaller core-valence (cc-pCVTZ) basis sets for N and O,[40] while for H the triple-ζ (TZ) basis[41] augmented with polarization functions has been used. The experimental equilibrium bond distance R(He−He) = 1.081 Å[42] has been taken for He_2^+, and the hemibonded structures of $(H_2O)_2^+$ and $(NH_3)_2^+$ with the direct bonds O−O and N−N (with R(O−O) = 2.023 Å and R(N−N) = 2.151 Å) have been taken from ref 43, where they were optimized at the MP2 level.

The two-center three-electron bond $(A-A)^+$ is at the HF level represented by double occupancy of the $\psi_+ = (a + b)/\sqrt{(2 + 2S)}$ bonding orbital between the A lone-pair orbitals (1s for He, $2p_\pi$ for H_2O and sp^3 for NH_3), and single occupancy of the antibonding combination $\psi_- = (a-b)/\sqrt{(2 - 2S)}$. There is a remarkable difference between the simple MO wave function for an electron-pair bond $\Psi_{pairbond} = |\psi_+{}^2|$ and the hemibond wave function $\Psi_{hemibond} = |\psi_+{}^2\psi_-\alpha|$ as far as the electron correlation is concerned. The electron pair bond, in particular at long distance, suffers from the well-known unwarranted inclusion of ionic configurations, $\Psi_{pairbond} = (^1/_2)\{|a^2| + |b^2| + |ab| - |\bar{a}b|\} = (1/\sqrt{2})\ \{\Psi^{ionic} + \Psi^{HL}\}$. In particular at long distances the 50% inclusion of ionic configurations deteriorates the quality of the wave function since the covalent Heitler−London wave function then becomes the exact solution. Combining with the doubly excited configuration $\Psi_{exc} = |\psi_-{}^2| = (1/\sqrt{2})\ \{\Psi^{ionic} - \Psi^{HL}\}$ is able to remove the ionic contributions. In terms of exchange−correlation holes: if we consider a reference electron close to nucleus b, for example, the HF wave function has equal probability for the second electron to be at either nucleus, i.e., the hole is delocalized over both nuclei (cf. ref 20) (it represents only exchange, which is just self-interaction correction in this case). On the other hand, the full exchange−correlation hole of Ψ^{HL} is localized at the site where the reference electron is located.[44] GGA exchange approximations work implicitly with localized holes and therefore incorporate the left−right correlation in a KS calculation on an electron pair bond, actually to a surprisingly quantitative accuracy.[8,13,36] The HF wave function of the hemibonded systems does not suffer from the left−right correlation error. When expanding $\Psi_{hemibond} = |\psi_+{}^2\psi_-\alpha|$ for He_2^+ at long bond distance one obtains $\Psi_{hemibond} = (1/\sqrt{2})\{|a\alpha b^2| - |a^2 b\alpha|\}$. At a long distance, the exact wave function approaches $\Psi_{hemibond} = (1/\sqrt{2})\ \{\hat{N}\hat{A}\Psi(He_a{}^+)\Psi(He_b) - \hat{N}\hat{A}\Psi(He_a)\Psi(He_b{}^+)\}$, where $\hat{N}$ and $\hat{A}$ are the normalization and antisymmetrization operators, respectively. In fact, completely different from H_2, the He_2^+ system at equilibrium distance can be considered to be aproaching the long distance limit. For H_2 at the bonding distance of $R_e = 0.7$ Å the $\langle a|b\rangle$ overlap is 0.8, whereas for He_2^+ at the R_e of 1.1 Å the overlap is only 0.23[43] (the He 1s is much more contracted), which is only reached in H_2 at a distance of 1.95 Å. So the MO wave function for He_2^+ does not exhibit a left−right correlation error but it does have two obvious errors. First, lack of intra-atomic correlation on the nonionized He atom, i.e., the configurations a^2 and b^2 should be correlated He wave functions. Second, the symmetrical effective field in the one-electron equations has a charge $+^1/_2$ at each He fragment, which is different from the charges 0 and +1 in the correlated wave function. This a rather large difference, in particular in view of the low nuclear charge $Z = 2$, so in a term like $|a\alpha b^2|$ the a orbital is too diffuse, and the b orbital is too contracted. We thus expect the CI calculations to correct first of all for the He atom dynamical correlation, which is known to have in He little effect on the one-electron energy terms, but also for the wrong orbital expansion and contraction, which will also affect the one-electron energies. Similar considerations hold for the other hemibonded systems.

TABLE 1: CI Coefficients of the HF Configuration and the Leading Coefficients among the Singly and Doubly Excited Configurations in the CISD Wavefunctions of A_2. ψ_+ Is $1\sigma_g$, $4a_g$, $3a_{1g}$ in He_2^+, $(H_2O)_2^+$ and $(NH_3)_2^+$ Respectively, ψ_- Is $1\sigma_u$, $4b_u$, $3a_{2u}$

		single excitations		double excitations	
molecule	HF	coeff	excitation type	coeff	excitation type
He_2^+	0.991	0.058	$1\sigma_g \rightarrow 3\sigma_g$	0.034	$1\sigma_g{}^2 \rightarrow 1\sigma_u 2\sigma_u$
$(H_2O)_2^+$	0.953	0.036	$4a_g \rightarrow 9a_g$	0.034	$3a_g 4a_g \rightarrow 4b_u 7b_u$
$(NH_3)_2^+$	0.949	0.054	$3a_{1g} \rightarrow 7a_{1g}$	0.037	$1e_u 3a_{1g} \rightarrow 3a_{2u} 2e_g$

TABLE 2: Total Energies of He_2^+, He, and He^+ (hartree) and Dissociation Energies of He_2^+ (kcal/mol) Calculated with ab Initio Methods

method	He^+	He	He_2^+	D_e
HF	−1.9999	−2.8616	−4.9228	38.47
CI		−2.9032	−4.9934	56.66
CI(corrected)		−2.9032	−4.9939	56.98
MP4[a]				55.3
CCSD(T)[a]				56.0
exp[b]/exact[c]	−2.0000	−2.9037		56.9

[a] Reference 19. [b] Reference 42. [c] Reference 45.

We have carried out CISD calculations for all systems. These are capable of fully correlating the lone pairs in the $A-A^+$ systems, but except for He_2^+ there will be size-inconsistency effects in these CISD wave functions we will have to correct for. The CISD wave functions Ψ^{CI} show the same pattern of configuration interaction for all three systems and Table 1 presents the CI coefficient of the HF configuration $\Psi^{HF}[\psi_+{}^2\psi_-{}^1]$ and the largest contributions among all singly and doubly excited configurations. The HF configuration completely dominates Ψ^{CI}, indicating there is no strong nondynamical correlation, the next largest (though much smaller) contribution comes from the configuration with a single excitation from ψ_+ which, by virtue of Brillouin's theorem, does not interact directly with Ψ^{HF}. These single excitations cannot be $\psi_+ \rightarrow \psi_-$ for symmetry reasons, they are all excitations out of ψ_+ to higher lying orbitals of the same symmetry whose primary function is to correct the one-electron density. Among doubly excited configurations the largest contribution comes from the configuration, which includes single excitation $\psi_+ \rightarrow \psi_-$, while another electron is excited to some unoccupied orbital of the proper symmetry from ψ_+ (in the case of He_2^+) or from another doubly occupied orbital. The corresponding CI coefficients are small and the values around 0.035 are remarkably similar for all three systems (See Table 1). This can be contrasted with the simple pattern of nondynamical left−right correlation in an ordinary covalent bond with a strong interaction between Ψ^{HF} and the doubly excited configuration with two electrons excited from ψ_+ to ψ_-. Evidently, this latter pattern cannot be realized in our A_2^+ case, since ψ_- is (singly) occupied in $\Psi^{HF}(A_2^+)$, and it is not required since the left−right correlation error that such excitations correct for is absent.

The energetics of the bonding and the CI effects can be seen from Tables 2−4, which present the total energies E of the systems A_2^+, A, and A^+ and the dissociation energies D_e of

TABLE 3: Total Energies of $(H_2O)_2{}^+$, H_2O, and $(H_2O)^+$ (hartree) and Dissociation Energies of $(H_2O)_2{}^+$ (kcal/mol) Calculated with ab Initio Methods

method	$(H_2O)^+$	H_2O	$(H_2O)_2{}^+$	D_e
HF	−75.6499	−76.0540	−151.7248	13.13
CI	−75.9141	−76.3598	−152.3003	16.57
CI(corrected)	−75.9245	−76.3742	−152.3570	36.58
MP4[a]				43.1
CCSD(T)[b]				39.2

[a] Reference 19. [b] Reference 20.

TABLE 4: Total Energies of $(NH_3)_2{}^+$, NH_3, and $(NH_3)^+$ (hartree) and Dissociation Energies of $(NH_3)_2{}^+$ (kcal/mol) Calculated with ab Initio Methods

method	$(NH_3)^+$	NH_3	$(NH_3)_2{}^+$	D_e
HF	−55.8952	−56.2152	−112.1370	16.69
CI	−56.1370	−56.4952	−112.6560	14.93
CI(corrected)	−56.1476	−56.5103	−112.7116	33.70
MP4[a]				37.9

[a] Reference 19.

$A_2{}^+$ calculated with the HF and CI methods (in the last case the energies obtained with and without size-consistency correction[38] are presented). The D_e values are compared with those calculated with the MP4,[19] CCSD(T)[19,20] and with the experimental data.[42] Note that, due to the larger basis set used in this paper, the HF total energies in Tables 2−4 are consistently lower than the corresponding energies reported in ref 43, while our CI total energies are lower than the best MP2 energies obtained in.[43]

We would like to stress, in particular, the high quality of the CISD calculation for the lightest $He_2{}^+$ system (See Table 2). The CISD $D_e = 56.66$ kcal/mol of $He_2{}^+$ is closer to the experimental value $D_e^{exp} = 56.9$ kcal/mol (corrected for the zero-point vibrational energy[19]) than the MP4 $D_e = 55.3$ kcal/mol and even than the CCSD(T) $D_e = 56.0$ kcal/mol of ref 19, as a consequence of our larger basis set. The size-consistency correction for $He_2{}^+$ is small since, as pointed out above, there is only one electron pair that has to be correlated and we do not need quadruple excitations to correlate two electron pairs simultaneously. Still, the size-consistency correction works in the right direction and the resulting corrected value $D_e = 56.98$ kcal/mol nearly coincides with D_e^{exp}. We note that correlation effects add 18.2 kcal/mol (18.5 after size-consistency correction) to the calculated D_e, which is 38.5 kcal/mol at HF level. For the simple $He_2{}^+$ system the origin of the correlation contribution to D_e is easy to trace. Since He^+ is a one-electron system, the only correlation contribution for the individual fragments He and He^+ comes from dynamical correlation of the 1s electron pair of the He atom. The CISD correlation energy for the He atom $E_c^{HF}(He) = E^{CI}(He) - E^{HF}(He) = -0.0416$ hartree (See Table 2) is very close to the conventional empirical correlation energy $E_c^{HF(emp)}(He) = -0.0420$ hartree.[45] The total correlation energy of $He_2{}^+$ (−0.071 H) contains apart from this expected −0.042 hartree dynamical correlation of a single He, see above, an additional −0.029 hartree = −18.2 kcal/mol. This is much smaller than the ca. 58 kcal/mol correlation correction to the H_2 bond energy at $R = 1.95$ Å (corresponding to $\langle a|b\rangle = 0.23$) in agreement with the lack of nondynamical correlation in the $He_2{}^+$ bond. The 18.2 kcal/mol correlation contribution is to be attributed to both dynamical correlation corrections to the electron−electron repulsion energy and to orbital and density shape corrections affecting one-electron energy terms (kinetic energy, electron−nuclear energy), see below.

TABLE 5: KS Energy Contributions T^s, V^s, $W_H{}^s$, $W_x{}^s$, ((3.1)−(3.5)) and Their Differences from HF Energy Components $\Delta T^{S,HF}$, $\Delta V^{S,HF}$, $\Delta W_H^{S,HF}$, $\Delta W_x^{S,HF}$, DFT Correlation Energy E_c^s and Its Kinetic and Potential Parts T_c^s and W_c^s and the HF Counterparts E_c^{HF}, T_c^{HF}, W_c^{HF} (Hartrees) for $A_2{}^+$

	$He_2{}^+$	$(H_2O)_2{}^+$	$(NH_3)_2{}^+$
T^s	4.926	151.663	112.179
$\Delta T^{s,HF}$	0.021	0.214	0.247
T_c^s	0.060	0.461	0.330
T_c^{HF}	0.082	0.674	0.577
V^s	−13.901	−439.421	−349.923
$\Delta V^{s,HF}$	−0.021	−0.402	−0.397
$W_H{}^s$	3.657	111.115	94.835
$\Delta W_H^{s,HF}$	−0.001	0.107	0.164
W_c^s	−0.132	−1.045	−0.858
W_c^{HF}	−0.131	−0.970	−0.868
$W_x{}^s$	−1.561	−17.460	−15.020
$\Delta W_x^{s,HF}$	0.002	0.016	0.005
E_c^s	−0.072	−0.584	−0.527
E_c^{HF}	−0.0706	−0.575	−0.519
$\Delta E_c^{s,HF}$	−0.002	0.065	−0.019

As was shown above, the CISD wave functions of the heavier systems $(H_2O)_2{}^+$ and $(NH_3)_2{}^+$ exhibit the same configuration interaction pattern as the one for $He_2{}^+$. However, CISD substantially underestimates the stability of $(H_2O)_2{}^+$ and $(NH_3)_2{}^+$ as compared to CCSD(T) of ref 20, and MP4 of ref 19 (See Tables 3 and 4). This is clearly the effect of size inconsistency of the restricted CI[46] for these systems with many electron pairs. The relatively large size-consistency corrections for $(H_2O)_2{}^+$ and $(NH_3)_2{}^+$, compared to the size-consistency correction for $He_2{}^+$, bring the CISD dissociation energies of $(H_2O)_2{}^+$ and $(NH_3)_2{}^+$ much closer to the size-consistency corrections of CCSD(T) and MP4 (See Tables 3 and 4). In fact, the corrected CISD $D_e = 36.6$ kcal/mol for $(H_2O)_2{}^+$ is slightly closer to the CCSD(T) $D_e = 39.2$ kcal/mol[20] (which, we believe, is the most accurate calculated value) than the MP4 $D_e = 43.1$ kcal/mol.[19] Thus, we expect that also for $(NH_3)_2{}^+$ the true dissociation energy is between the corrected CISD $D_e = 33.7$ kcal/mol and the MP4 $D_e = 37.9$ kcal/mol.

III. Comparison of the KS and HF One-Electron Solutions for $A_2{}^+$

The correlated electron densities $\rho^{CI}(\mathbf{r})$ of the CISD wave functions of $He_2{}^+$, $(H_2O)_2{}^+$, and $(NH_3)_2{}^+$ have been used to generate the Kohn−Sham orbitals $\psi_i{}^s(\mathbf{r})$ and potential $v_s(\mathbf{r})$ for these systems. The KS solution has been obtained with the iterative procedure of ref 47, which is based on the theory of linear response of the KS orbitals to a potential change δv_s. The accuracy of this solution can be characterized by the absolute integral error $\Delta\rho = \int|\rho^s(\mathbf{r}) - \rho^{CI}(\mathbf{r})|\,d\mathbf{r}$ of the density $\rho^s(\mathbf{r})$ obtained from the generated KS orbitals $\psi_i{}^s(\mathbf{r})$. A rather accurate KS solution has been constructed for $He_2{}^+$ with $\Delta\rho$ of only 0.0003 *e*, while the KS solutions for $(H_2O)_2{}^+$ and $(NH_3)_2{}^+$ have larger errors of 0.007 and 0.0045 *e*. For the energy terms displayed in Table 5−7 the difference between $\rho^s = \sum_{i=1}{}^N|\psi_i{}^s|^2$ and ρ^{CI} is insignificant.

Using $\rho^s(\mathbf{r})$ and $\{\psi_i{}^s(\mathbf{r})\}$, the KS energy contributions have been calculated and, to assess the effect of electron correlation on the KS solution, they are compared in Table 5 with the HF ones. The total energies E^{KS} and E^{HF} of the KS and HF

TABLE 6: Comparison of the Total Energies of He_2^+, He, and He^+ (hartree) and Dissociation Energies of He_2^+ (kcal/mol) Calculated with the CI and Self-Consistent GGA Methods

method	He^+	He	He_2^+	D_e	error[b]
CI	−1.9999[a]	−2.9032	−4.9934	56.66	−0.30
BP	−1.9921	−2.9068	−5.0307	82.66	26.36
BLYP	−1.9897	−2.9069	−5.0322	85.09	28.19
PW	−1.9960	−2.9002	−5.0203	77.87	21.57

[a] The HF energy. [b] Error of D_e (kcal/mol compared to the experimental value of 56.9 kcal/mol.[42]

TABLE 7: Comparison of the KS and GGA Exchange and Correlation Contributions to the Dissociation Energy of He_2^+ (kcal/mol)[a]

	KS	BP	BLYP	PW
D_e^x	−55.47	−25.32(30.15)	−25.32(30.15)	−24.79(30.68)
D_e^c	19.11	13.55(−5.56)	12.65(−6.46)	8.25(−10.86)
D_e^{xc}	−36.36	−11.77(24.69)	−12.67(23.79)	−16.54(19.82)

[a] The GGA Contributions are calculated non-self-consistently, i.e., not with ρ^{GGA} but with the KS density ρ^s $(=\rho^{CI})$ in $E_{xc}{}^{GGA}[\rho]$ (the differences with respect to KS are indicated within parentheses).

determinants are expressed through the corresponding densities $\rho^{s/HF}(\mathbf{r})$, spin-densities $\rho_\sigma{}^{s/HF}(\mathbf{r})$, and orbitals $\{\psi_{i\sigma}{}^{s/HF}(\mathbf{r})\}$

$$E^{KS/HF} = T^{s/HF} + V^{s/HF} + W_H^{s/HF} + W_x^{s/HF} \tag{3.1}$$

We denote the one-electron energies by T (kinetic energy) and V (electron−nuclear energy), and the two-electron energy and its components by$W$ (see for notation and explanation ref 48). Explicitly, in (3.1) $T^{s/HF}$ is the kinetic energy

$$T^{s/HF} = \sum_\sigma \sum_{i=1}^{N_\sigma} \int d\mathbf{r}\, \psi_{i\sigma}^{s/HF*}(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_{i\sigma}^{s/HF*}(\mathbf{r}) \tag{3.2}$$

$V^{s/HF}$ is the electron−nuclear attraction energy

$$V^{s/HF} = -\sum_j \int d\mathbf{r}\, \frac{Z_j \rho^{s/HF}(\mathbf{r})}{|\boldsymbol{r} - \boldsymbol{R}_j|} \tag{3.3}$$

$W_H^{s/HF}$ is the Hartree energy of the electron−electron electrostatic repulsion

$$W_H^{s/HF} = \frac{1}{2} \int d\mathbf{r}_1\, d\mathbf{r}_2 \frac{\rho^{s/HF}(\mathbf{r}_1) \rho^{s/HF}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{3.4}$$

and $W_x^{s/HF}$ is the exchange energy

$$W_x^{s/HF} = \frac{1}{2} \sum_\sigma \int d\mathbf{r}_1\, d\mathbf{r}_2 \frac{\rho_\sigma^{s/HF}(\mathbf{r}_1) \rho_{x\sigma}^{s/HF}(\mathbf{r}_2|\mathbf{r}_1)}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{3.5}$$

expressed via the exchange (Fermi) hole function $\rho_{x\sigma}^{s/HF}(\mathbf{r}_2|\mathbf{r}_1)$, the latter being determined from$\rho_\sigma^{s/HF}(\mathbf{r})$ and $\{\psi_{i\sigma}^{s/HF}(\mathbf{r})\}$

$$\rho_{x\sigma}^{s/HF}(\mathbf{r}_2|\mathbf{r}_1) = -\frac{1}{\rho_\sigma^{s/HF}(\mathbf{r}_1)} \sum_{i=1}^{N_\sigma} \sum_{j=1}^{N_\sigma} \psi_{i\sigma}^{s/HF*}(\mathbf{r}_1) \psi_{j\sigma}^{s/HF}(\boldsymbol{r}_1) \psi_{j\sigma}^{s/HF*}(\mathbf{r}_2) \psi_{i\sigma}^{s/HF}(\mathbf{r}_2) \tag{3.6}$$

The correlation correction W_c to the electron−electron interaction energy is defined as the difference between the exact W, as approximated here by the CI calculation, and the hartree and exchange contributions,

$$W_c^{s/HF} = W - W_H^{s/HF} - W_X^{s/HF} \tag{3.7}$$

Just as the exchange energy can be obtained by integrating the density with the exchange hole potential, the correlation correction W_c can be by obtained by integrating the density against the Coulomb hole potential.[48] Note that the total correlation energy in the KS case has only components T_c^s and W_c^s, since the KS density is equal to the CI one, whereas the HF correlation energy also contains electron−nuclear and electron−electron Hartree energy corrections:

$$E_{cS} = T_c^s + W_c^s \tag{3.8}$$

$$E_c^{HF} = T_c^{HF} + V_c^{HF} + W_{H,c}^{HF} + W_c^{HF}$$

Both KS and HF solutions for the open-shell systems A_2^+ are of the restricted type, in the sense that the orbitals $\{\psi_{i\sigma}^{s/HF}(\mathbf{r})\}$ are the same for different spins σ. This will have only minor influence on the energy terms that are compared in Table 5, although of course unrestricted calculations make considerable difference for other properties like spin density at the nucleus. Table 5 presents the KS quantities T^s, V^s, W_H^s, W_x^s, the KS correlation energy $E_c{}^s$, and its kinetic and potential parts $T_c{}^s$ and $W_c{}^s$ as well as the differences $\Delta T^{s,HF}$, $\Delta V^{s,HF}$, $\Delta W_H^{s,HF}$, $\Delta W_x^{s,HF}$, between the KS and HF energies. It also contains the conventional correlation energy E_c^{HF} and its components T_c^{HF}, W_c^{HF}, $V_c^{HF} \equiv \Delta V^{s,HF}$ and $W_{H,c}^{HF} \equiv \Delta W_H^{s,HF}$. We refer to refs 8, 48, and 49 for explanation and other applications of this type of energy decomposition.

One can conclude from the He_2^+ column of Table 5, by comparing to similar results for He atom (see refs 6 and 44) that the correlation effects in He_2^+ have atomic and molecular contributions of the same order of magnitude. For instance, the correlation correction to the electron−electron repulsion energy has a negligible contribution $W_{H,c}^{HF} \equiv \Delta W_H^{s,HF}$ from the effect of the density change $\rho^{HF} \rightarrow \rho^s$ on the Hartree term, W_H, and is almost completely a Coulomb hole contribution W_c^{HF} of −0.131 H. In the He atom this is −0.077 H, so the dynamical correlation between the three electrons of He_2^+ is indeed larger, but not nearly in the proportion of three pairwise interactions in He_2^+ to one pair interaction in He. This confirms our expectation on the basis of the wave functions, see section II. There are more significant changes in the one-electron energies of He_2^+ than of He atom, for instance T_c^{HF} is +0.082 H, compared to +0.04 H in He. This indicates a net contraction effect of the correlation on the density, which is in agreement with the negative $V_c^{HF}(\Delta V^{s,HF})$ of −0.021 H, compared to only −0.004 H in He. These results confirm the expectation that He_2^+ has in addition to the dynamical correlation of the He electron pair relatively small additional dynamical correlation effects with the third electron, and somewhat larger one-electron energy effects due to the different charges of the symmetrical density distribution in the HF wave function and the unsymmetrical charges in the VB structures. The typical large nondynamical correlation effects of the electron pair bond (cf. H_2 at $R = 1.95$ Å) are absent. We note that, as always[8,49] the "errors" of the KS determinant and the HF determinant with respect to the correlated wave function are not so different and to the extent they are, as showing up in $\Delta T^{s,HF} = 0.021$ hartree and $\Delta V^{s,HF} = -0.021$ hartree, they largely cancel. As a result, the correlation energies E_c^s and E_c^{HF} are very close.

In the case of $(H_2O)_2^+$ and $(NH_3)_2^+$ correlation appears to produce an appreciable contraction of the correlated density around the nuclei compared to the HF one. These numbers are however dominated by the correlation effects in the two fragments, where the correlation in the A−H bonds will already produce this effect, and it is much harder to draw conclusions about the correlation effects in the three-electron bond. Note (cf. Table 4) that the correlation energies in NH_3^+ and NH_3 are −0.252 and −0.295 hartree, respectively, summing up to −0.547 hartree. The correlation energy of $(NH_3)_2^+$ is with −0.575 only little larger. Because of the contraction (in monomers as well as dimers), the differences of the electron−nuclear attraction energies $\Delta V^{s,HF}$ are negative, while those of the kinetic $\Delta T^{s,HF}$ and Hartree $\Delta W_H^{s,HF}$ energies are positive. Again, as in the case of He_2^+, compensation of differences of opposite sign occurs, and moreover $\Delta W_x^{s,HF}$ are small, so that the total energies E^{KS} and E^{HF} of the KS and HF determinants are close to each other. As a matter of fact the KS and conventional (with the HF reference) correlation energies $E_c^{s/HF}$

$$E_c^{s/HF} = E^{CI} - E^{KS/HF} \tag{3.9}$$

are very close and their difference $\Delta E_c^{s,HF} = E_c^s - E_c^{HF} = E^{HF} - E^{KS}$ is very small (certainly percentage wise). Note that the HF determinant is, by definition, the one with the lowest possible energy, so that $\Delta E_c^{s,HF}$ should be negative. This is true for He_2^+ and $(NH_3)_2^+$, while for $(H_2O)_2^+$ a positive $\Delta E_c^{s,HF}$ value has been obtained, which indicates that the KS solution in this case has not been obtained to sufficient accuracy to obtain a meaningful $\Delta E_c^{s,HF}$. This is, apparently, due to the influence on the CI and KS solutions for $(H_2O)_2^+$ of the size-inconsistency effect discussed in section III.

Just as the HF orbitals discussed in section II, the KS orbitals of the two-center three-electron bond are well represented with the doubly occupied bonding orbital $\psi_+ = (a + b)/\sqrt{(2+2S)}$ and the singly occupied antibonding orbital $\psi_- = (a - b)/\sqrt{(2-2S)}$. Inserting these orbitals in (3.6) and neglecting the two-center overlap $a(\mathbf{r})b(\mathbf{r})$, one can obtain an estimate of the exchange hole functions $\rho_{x\alpha}^s(\mathbf{r}_2|\mathbf{r}_1)$ for the major-spin α and $\rho_{x\beta}^s(\mathbf{r}_2|\mathbf{r}_1)$ for the minor-spin β of He_2^+

$$\rho_{x\alpha}^s(\mathbf{r}_2|\mathbf{r}_1) = -\frac{1}{\rho_\alpha(\mathbf{r}_1)}[\psi_{+\alpha}(\mathbf{r}_1)^2\psi_{+\alpha}(\mathbf{r}_2)^2 + \psi_{-\alpha}(\mathbf{r}_1)^2\psi_{-\alpha}(\mathbf{r}_2)^2 + 2\psi_{+\alpha}(\mathbf{r}_1)\psi_{-\alpha}(\mathbf{r}_1)\psi_{+\alpha}(\mathbf{r}_2)\psi_{-\alpha}(\mathbf{r}_2)] \approx -\frac{a^2(\mathbf{r}_1)a^2(\mathbf{r}_2) + b^2(\mathbf{r}_1)b^2(\mathbf{r}_2)}{a^2(\mathbf{r}_1) + b^2(\mathbf{r}_1)} \tag{3.10}$$

$$\rho_{x\beta}{}^s(\mathbf{r}_2|\mathbf{r}_1) = -\psi_{+\beta}(\mathbf{r}_1)^2 \approx -\frac{1}{2}[a^2(\mathbf{r}_1) + b^2(\mathbf{r}_1)] \tag{3.11}$$

It follows from (3.10) that, for an α spin electron, the exchange hole is localized around the reference electron ($\mathbf{r}_1\alpha$). Indeed, if the reference electron is on the atom He_A with the orbital $a(\mathbf{r})$, $\mathbf{r}_1 \in \Omega_A$, the exchange hole (3.10) in the distribution of α spin electrons is, essentially, $-a^2(\mathbf{r}_2)$, while if $\mathbf{r}_1 \in \Omega_B$, it is $-b^2(\mathbf{r}_2)$. Such a localized hole is what the GGA functionals implicitly employ. They are therefore expected to perform well for α spin.

In contrast, for the single β electron the exchange hole is just the delocalized self-interaction hole $-\psi_+{}^2(\mathbf{r}_2)$. The exchange GGA functionals make a large error here, since they employ a localized hole and are therefore much too stabilizing, cf. the case of H_2^+. Since He_2^+ is rather far to the elongated bond side when comparing to H_2^+, the error will be as large as it is in H_2^+ at long bond length.[18]

Turning now to the correlation holes, we note that when an α reference electron is close to atom He_A say, the other α electron will be at He_B, but the β electron will be equally likely at He_A and He_B. So there is no left−right correlation hole in the β electron density around an α reference electron. Similarly, there will be no left−right corrrelation hole in the α electron density around the β electron. There will of course be some dynamical correlation between the α and β electrons. The lack of left−right Coulomb correlation in He_2^+ is actually a crucial difference between He_2^+ and H_2. In H_2 at long bond distance the α electron is in *a* when the β electron is in *b*. Therefore, the localized exchange hole of GGA's in the α spin electron distribution, which is in fact erroneous, may be said to mimick Coulomb correlation between α and β electrons and the GGAs are actually performing reasonably in H_2. In He_2^+, however, as in H_2^+, this left−right correlation between the α and β electrons is absent and the localized hole around the β electron of the GGA exchange functionals is mimicking left−right correlation with the electrons of other spin that is spurious in this case.

Considering the GGA correlation functionals, we note that they usually reproduce well the dynamical correlation in atomic systems. Thus, they are expected to perform reasonably also for He_2^+, with its dynamical correlation effects as discussed in section II. In the next section we investigate whether these considerations provide a basis for understanding the performance of GGAs and meta-GGAs.

IV. Assessment of GGAs and Meta-GGAs

In this section the CI results of section II and the KS solution of section III are employed to analyze the performance of DFT generalized gradient approximations (GGAs) and meta-GGAs for A_2^+. GGA models the exchange−correlation (xc) energy functional $E_{xc}[\rho]$

$$E_{xc}^{GGA}[\rho] = \int e_{xc}^{GGA}(\rho(\mathbf{r}),\nabla\rho(\mathbf{r}))\,d\mathbf{r} \tag{4.1}$$

with the xc energy density $E_{xc}^{GGA}(\rho(\mathbf{r}),\nabla\rho(\mathbf{r}))$, which is an explicit function of the density $\rho(\mathbf{r})$ and its gradient $\nabla\rho(\mathbf{r})$, while meta-GGAs employ also the kinetic energy density $\tau(\mathbf{r})$

$$\tau_\sigma(\mathbf{r}) = \frac{1}{2}\sum_{i=1}^{N_\sigma}|\nabla\psi_{i\sigma}(\mathbf{r})|^2 \tag{4.2}$$

and/or the Laplacian $\nabla^2\rho(\mathbf{r})$

$$E_{xc}^{meta-GGA}[\rho] = \int e_{xc}^{meta-GGA}(\rho(\mathbf{r}),\ \nabla\rho(\mathbf{r}),\ \tau(\mathbf{r}),\ \nabla^2\rho(\mathbf{r}))\,d\mathbf{r} \tag{4.3}$$

Table 6 compares the CI total and dissociation energies for He_2^+ with those calculated self-consistently with three standard GGA functionals, namely, with the xc functional of Perdew and Wang (PW91),[17,50,51] the combination BP of the exchange functional of Becke (B88)[16] and the correlation functional of Perdew (P86)[14] and the combination BLYP of the same exchange functional B88 with the correlation functional of Lee, Yang, and Parr (LYP).[15] The self-consistent GGA calculations have been performed in the same basis as was used in the CI calculations by means of a Gaussian orbital density functional code[6,12,52] based on the ATMOL package.

The GGAs of Table 6 reproduce rather accurately the total energies of the atomic systems He and He^+, but they consistently overestimate the energy of He_2^+. This leads to the overestimation of the dissociation energy of He_2^+ to He and He^+. The corresponding errors are, with ca. 25 kcal/mol (ca. 40%), large. To trace their origin, one can compare the GGA and the accurate KS quantities. The accurate KS quantities are given in the second column of Table 7. The exchange energies that enter D_e^x are calculated from the HF expression ((3.5) and (3.6)) but using the KS orbitals. The KS corrrelation contributions use the difference between the exact (CI) total energy and the energy of the KS determinant E^{KS} as the correlation energies for the various systems. So if we add to D_e^{xc} the rest of the energy terms ($T^s[\rho^s]$, $V^s[\rho^s]$, and $W_H^s[\rho^s]$), we obtain the CI D_e. In the other columns the GGA numbers are given. These are all calculated with the same KS density ρ^s substituted in the various $E_{xc}^{GGA}[\rho]$ rather than with the different self-consistent GGA densities ρ^{GGA}. However, the densities ρ^s and ρ^{GGA} do not differ much and the $E_{xc}^{GGA}[\rho^s]$ are rather close to the $E_{xc}^{GGA}[\rho^{GGA}]$. When one compares the self-consisten GGA values for the other energy terms ($T^s[\rho^s]$, $V^s[\rho^s]$, and $W_H^s[\rho^s]$) with the KS values, the terms may individually differ between KS and GGA, but their sum is always close. Therefore, the errors in the GGA exchange−correlation terms D_e^{xc} in Table 7 are actually close to the total errors in the GGA dissociation energies in Table 6. So we may use the errors in Table 7 to analyze the cause of the GGA errors.

The KS exchange contribution D_e^x is quite negative (−55.5 kcal/mol) because the exchange energy of the fragments is more stabilizing than that of the He_2^+ molecule. This is the case because for both He and He^+ the exchange energy is just selfinteraction corrections for localized 1s electrons, three in total, while for He_2^+ we have seen that this the case for the two α spin electrons but the exchange hole for the β electron (also just selfinteraction correction) is delocalized and therefore the exchange energy much less stabilizing. The GGA exchange functionals do not faithfully describe this delocalized hole for the β electron, they have implicitly a too localized hole around the β electron and a too stabilizing exchange energy in He_2^+. This implies that they will increase the dissociation energy relative to the KS exchange energy. The error is large, ca. 30 kcal/mol.

The KS correlation contribution D_e^c increases the dissociation energy, i.e., the correlation energy is more stabilizing for He_2^+ than for He and He^+. The GGA correlation functionals do exhibit this effect, but they tend to underestimate correlation in He_2^+. A possible explanation is that, though reproducing properly the short-range dynamical correlation of the electron pair of He, the GGA correlation functionals cannot fully grasp the relatively long-range dynamical correlation of this electron pair with the unpaired electron. The result is that the GGA correlation functionals decrease the dissociation energy relative to the KS correlation energy, i.e., they make errors of opposite sign compared to the GGA exchange functionals, but the errors are much smaller, see Table 7.

In conclusion then the GGA errors in Table 6 are caused by the large errors in the GGA exchange energies, which are actually somewhat compensated (but not completely) by smaller errors of opposite sign for the GGA correlation errors. The large exchange error arises from the unduly localized GGA exchange hole for the β electron.

TABLE 8: Dissociation Energies (kcal/mol) Obtained with the GGA (Post-LDA Calculations[a]

molecule	LDA	BP	BLYP	BOP	FT97
He_2^+	86.0(29.1)	83.5(26.6)	82.9(26.0)	83.9(27.0)	82.2(25.3)
$(H_2O)_2^+$	66.7(27.5)	55.9(16.7)	55.8(16.6)	54.0(14.8)	54.0(14.8)
$(NH_3)_2^+$	56.2(22.4)	46.0(12.2)	45.7(11.9)	44.4(10.6)	45.6(11.8)
molecule	**PW**	**PBE**	**revPBE**	**HCTH/93**	**HCTH/402**
He_2^+	78.5(21.6)	77.6(20.7)	77.4(20.5)	79.1(22.2)	78.5(21.6)
$(H_2O)_2^+$	57.7(18.5)	59.8(20.6)	56.8(17.6)	52.4(13.2)	54.0(14.8)
$(NH_3)_2^+$	47.8(14.0)	49.7(15.9)	46.9(13.1)	43.0(9.2)	44.2(10.4)

[a] Errors with respect to the reference data are given in parentheses.

TABLE 9: Dissociation Energies (kcal/mol) Obtained with the Meta-GGA (Post-LDA Calculations

molecule	FT98	BLAP3	Bmτ1	PKZB	PKZB−KCIS
He_2^+	85.2(28.3)	78.6(21.7)	78.3(21.4)	78.0(21.1)	78.3(21.4)
$(H_2O)_2^+$	55.2(16.0)	53.0(13.8)	52.6(13.4)	51.1(11.9)	52.5(13.3)
$(NH_3)_2^+$	45.0(11.2)	43.6(9.8)	43.3(9.5)	41.4(7.6)	42.7(8.9)

molecule	VS98
He_2^+	75.8(18.9)
$(H_2O)_2^+$	53.0(13.8)
$(NH_3)_2^+$	43.8(10.0)

[a] Errors with respect to the reference data are given in parentheses.

The functionals BP, BLYP and PW considered in Tables 6 and 7 were developed in the period 1986−1992 and they have become standard DFT tools. To test more recent GGAs as well as meta-GGAs, some post-local-density-approximation (LDA) of He_2^+, $(H_2O)_2^+$, and $(NH_3)_2^+$ have been performed with the Amsterdam Density Functional (ADF2000) package.[53] Besides BP, BLYP, and PW, the GGAs tested are the xc functional of Perdew, Burke, and Ernzerhof (PBE)[54] as well as its revised version (revPBE),[55] the xc functional of Filatov and Thiel (FT97),[56] the xc functionals of Hamprecht, Cohen, Tozer, and Handy (HCTH/93 and HCTH/402)[57,58] parametrized for test sets of 93 and 402 molecules, respectively, and the combination (BOP) of the exchange functional B88[16] with the one-parameter progressive (OP) approximation of Tsuneda, Suzumura, and Hirao[59] to the correlation functional of Colle and Salvetti.[60] Meta-GGAs are the combinations (BLAP3 and Bmτ1) of the exchange functional B88 with the correlation functional of Proynov, Sirois, and Salahub (LAP3)[32] and with the recent extension of LAP3 by Proynov, Chermette, and Salahub (mτ1),[61] the xc functional of Filatov and Thiel (FT98),[34] the xc functional of Van Voorhis and Scuseria (VS98),[33] the xc functional of Perdew, Kurth, Zupan, and Blaha (PKZB),[35] and the combination (PKZB−KCIS) of the exchange functional PKZB[35] with the correlation functional of Krieger, Chen, Iafrate, and Savin (KCIS).[62] All calculations have been performed in basis sets of Slater-type orbitals (STOs) (6s3p2d for H and He and 8s6p3d2f for O and N) with the geometry optimized at the LDA level.

Tables 8 and 9 present the dissociation energies of He_2^+, $(H_2O)_2^+$, and $(NH_3)_2^+$ calculated with GGAs and meta-GGAs as well as the corresponding errors with respect to the experimental $D_e = 56.9$ kcal/mol for He_2^+,[42] CCSD(T) $D_e = 39.2$ kcal/mol for $(H_2O)_2^+$, [20] and the corrected CISD $D_e = 33.8$ kcal/mol for $(NH_3)_2^+$. All GGAs and meta-GGAs consistently overestimate the stability of A_2^+ resulting in significant errors, so that the analysis given above is also valid in this case. The standard LDA yields the largest errors and the gradient as well as higher-order corrections incorporated in GGAs and meta-GGAs produce, as a rule, a definite improvement.

Meta-GGAs (with the exception of FT98) appear to produce slightly better dissociation energies (See Table 9) compared to GGAs (See Table 8), still both groups of methods show a similar quality of the results. For He_2^+ revPBE yields the least error $\Delta D_e = 20.5$ kcal/mol among GGAs, while VS98 does this among meta-GGAs with $\Delta D_e = 18.9$ kcal/mol. For $(H_2O)_2^+$

and $(NH_3)_2^+$ HCTH/93 is the best among GGAs with errors of 13.2 and 9.2 kcal/mol, respectively, while PKZB yields the least meta-GGA errors of 11.9 and 7.6 kcal/mol. Note that in all cases the errors decrease for a system with a more diffuse valence density in the series $He_2^+ > (H_2O)_2^+ > (NH_3)_2^+$. A possible interpretation of this trend is that GGA/meta-GGA xc functionals depend solely on the local density $\rho(\mathbf{r})$ and the related semilocal quantities $\nabla\rho(\mathbf{r})$, $\nabla^2\rho(\mathbf{r})$, and $\tau(\mathbf{r})$, so that for more diffuse densities the effective size of the corresponding localized xc hole becomes relatively larger and closer to that of the delocalized KS hole, which results in smaller GGA/meta-GGA errors.

To conclude, Tables 8 and 9 show that, despite a definite improvement, neither recent GGAs, nor meta-GGAs have achieved a definite breakthrough in accuracy in this difficult case and the corresponding errors are still relatively large compared to the desired chemical accuracy. Since self-interaction errors are important in these molecules, one has to conclude that the meta-GGA's do not seem to achieve significant self-interaction correction.

On the basis of the present discussion, one can expect that hybrid DFT functionals, which include a portion of the exact KS exchange energy (3.5), should improve upon standard GGAs for A_2^+ and the results of calculations with the hybrid functionals B3LYP and BH&HLYP reported in refs 18−20 confirm these expectations. While the quality of B3LYP for He_2^+, $(H_2O)_2^+$ and $(NH_3)_2^+$ is comparable with those of meta-GGAs in Table 9, BH&HLYP, which includes a larger portion of the exact exchange, reduces the error of the dissociation energies of $(H_2O)_2^+$ and $(NH_3)_2^+$ to 1−2 kcal/mol compared to the ab initio data. Still, the BH&HLYP error for He_2^+ remains large, it amounts to 14 kcal/mol.[19] In the latter case a larger proportion of exact exchange might bring improvement. The fact that the amount that is required to obtain correct results is not known a priori limits the usefulness of exact exchange admixing. One may also consider correcting for the self-interaction error directly, and recently an improved dissociation energy, bond length and dissociation curve have been obtained for He_2^+ with an approximate treatment of the self-interaction correction to LDA and GGA functionals.[63]

V. Conclusions

In this paper the difficult case, for DFT methods, of the radical cations He_2^+, $(H_2O)_2^+$, $(NH_3)_2^+$ with two-center three-electron A−A bonds has been investigated at the CI, accurate KS, GGA, and meta-GGA levels. The correlation of the three electrons of the A−A bond has been analyzed. It is predominantly dynamical correlation of two electrons in a He closed shell plus some dynamical electron correlation of these electrons with the third electron on He^+, plus correlation corrections to the one-electron energy terms. This correlation shows up in a characteristic CI pattern. The CISD calculation of He_2^+ yields a calculated value of the dissociation energy D_e which is very close to experiment. CISD calculations of $(H_2O)_2^+$ and $(NH_3)_2^+$ suffer from the size-inconsistency effect, the size-extensivity correction repairs this effect for the calculated energies, so that the corrected CISD D_e value for $(H_2O)_2^+$ becomes close to the benchmark CCSD(T) value of ref 20.

The Kohn−Sham solutions of He_2^+, $(H_2O)_2^+$, and $(NH_3)_2^+$ have been constructed from the CI densities and the components of the total energies E^{KS} and E^{HF} of the KS and HF determinants are compared. In all cases the E^{KS} and E^{HF} values are close to each other, and so are the corresponding exchange energies W_x^s, W_x^{HF}, and correlation energies E_c^{HF} and E_c^s.

Assessment of seven different GGA and six meta-GGA methods has shown that, despite the recent intensive methodical development, the radical cations A_2^+ remain a difficult case for DFT. All methods tested consistently overestimate the stability of A_2^+, the corresponding D_e errors decrease for more diffuse valence densities in the series $He_2^+ > (H_2O)_2^+ > (NH_3)_2^+$. On average, meta-GGAs appear to perform slightly better than GGAs and both groups of methods provide a definite improvement over LDA. Still, even the best performers, like PKZB or HCTH/93, produce large errors comparable to those of the other functionals.

Comparison of the BP, BLYP, and PW exchange and correlation energies with the corresponding KS benchmark quantities for He_2^+ has indicated that the approximate exchange functionals are responsible for the errors of GGA-type methods. They characteristically overestimate exchange in A_2^+, so that the combined xc contribution to D_e is overestimated by about 25 kcal/mol. The cause for this overestimation of the exchange has been traced to the automatic inclusion of left−right correlation by the functionals, by virtue of their localized holes, while in the present systems this left−right correlation is absent. So there is a typical difference between a two-center two-electron bond, with left−right correlation present and therefore correctly included by the exchange functional, and a two-center three-electron bond where left−right correlation is absent so inclusion by the GGA functionals becomes spurious. We note that for the two-center ($m = 2$) three-electron ($n = 3$) A−A bond we have a fractional ratio $n/m = {}^3/_2$. This supports the qualitative rule of ref 13, which predicts a possible failure of GGAs for a chemical bond with fractional ratio ${}^n/_m$.

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