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Difficulties of Density Functional Theory in Investigating Addition Reactions of the Hydrogen Atom

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Received: July 18, 1996; In Final Form: September 18, 1996[®]

A comparison of results obtained by three widely used DFT formalisms (BLYP, B3LYP, and BH&HLYP) with those of MO methods (MP2 and CCSD(T)) points out that the DFT approaches under consideration fail to predict the behavior of the hydrogen atom in its addition and elimination reactions, either in radicals and radical cations or in triplet states. While in some cases DFT cannot recover the existence of low-lying transition structures, in other cases the relevant transition structures could be located using DFT, but the associated barrier heights are too low relative to MO values, and serious geometrical deviations occur. Calculations using the 6-31G(d,p) and 6-311++G(d,p) basis sets show that the basis exerts a significant effect on DFT results. It can be seen that the hybrid DFT schemes which include some exact HF exchange (BH&HLYP and B3LYP) yield an improvement over the pure DFT BLYP functional (with respect to the MO values), although serious discrepancies still exist.

Introduction

Despite the great success of density functional theory (DFT) in calculating energetic and molecular properties of equilibrium structures, it appears that this method, with the currently available functionals, encounters some serious difficulties in constructing the minimum-energy reaction paths of some specific chemical reactions.^{1–5} In particular, DFT fails to recover the basic properties of the hydrogen transfer process in a simple case such as the $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ reaction.¹ In the course of our theoretical study on radical cations⁶ and triplet species⁷ making use of DFT methods, we have regularly observed the rather erratic behavior in treating the addition or elimination reactions of the hydrogen atom. Despite its simplicity, H-loss plays a primordial role in the chemical reactivity of radical cations and hence in the interpretation of results obtained from mass spectrometric-based techniques. The opposite reaction, namely the addition of a hydrogen atom to a cation, is often characterized by a small barrier height. Nevertheless, this barrier has to be taken into account, for example, in determining the heat of formation of the cation from its measured appearance potential. Neglecting this barrier often leads to a significant error in the evaluation of the corresponding heat of formation (up to 20 kJ/mol).⁸ On the contrary, the 1,2-shift of the hydrogen is relatively well described by DFT methods,⁷ even though the barrier heights are consistently smaller than those obtained by high-level ab initio molecular orbital calculations.

In the present article, we wish to point out the difficulties with DFT treatments of the addition–elimination reactions involving hydrogen atoms, in radicals, radical cations, or triplet states. This problem appears to be a rather general phenomenon.

Computational Details

We have considered the BLYP, B3LYP and BH&HLYP methods which are among the most widely used DFT methods. The BLYP method is based purely on Kohn–Sham DFT formalism, including the standard local Slater exchange functional and the gradient-corrected Becke (exchange)⁹ and Lee–Yang–Parr (correlation)¹⁰ functionals. The B3LYP method,^{10,11,13} on the other hand, is based on an adiabatic connection scheme

which involves the mixing of some exact Hartree–Fock exchange (the Becke three-parameter fit). A third functional, which consists of a “half-and-half” mixture between Hartree–Fock-like and local Slater exchange (50% HF, 50% Slater) was also used in combination with the LYP correlation functional; it is denoted BH&HLYP.^{10,12,13} For the purpose of comparison, MO calculations have also been carried out at the second-order perturbation theory (MP2) and coupled-cluster (CCSD(T)) approximations. Basis sets of different qualities have been employed, including the 6-31G(d,p), 6-311++G(d,p), and 6-311++G(3df,3pd). All calculations have been performed with the aid of the GAUSSIAN 92/DFT program.¹³

Results and Discussion

In what follows, the performances of the DFT methods (BH&HLYP, B3LYP, and BLYP) and both correlated MO methods (MP2 and CCSD(T)) are compared with each other in calculating geometries of transition structures and associated barrier heights for various addition reactions of the hydrogen atom. We have chosen a sample of typical cases, including different electronic states. Figure 1 shows the species under consideration, namely the radicals $\text{H}_2\text{CP}^\bullet$, $\text{H}_2\text{CN}^\bullet$, HCO^\bullet , and HCS^\bullet , the cations HCO^+ and HCS^+ , and a few neutral, closed-shell molecules: ethylene, silene, and $\text{HN}=\text{C}=\text{O}$. For the addition of a hydrogen atom to radicals, we consider only the triplet products which are excited states of the corresponding neutral closed-shell species (only in the triplet state, the H-addition to radicals is associated with an energy barrier). For reactions to cations and neutral species, the additions occur on the ground doublet electronic states. While **X** designates a minimum on the potential energy surface, **TSX** represents the corresponding transition structure for hydrogen addition. Consecutively, we will discuss the calculated geometries and barrier heights obtained from the computational schemes mentioned above.

Geometries of Transition Structures

Geometries were optimized at the MP2, CCSD(T), BH&HLYP, B3LYP, and BLYP levels of theory, using the 6-31G(d,p) and 6-311++G(d,p) basis sets. It might be necessary to include diffuse functions on the heavy atoms as well as on hydrogens

[®] Abstract published in *Advance ACS Abstracts*, November 1, 1996.

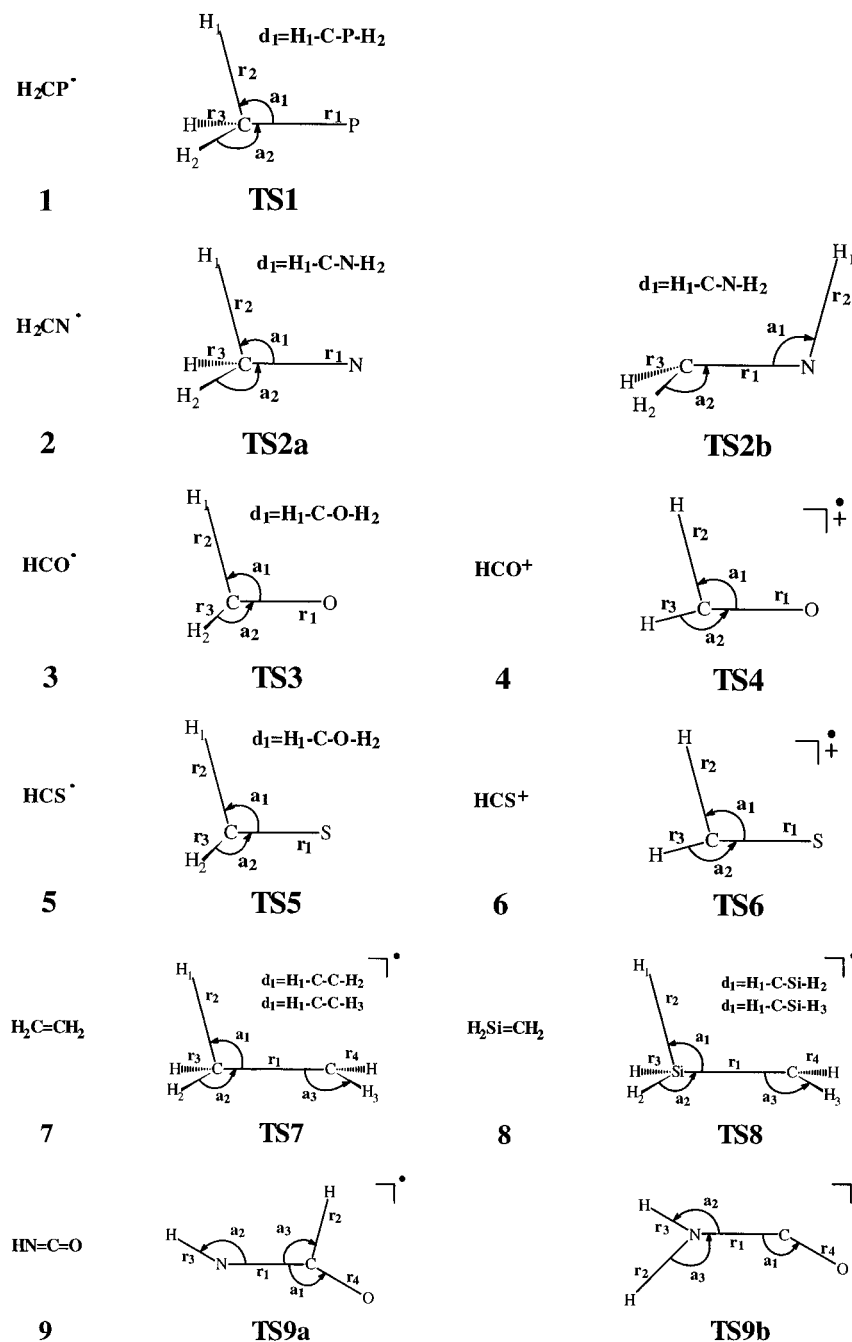


Figure 1. Geometrical parameters of different transition structures for hydrogen addition reactions.

when dealing with long bond distances. Some of the CCSD(T)/6-311++G(d,p) geometries were not computed due to their high computational demand; they were replaced by single-point calculations at the corresponding CCSD(T)/6-31G(d,p) geometry. A characterization of each stationary point was carried out by calculating the eigenvalues of the Hessian matrix and its associated normal modes of vibration, using the MP2, BH&HLYP, B3LYP, and BLYP methods, again in conjunction with both 6-31G(d,p) and 6-311++G(d,p) basis sets. Thus, except for CCSD(T) levels, the zero-point energies (ZPE) can be computed at each of the latter levels. The computed zero-point energies are uniformly scaled by the usual scaling factors of 0.94 for MP2/6-31G(d,p), 0.95 for MP2/6-311++G(d,p) and the recently suggested factors of 0.995 and 0.963 for BLYP and B3LYP, respectively.¹⁴ No scaling factors for the BH&HLYP method are readily available.

Table 1 lists the geometrical parameters for the transition structures that are defined in Figure 1. Only the important

parameters are listed, a full list of parameters, however, is supplied as Supporting Information. Geometries of the reactants are omitted for the sake of simplicity. All correlated MO methods predict the existence of a transition state for each addition considered, and the parameters are comparable to each other. The DFT methods, however, seem to suffer from serious deficiencies in that they do not succeed in finding certain transition structures, more specifically for the additions to $\text{H}_2\text{-CP}^\bullet$, HCO^+ , HCS^+ , and $\text{H}_2\text{Si=CH}_2$. For HCS^\bullet and ethylene, BLYP/6-31G(d,p) predicts no transition state for the addition, whereas the 6-311++G(d,p) basis set actually does lead to a transition structure. This fact can no doubt be attributed to a basis set deficiency and shows that diffuse functions are needed to properly treat long bond distances. Note that the intermolecular C-H distance predicted by BLYP/6-311++G(d,p) amounts to 2.628 Å for HCS^\bullet and 2.431 Å for ethylene, whereas the corresponding CCSD(T) bond distances are 2.042 Å and 1.973 Å, respectively.

TABLE 1: Geometrical Parameters for Transitions Structures of Various Hydrogen Additions^a

			6-31G(d,p)					6-311++G(d,p)				
			MP2	CCSD(T)	BH&HLYP	B3LYP	BLYP	MP2	CCSD(T)	BH&HLYP	B3LYP	BLYP
H ₂ C=P• + H•	TS1	<i>r</i> 2	2.362	2.261				2.329	2.301			
H ₂ C=N• + H•	TS2a	<i>r</i> 1	1.258	1.281	1.250	1.256	1.263	1.252	1.275	1.247	1.252	1.259
		<i>r</i> 2	1.873	1.920	2.174	2.218	2.327	1.877	1.948	2.113	2.141	2.204
	TS2b	<i>r</i> 1	1.250	1.282	1.253	1.258	1.264	1.246	1.276	1.248	1.252	1.258
		<i>r</i> 2	1.498	1.596	1.674	1.774	1.904	1.489	1.612	1.670	1.770	1.887
		<i>a</i> 1	125.7	120.3	120.6	122.6	123.9	128.3	121.9	121.9	123.9	125.1
HCO• + H•	TS3	<i>r</i> 2	1.509	1.701	1.825	1.922	2.038	1.687	1.714	1.815	1.911	2.013
		<i>a</i> 1	107.2	105.8	104.9	106.9	108.2	102.4	107.1	106.0	108.0	109.2
HCO ⁺ + H•	TS4	<i>r</i> 2	1.613	1.841				1.607	1.869			
		<i>a</i> 2	157.5	160.4				157.0	161.8			
HCS• + H•	TS5	<i>r</i> 1	1.560	1.591	1.564	1.577		1.556	1.585	1.560	1.572	1.586
		<i>r</i> 2	1.853	2.002	2.244	2.436		1.865	2.042	2.236	2.401	2.628
		<i>a</i> 1	106.9	107.3	107.3	110.1		108.3	108.3	108.1	110.4	112.0
		<i>d</i> 1	94.4	95.6	91.9	89.5		93.1	94.1	91.8	90.1	88.1
HCS ⁺ + H•	TS6	<i>r</i> 1	1.453	1.500				1.450	1.496			
		<i>r</i> 2	1.890	2.019				1.898	2.048			
H ₂ C=CH ₂ + H•	TS7	<i>r</i> 1	1.333	1.356	1.329	1.335		1.335	1.357	1.330	1.336	1.343
		<i>r</i> 2	1.862	1.931	2.182	2.374		1.868	1.973	2.120	2.228	2.431
		<i>a</i> 1	107.2	107.1	104.7	103.5		107.7	107.3	105.6	105.0	104.0
		<i>d</i> 1	96.8	96.8	92.8	91.6		96.9	96.6	93.4	92.7	91.6
H ₂ Si=CH ₂ + H•	TS8	<i>r</i> 1	1.677	1.721				1.673				
		<i>r</i> 2	2.803	2.920				2.775				
		<i>r</i> 3	1.466	1.470				1.467				
		<i>a</i> 1	106.2	107.6				100.3	<i>b</i>			
HN=C=O + H•	TS9a	<i>r</i> 1	1.265	1.255	1.231	1.240	1.250	1.269			1.235	1.244
		<i>r</i> 2	1.300	1.580	1.602	1.700	1.791	1.281			1.683	1.767
		<i>a</i> 1	152.7	155.7	157.7	158.8	159.5	151.6			159.1	159.8
		<i>a</i> 3	112.7	101.4	99.8	100.2	100.3	112.7			100.0	100.2
	TS9b	<i>r</i> 1	1.243	1.249	1.224	1.233	1.243	1.242			1.227	1.236
		<i>r</i> 2	1.411	1.536	1.558	1.650	1.761	1.407			1.658	1.767

^a See Figure 1 for definitions. Bond lengths are given in angstroms and bond angles in degrees. ^b These optimizations were not carried out due to the large amount of computer time that would be needed.

Clearly, the most significant parameter in discussing these geometries is the intermolecular bond distance between the incoming hydrogen atom and the atom to which it adds. This is, in all cases, the *r*2 parameter given in Table 1. As expected, both MP2 and CCSD(T) geometries are comparable, with a general tendency of CCSD(T) to increase *r*2 by approximately 0.12 Å using the smaller basis set and by 0.11 Å using the larger one (as compared with MP2 values). Considering the small basis set optimizations and taking the CCSD(T) values as references, it appears that both B3LYP and BLYP suffer from severe deviations concerning the intermolecular distance *r*2. On the average, B3LYP overestimates this distance by 0.26 Å, while BLYP does even worse with an average overestimation of 0.30 Å. The BH&HLYP method also leads to an overestimation of *r*2 relative to CCSD(T) values, but this amounts only to 0.14 Å. Using the larger 6-311++G(d,p) basis set, the errors in B3LYP and BH&HLYP are reduced to 0.23 and 0.13 Å, respectively. For BLYP, however, it now even amounts up to 0.37 Å. This large deviation originates from the refinding of **TS5** and **TS7**, which did not exist at the BLYP/6-31G(d,p) level. The fact that B3LYP and BH&HLYP perform better than BLYP, is probably due to their inclusion of exact Hartree–Fock exchange,^{1,4} which is lacking in the BLYP functional. Apparently, the long-range interactions, represented in the nonlocal part of the exchange, are not well reproduced by pure DFT. Although its description can be improved by the inclusion of Hartree–Fock exchange, the deficiency is not fully overcome. While yielding much less severe deviations than B3LYP and BLYP, BH&HLYP is still not able to refind certain transition states (**TS1**, **TS4**, **TS6**, and **TS8**).

Barrier Heights. Table 2 shows the barrier heights for H-addition computed at the MP2, CCSD(T), BH&HLYP, B3LYP, and BLYP levels with both 6-31G(d,p) and 6-311++G(d,p) basis sets. Concerning the MO methods, CCSD(T) lowers,

in general, the barriers significantly as compared with MP2. Regarding the DFT methods, it is seen that they drastically underestimate the barrier heights, especially when using the rather modest 6-31G(d,p) basis set. Use of the 6-311++G(d,p) basis set raises, however, all barriers and enables the BLYP functional to recover **TS5** and **TS7**, for which it failed with the smaller basis set. It has to be noted that in almost all cases BH&HLYP yields results closer to the CCSD(T) values than B3LYP, which is in turn performing better than BLYP.

Table 3 contains the barrier heights for the various hydrogen addition reactions obtained at the CCSD(T), BH&HLYP, B3LYP, and BLYP levels with the 6-311++G(3df,3pd) basis set. Concerning the CCSD(T) results, the barrier heights are further lowered with respect to the two smaller basis sets. A significant basis set dependence is thus noted for MO methods. While it is clear that extension of the basis set up to 6-311++G(d,p) has a considerable effect on the DFT results, the basis set effect is no longer operative on going to the larger 6-311++G(3df,3pd) set, as expected for DFT methods. This suggests that the encountered difficulties, although partly corrected with large basis sets, are mainly due to fundamental deficiencies of the model. In accordance with Baker et al.,¹ the importance of the exact Hartree–Fock exchange potential can be demonstrated (Table 2): the hybrid methods (BH&HLYP and B3LYP) clearly perform better than the pure DFT BLYP method. Considering the two hybrid functionals, the one which contains the most Hartree–Fock exchange, namely BH&HLYP, yields results in closer agreement with MO values than B3LYP, although neither B3LYP nor BH&HLYP is able to describe—even qualitatively—certain reactions. As Johnson et al. argued,² a good part of this error may arise from self-interaction.

TABLE 2: Barrier Heights for Various Hydrogen Addition Reactions, Obtained by Different MO and DFT Methods (kJ/mol)

		6-31G(d,p)					6-311++G(d,p)				
		MP2 ^a	CCSD(T) ^a	BH&HLYP ^b	B3LYP ^c	BLYP ^d	MP2 ^e	CCSD(T) ^e	BH&HLYP ^f	B3LYP ^g	BLYP ^h
H ₂ C=P• + H•	TS1	4.8	8.2				5.4	6.5			
H ₂ C=N• + H•	TS2a	29.5	20.6	3.9	3.7	3.2	29.1	17.9	6.9	7.0	6.9
	TS2b	39.2	34.6	23.8	12.8	7.1	40.0	35.8	25.8	15.1	10.1
HCO• + H•	TS3	74.3	41.1	18.1	11.3	7.7	65.0	36.5	20.1	13.5	10.4
HCO ⁺ + H•	TS4	55.5	25.2				45.6	19.5			
HCS• + H•	TS5	17.8	19.6	6.4	3.1		13.3	14.5	7.4	4.4	3.6
HCS ⁺ + H•	TS6	87.7	27.0				81.9	23.5			
H ₂ C=CH ₂ + H•	TS7	52.5	25.8	3.3	1.1		51.8	23.8	6.7	4.3	3.1
H ₂ Si=CH ₂ + H•	TS8	36.7	8.0				35.0	5.9 ⁱ			
HN=C=O + H•	TS9a	113.9	59.8	42.7	28.6	20.4	106.2	53.9 ⁱ	45.1	31.9	24.5
	TS9b	81.5	55.6	34.6	18.5	9.5	68.0	46.4 ⁱ	34.4	19.3	11.5

^a With scaled ZPE(MP2/6-31G(d,p)) correction. ^b With scaled ZPE(BH&HLYP/6-31G(d,p)) correction. ^c With scaled ZPE(B3LYP/6-31G(d,p)) correction. ^d With scaled ZPE(BLYP/6-31G(d,p)) correction. ^e With scaled ZPE(MP2/6-311++G(d,p)) correction. ^f With scaled ZPE(BH&HLYP/6-311++G(d,p)) correction. ^g With scaled ZPE(B3LYP/6-311++G(d,p)) correction. ^h With scaled ZPE(BLYP/6-311++G(d,p)) correction. ⁱ Based on CCSD(T)/6-31G(d,p) geometry.

TABLE 3: Barrier Heights for Various Hydrogen Addition Reactions, Obtained by Different MO and DFT Methods (kJ/mol)

		6-311++G(3df,3pd)			
		CCSD(T) ^a	BH&HLYP ^b	B3LYP ^c	BLYP ^d
H ₂ C=P• + H•	TS1	5.3			
H ₂ C=N• + H•	TS2a	13.0	7.1	6.9	6.9
	TS2b	29.1	25.0	14.7	9.7
HCO• + H•	TS3	28.6	19.3	12.5	9.6
HCO ⁺ + H•	TS4	11.9			
HCS• + H•	TS5	9.2	7.4	4.4	3.5
HCS ⁺ + H•	TS6	17.0			
H ₂ C=CH ₂ + H•	TS7	18.7	6.8	4.7	4.7
H ₂ Si=CH ₂ + H•	TS8	4.2 ^e			
HN=C=O + H•	TS9a	48.0 ^e	44.2	30.9	23.5
	TS9b	42.6 ^e	36.8	21.4	13.1

^a Based on CCSD(T)/6-311++G(d,p) geometry and scaled ZPE(MP2/6-311++G(d,p)) correction. ^b Based on BH&HLYP/6-311++G(d,p) geometry and ZPE(BH&HLYP/6-311++G(d,p)) correction. ^c Based on B3LYP/6-311++G(d,p) geometry and scaled ZPE(B3LYP/6-311++G(d,p)) correction. ^d Based on BLYP/6-311++G(d,p) geometry and scaled ZPE(BLYP/6-311++G(d,p)) correction. ^e Based on CCSD(T)/6-31G(d,p) geometry.

Conclusions

In summary, a comparative test between three popular DFT methods (BH&HLYP, B3LYP, and BLYP) and two MO methods (CCSD(T) and MP2) has been carried out to investigate their performance in describing addition reactions of the hydrogen atom, either in radicals and radical cations or in triplet states. Large basis sets (up to 6-311++G(3df,3pd)) were used to minimize basis set effects. The DFT methods are shown to suffer from serious difficulties in treating these reactions: either no transition structure can be found at all, or when a transition structure is actually located, serious discrepancies are found, both geometrical and energetical, as compared to ab initio calculations. Typically, BLYP and B3LYP overestimate the intermolecular bond length by approximately 0.3 Å relative to CCSD(T) bond lengths, and the barrier heights are in almost all cases more than 50% too low, again relative to CCSD(T) values. Using the BH&HLYP functional, results considerably closer to the MO values are obtained, both concerning geom-

etries and barrier heights. It is shown that BH&HLYP and B3LYP, probably due to their inclusion of Hartree–Fock exchange, perform better than BLYP. The basis set has a considerable effect on DFT, but this effect is, as expected, much larger for the MO methods. Although extension of the basis set and inclusion of Hartree–Fock exchange may enhance the reliability of DFT, unacceptable deviations with respect to ab initio MO theory still remain, at least for the functionals investigated in this work.

Acknowledgment. The authors are indebted to the Belgian National Fund for Scientific Research (NFWO), the Flemish Government (DWTC; GOA) for continuing support and the K. U. Leuven Computing Centre for generous allocations of computer time.

Supporting Information Available: Table containing geometrical parameters for transition structures (2 pages). Ordering information is given on any current masthead page.

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JP962191R