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# Computation of electron affinities of O and F atoms, and energy profile of F–H<sub>2</sub> reaction by density functional theory and *ab initio* methods

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The validity of hybrid and nonlocal DFT methods are tested on examples of systems which are difficult to model by way of quantum chemistry techniques. The electron affinities for the oxygen and fluorine atoms were calculated. The exothermicity, the barrier for the fluorine atom reaction with the hydrogen molecule, and the energy of the H–F bond and its distance were computed with DFT methods, as well as, with ROHF, MPn, and QCISD(T) *ab initio* methods. The computations were performed by using various basis sets, with 6-311++G(3*df*,3*pd*) as the largest. The obtained results are compared with the experimental values. The results of the Becke3LYP hybrid method is in qualitative agreement with experimental results and in the majority of the cases reassembles the high cost QCISD(T) calculation results. Considering the modest computational cost for DFT methods, Becke3LYP/6-311++G(2*d*,2*p*) is suggested as the standard theory model for computation, and Becke3LYP/6-311++G(3*df*,3*pd*) as the model for generating highly accurate results. They should be applicable to relatively sizable chemical systems. © 1996 American Institute of Physics. [S0021-9606(96)02511-4]

## INTRODUCTION

DFT methods<sup>1</sup> are computationally less expensive than the current correlated techniques of *ab initio* quantum chemistry.<sup>2</sup> It was shown that local density approximation (LDA) results for the energetics of atoms and molecules are dramatically improved when the density gradient correlations are included.<sup>3</sup> In comparison with the experimental thermochemical data, the average error is 3.7 kcal/mol, relatively close to 1.6 kcal/mol when obtained with the G1 procedure.<sup>3</sup>

The hybrid of Hartree–Fock (HF) and DFT methods seem to further reduce the difference between the calculated and experimental energies and geometries. The hybrid methods (Becke3LYP), developed by Gill, Johnson, Pople, and Frisch, combined the nonlocal exchange functional by Becke<sup>4</sup> and nonlocal correlation functional of Lee, Yang, and Parr (LYP)<sup>5</sup> in combination with the self-consistent field (SCF) HF densities. We have applied this and other hybrid DFT methods for the computation of structures that require a high level of correlated *ab initio* techniques. The structural parameters and energies for the nitric oxide dimer,<sup>6</sup> nitrogen oxides,<sup>7</sup> sulfur–fluoride,<sup>8</sup> nitrogen–fluoride,<sup>9</sup> and oxygen–fluoride<sup>10</sup> compounds are almost indistinguishable from the experimental results. We have also used these methods for modeling the transition state structures in fluorine rearrangement reactions<sup>8</sup> and Diels–Alder reactions.<sup>11</sup> The obtained activation energies are very close to those obtained experimentally. In fact, the accuracy in predicting activation energies has encouraged us to seek the possibility of applying the hybrid DFT methods to large organic molecules. Presently, the computational capabilities are still insufficient to efficiently perform full DFT optimization of sizable organic molecules with large basis sets. We have demonstrated that the single point hybrid DFT calculations on AM1 optimized geometries produce activation energies of the Diels–

Alder reactions that are 1–3 kcal away from the experimental results.<sup>12</sup>

The motivation for this paper is twofold. First, although DFT calculations are becoming a very popular tool for the computational chemist excluding ourselves, there are not very many studies which use the hybrid DFT methods for solving systems which are difficult by using quantum chemistry methods. Furthermore, this approach should be valuable for the study of energetic heterocyclic compounds that contain many electronegative atoms such as N, O, S, and F. In their decomposition reactions, the fluorine radical formation and the hydrogen abstraction reactions are highly possible. To evaluate the suitability of the hybrid DFT methods for studying these systems, we have computed the electron affinities for F and N, and the activation barrier and exothermicity for F+H<sub>2</sub>→HF+H. The *ab initio* computation of these properties was performed previously by Scuseria.<sup>13</sup>

## COMPUTATIONAL METHODS

All of the calculations were performed with the GAUSSIAN 92<sup>14</sup> implementation of the density functional theory. The optimizations were performed without any geometric restrictions, except in the case of the linear transition state structure, using the default Gaussian convergence criteria. The local spin density approximation (LSDA) calculations were performed with the functional included in GAUSSIAN 92/DFT. It is a combination of the Slater exchange functional and VWN correlation functional for the DFT calculation.<sup>15</sup> LSDA is not uniquely defined in the literature. Four different DFT hybrid methods were used BHandH, BHandHLYP, Becke3LYP and Beck3P86. The BHandH method includes 50% HF exchange and 50% Slater exchange<sup>16</sup> with no correlation functional. BHandHLYP is the Becke 50–50 method with LYP<sup>5</sup> correlation added. Becke3LYP is Becke's three-parameter functional<sup>4</sup> with the nonlocal correlation provided

TABLE I. Electron affinity (eV) of the oxygen atom.

Theory model	$E(O)/(hartree)$	$E(O^-)/(hartree)$	E.A.
ROHF/6-31+G( <i>d,p</i> )	-74.781 449 5	-74.762 721 5	-0.51
ROHF/6-311+G(2 <i>d,2p</i> )	-74.802 121 0	-74.782 572 1	-0.53
ROHF/6-311++G(3 <i>df,3pd</i> )	-74.802 915 7	-74.783 145 0	-0.54
HF/6-31+G( <i>d,p</i> )	-74.786 763 9	-74.766 618 6	-0.55
HF/6-311+G(2 <i>d,2p</i> )	-74.808 059 4	-74.786 903 3	-0.58
HF/6-311++G(2 <i>d,2p</i> )	-74.809 340 4	-74.787 979 3	-0.58
LSDA/6-31+G( <i>d,p</i> )	-74.651 310 9	-74.742 694 2	-2.49
LSDA/6-311+G(2 <i>d,2p</i> )	-74.673 847 8	-74.765 035 2	2.48
LSDA/6-311++G(3 <i>df,3pd</i> )	-74.674 573 6	-74.765 571 2	2.49
BHandH/6-31+G( <i>d,p</i> )	-74.630 714 1	-74.667 549 4	1.00
BHandH/6-311+G(2 <i>d,2p</i> )	-74.651 979 0	-74.688 368 6	0.99
BHandH/6-311++G(3 <i>df,3pd</i> )	-74.652 847 5	-74.689 054 0	0.99
BHandHLYP/6-31+G( <i>d,p</i> )	-75.048 621 7	-75.088 722 3	1.09
BHandHLYP/6-311+G(2 <i>d,2p</i> )	-75.070 396 0	-75.109 915 7	1.08
BHandHLYP/6-311++G(3 <i>df,3pd</i> )	-75.071 313 4	-75.110 652 7	1.07
Becke3LYP/3-21G*	-74.660 282 6	-74.587 464 3	-1.98
Becke3LYP/6-31G( <i>d</i> )	-75.060 618 0	-75.052 709 5	-0.22
Becke3LYP/6-31G( <i>d,p</i> )	-75.060 618 0	-75.052 709 5	-0.22
Becke3LYP/6-31+G( <i>d,p</i> )	-75.067 586 5	-75.127 219 7	1.62
Becke3LYP/6-311+G(2 <i>d,2p</i> )	-75.090 032 0	-75.149 209 7	1.61
Becke3LYP/6-311++G(3 <i>df,3pd</i> )	-75.090 887 2	-75.149 874 4	1.61
Becke3P86/6-31+G( <i>d,p</i> )	-75.199 911 6	-75.276 511 3	2.08
Becke3P86/6-311+G(2 <i>d,2p</i> )	-75.221 834 7	-75.298 042 9	2.07
Becke3P86/6-311++G(3 <i>df,3pd</i> )	-75.222 773 8	-75.298 768 7	2.07
BLYP/6-31+G( <i>d,p</i> )	-75.056 063 9	-75.119 409 4	1.72
BLYP/6-311+G(2 <i>d,2p</i> )	-75.079 408 0	-75.142 274 5	1.71
BLYP/6-311++G(3 <i>df,3pd</i> )	-75.080 251 6	-75.142 927 2	1.71
BP86/6-31+G( <i>d,p</i> )	-75.057 421 9	-75.124 568 8	1.83
BP86/6-311+G(2 <i>d,2p</i> )	-75.080 019 6	-75.146 768 0	1.82
BP86/6-311++G(3 <i>df,3pd</i> )	-75.080 956 6	-75.147 480 7	1.81
MP2/6-31+G( <i>d,p</i> )	-74.885 291 0	-74.925 247 0	2.52
MP2/6-311+G(2 <i>d,2p</i> )	-74.935 174 4	-74.977 821 9	1.16
MP2/6-311++G(3 <i>df,3pd</i> )	-74.952 421 3	-75.000 575 2	1.31
MP3/6-31+G( <i>d,p</i> )	-74.898 515 2	-74.930 774 0	0.88
MP3/6-311+G(2 <i>d,2p</i> )	-74.948 793 2	-74.982 219 1	0.91
MP3/6-311++G(3 <i>df,3pd</i> )	-74.968 321 6	-75.006 355 2	1.03
MP4SDQ/6-31+G( <i>d,p</i> )	-74.900 805 3	-74.935 135 6	0.93
MP4SDQ/6-311+G(2 <i>d,2p</i> )	-74.950 407 1	-74.985 767 1	0.96
MP4SDQ/6-311++G(3 <i>df,3pd</i> )	-74.967 809 6	-75.009 225 0	1.13
QCISD/6-31+G( <i>d,p</i> )	-74.901 733 4	-74.936 844 8	0.96
QCISD/6-311+G(2 <i>d,2p</i> )	-74.951 106 6	-74.987 105 6	0.98
QCISD/6-311++G(3 <i>df,3pd</i> )	-74.968 900 5	-75.010 329 3	1.13
QCISD(T)/6-31+G( <i>d,p</i> )	-74.902 726 4	-74.939 374 6	1.00
QCISD(T)/6-311+G(2 <i>d,2p</i> )	-74.953 397 8	-74.992 508 1	1.01
QCISD(T)/6-311++G(3 <i>df,3pd</i> )	-74.972 020 8	-75.017 396 9	1.23
Experimental <sup>a</sup>	-75.067 3	-75.121 0	1.46

<sup>a</sup>Reference 25.

by the LYP<sup>5</sup> expression. Becke3P86 is Becke's 3<sup>4</sup> functional parameters with the nonlocal correlation provided by the Perdew 86 expression.<sup>17</sup> For comparison of the computational results, two *ab initio* methods, a spin-restricted open-shell Hartree–Fock (ROHF) self-consistent field<sup>18</sup> 2nd, 3rd, and 4th order Møller–Plesset perturbation theory,<sup>19</sup> and QCISDT<sup>20</sup> were used implementing the standard Gaussian basis sets [6-31+G(*d,p*), 6-311+G(2*d,2p*), and 6-311++G(3*df,3pd*)].<sup>21</sup> The search for the transition state structures and their verification<sup>22</sup> was performed as described previously.<sup>23</sup> The initial optimization with GAUSSIAN was performed with “rhf sto-3G test opt=(ef,ts,calcfc) scf=direct” to obtain one imaginary frequency. After the first

cycle, the optimization was aborted, and the input file was modified to the “DFT or *ab initio* method 6-31+G(*d,p*) test opt=(ef,ts,readfc) scf=direct” while keeping the file name constant and linking calculations in the chain with “--link1--” command.

## RESULTS AND DISCUSSION

To validate the comparison between different *ab initio* and DFT methods, all calculations were performed with the same three different basis sets. First, we investigated the electron affinity (E.A.) of the oxygen atom (Table I). It is known that SCF-HF *ab initio*<sup>13</sup> methods do not produce ac-

TABLE II. Electron affinity (eV) of the fluorine atom and heat of  $F+H \rightarrow HF$ .

Theory model	$E(F)$ (hartree)	$E(F^-)$ (hartree)	E.A.	$r(HF)$ (°)	$E(H)$ (hartree)	$E(HF)$ (hartree)	$\Delta E$
ROHF/6-31+G( <i>d,p</i> )	-99.368 358 9	-99.418 586 4	1.37	0.902	-0.498 232 9 <sup>a</sup>	-100.024 306 8	98.97
ROHF/6-311+G(2 <i>d,2p</i> )	-99.396 358 1	-99.445 655 7	1.34	0.897	-0.499 809 8	-100.055 567 0	100.02
ROHF/6-311++G(3 <i>df,3pd</i> )	-99.397 084 0	-99.445 655 7	1.32	0.897	-0.499 817 9	-100.058 122 0	101.17
LSDA/6-31+G( <i>d,p</i> )	-99.242 820 3	-99.414 294 0	4.64	0.936	-0.493 936 9	-99.998 618 2	164.32
LSDA/6-311+G(2 <i>d,2p</i> )	-99.276 128 4	-99.444 003 3	4.57	0.931	-0.496 113 6	-100.032 586 2	163.37
LSDA/6-311++G(3 <i>df,3pd</i> )	-99.276 897 5	-99.444 003 7	4.55	0.930	-0.496 241 1	-100.035 073 8	164.36
BHandH/6-31+G( <i>d,p</i> )	-99.219 411 6	-99.327 904 7	3.20	0.917	-0.475 996 0	-99.920 565 9	141.29
BHandH/6-311+G(2 <i>d,2p</i> )	-99.248 194 2	-99.355 628 2	2.92	0.912	-0.477 907 6	-99.952 445 6	141.99
BHandH/6-311++G(3 <i>df,3pd</i> )	-99.249 122 5	-99.355 628 2	2.90	0.912	-0.477 977 6	-99.954 983 3	143.00
BHandHLYP/6-31+G( <i>d,p</i> )	-99.705 152 2	-99.813 022 8	2.94	0.915	-0.496 834 3	-100.410 591 2	130.90
BHandHLYP/6-311+G(2 <i>d,2p</i> )	-99.734 561 4	-99.841 084 4	2.90	0.910	-0.498 545 4	-100.442 901 7	131.00
BHandHLYP/6-311++G(3 <i>df,3pd</i> )	-99.735 531 1	-99.841 084 4	2.87	0.910	-0.498 600 0	-100.445 299 1	132.51
Becke3LYP/6-31+G( <i>d,p</i> )	-99.730 585 0	-99.859 698 1	3.51	0.927	-0.500 272 8	-100.451 373 5	138.37
Becke3LYP/6-311+G(2 <i>d,2p</i> )	-99.760 774 3	-99.888 693 4	3.48	0.922	-0.502 155 9	-100.484 683 5	139.15
Becke3LYP/6-311++G(3 <i>df,3pd</i> )	-99.761 676 8	-99.888 693 4	3.46	0.922	-0.502 256 9	-100.486 982 0	139.96
Becke3P86/6-31+G( <i>d,p</i> )	-99.881 294 3	-100.027 919 6	3.99	0.925	-0.516 818 6	-100.624 580 7	142.11
Becke3P86/6-311+G(2 <i>d,2p</i> )	-99.910 856 1	-100.056 581 5	3.97	0.920	-0.518 515 1	-100.657 257 7	143.00
Becke3P86/6-311++G(3 <i>df,3pd</i> )	-99.911 814 7	-100.056 581 5	3.94	0.919	-0.518 572 0	-100.659 556 3	143.80
BLYP/6-31+G( <i>d,p</i> )	-99.720 973 3	-99.853 940 3	3.62	0.939	-0.495 446 2	-100.440 137 8	140.38
BLYP/6-311+G(2 <i>d,2p</i> )	-99.752 227 5	-99.883 903 9	3.58	0.933	-0.497 554 8	-100.474 593 8	141.07
BLYP/6-311++G(3 <i>df,3pd</i> )	-99.753 123 3	-99.883 903 9	3.56	0.933	-0.497 721 5	-100.476 815 4	141.80
BP86/6-31+G( <i>d,p</i> )	-99.722 029 0	-99.858 809 2	3.72	0.936	-0.498 105 0	-100.449 674 6	144.04
BP86/6-311+G(2 <i>d,2p</i> )	-99.752 432 3	-99.888 233 8	3.70	0.931	-0.500 025 1	-100.483 279 1	144.84
BP86/6-311++G(3 <i>df,3pd</i> )	-99.753 389 7	-99.888 233 8	3.67	0.931	-0.500 140 7	-100.485 489 2	145.55
MP2/6-31+G( <i>d,p</i> )	-99.498 820 2	-99.623 846 7	3.40	0.926		-100.215 809	137.27
MP2/6-311+G(2 <i>d,2p</i> )	-99.578 603 5	-99.703 831 0	3.41	0.918		-100.302 993	140.92
MP2/6-311++G(3 <i>df,3pd</i> )	-99.602 117 1	-99.732 134 3	3.54	0.917		-100.332 820	144.88
MP3/6-31+G( <i>d,p</i> )	-99.506 687 2	-99.613 630 0	2.91	0.921		-100.214 847 2	131.73
MP3/6-311+G(2 <i>d,2p</i> )	-99.587 214 2	-99.692 152 4	2.86	0.912		-100.300 780 1	134.13
MP3/6-311++G(3 <i>df,3pd</i> )	-99.612 300 2	-99.721 988 1	2.98	0.911		-100.331 884 5	137.90
MP4SDQ/6-31+G( <i>d,p</i> )	-99.509 133 6	-99.623 356 7	3.11	0.926		-100.222 985 3	135.30
MP4SDQ/6-311+G(2 <i>d,2p</i> )	-99.588 593 2	-99.700 311 8	3.04	0.918		-100.311 041 0	139.70
MP4SDQ/6-311++G(3 <i>df,3pd</i> )	-99.613 404 1	-99.729 410 9	2.90	0.917		-100.343 061 4	144.22
QCISD/6-31+G( <i>d,p</i> )	-99.509 948 3	-99.622 686 0	3.07	0.925		-100.219 598 9	132.66
QCISD/6-311+G(2 <i>d,2p</i> )	-99.589 168 0	-99.699 550 2	3.00	0.915		-100.304 479 8	135.22
QCISD/6-311++G(3 <i>df,3pd</i> )	-99.613 875 6	-99.728 524 2	3.12	0.914		-100.334 895 0	138.80
QCISD(T)/6-31+G( <i>d,p</i> )	-99.511 208 7	-99.624 944 4	3.09	0.917		-100.221 843 2	133.28
QCISD(T)/6-311+G(2 <i>d,2p</i> )	-99.592 086 4	-99.705 563 9	3.09	0.917		-100.309 831 2	136.75
QCISD(T)/6-311++G(3 <i>df,3pd</i> )	-99.617 804 0	-99.736 495 5	3.23	0.916		-100.341 660 0	140.58
Experimental	-99.731 3 <sup>a</sup>	-99.856 3 <sup>b</sup>	3.40 <sup>b</sup>	0.917 <sup>c</sup>			141.20 <sup>c</sup>

<sup>a</sup>Hydrogen atom is calculated only at the Hartree-Fock level; with only one electron, correlation is not a factor in this system.

<sup>b</sup>Reference 25.

<sup>c</sup>Reference 26.

ceptable results and that the CCSD(T) considerably improves the computational results. It was also determined that BLYP<sup>24</sup> calculations overestimate the energy, if compared with the experimental value (1.46 eV).<sup>25</sup> All our HF calculations predict negative electron affinities (around -0.6 eV). The local spin density approximation (LSDA) produced results that overestimate the electron affinity by 1 eV (Table I). Both BHandH hybrid DFT methods compute E.A. values that are much closer to the experimental value. The best results were obtained with DFT methods by using the Becke3LYP hybrid [Becke3LYP/6-31+G(*d,p*)] DFT model. There is considerable basis set dependence. Thus 3-21G\*, 6-31G(*d*), and 6-31G(*d,p*) do not produce satisfactory results. Polarization functional must be present. With Becke3LYP/6-31+G(*d,p*), the total energy for the oxygen radical agrees to four digits while, the oxygen anion agrees to three digits. The predicted electron affinity is 0.16 eV

different than the experimental value (Table I). These results are better than any *ab initio* method (HF, MPn, and QCISD) used in this study. The nonlocal (BLYP and BP86) DFT methods overestimate the E.A., but results are still better than HF and are comparable in quality to the MPn *ab initio* calculations.

Even better DFT results are obtained when the fluorine electron affinity and energy of the H-F bond is computed (Table II). The HF calculations produce results that are unacceptable. The computed electron affinity is more than 2 eV below the experimental value. Almost the same value for the LSDA local DFT method overestimates the electron affinity. Every other DFT method had shown considerable improvement over HF and LSDA computed results. The best agreement of total energies for the fluorine radical and anion is again obtained with the Becke3LYP/6-31+G(*d,p*) theory model. The obtained electron affinity of the F atom differs by

TABLE III. Classical barrier height ( $\Delta E_I$ ) and exothermicity ( $\Delta E_{II}$ ) in kcal/mol for  $F+H_2 \rightarrow HF+H$  calculated with the assumption that the transition state structure is linear.

Theory model	$r_{HH}(\text{\AA})$	$r_{HF}(\text{\AA})$	$E_{H_2}(\text{hartree})$	$E_{TS}(\text{hartree})$	$\Delta E_I$	$\Delta E_{II}$
ROHF/6-31+G( <i>d,p</i> )	0.831	1.176	-1.131 333 5	-100.453 433 7	29.03	14.33
ROHF/6-311+G(2 <i>d,2p</i> )	0.828	1.178	-1.133 003	-100.483 971 9	28.48	16.32
ROHF/6-311++G(3 <i>df,3pd</i> )	0.829	1.179	-1.133 073 9	-100.486 180 9	27.60	17.43
LSDA/6-31+G( <i>d,p</i> )			-1.171 246 1			49.25
LSDA/6-311+G(2 <i>d,2p</i> )			-1.172 710 0			50.11
LSDA/6-311++G(3 <i>df,3pd</i> )			-1.172 729 6			51.26
Becke3LYP/6-31+G( <i>d,p</i> )	0.743	2.908	-1.178 539 3	-100.908 985 2	0.09	26.68
Becke3LYP/6-311+G(2 <i>d,2p</i> )	0.743	2.909	-1.180 012 7	-100.940 620 4	0.11	28.90
Becke3LYP/6-311++G(3 <i>df,3pd</i> )	0.743	2.908	-1.180 033 9	-100.941 603 1	0.07	29.82
Becke3P86/6-31+G( <i>d,p</i> )	0.744	2.874	-1.214 172 8	-101.095 037 2	0.27	28.82
Becke3P86/6-311+G(2 <i>d,2p</i> )	0.744	2.878	-1.215 551 3	-101.126 018 3	0.25	30.98
Becke3P86/6-311++G(3 <i>df,3pd</i> )	0.744	2.880	-1.215 579 4	-101.127 069 3	0.21	31.83
BLYP/6-31+G( <i>d,p</i> )	0.748	3.452	-1.167 912 2	-100.888 866 7	0.01	29.30
BLYP/6-311+G(2 <i>d,2p</i> )	0.747	3.442	-1.169 600 9	-100.921 734 7	0.06	31.58
BLYP/6-311++G(3 <i>df,3pd</i> )	0.748	3.009	-1.169 614 8	-100.922 912 0	0.11	32.50
BP86/6-31+G( <i>d,p</i> )	0.752	2.943	-1.176 465 0	-100.898 333 1	0.10	30.92
BP86/6-311+G(2 <i>d,2p</i> )	0.752	2.949	-1.177 890 5	-100.930 141 2	0.12	33.24
BP86/6-311++G(3 <i>df,3pd</i> )	0.752	2.941	-1.177 904 2	-100.931 153 9	0.09	34.09
MP2/6-31+G( <i>d,p</i> )	0.772	1.394	-1.131 333 5	-100.645 905 9	6.64	36.12
MP2/6-311+G(2 <i>d,2p</i> )	0.773	1.398	-1.133 003	-100.732 071 4	5.83	38.55
MP2/6-311++G(3 <i>df,3pd</i> )	0.769	1.424	-1.133 073 9	-100.759 798 8	4.56	41.15
QCISD(T)/6-31+G( <i>d,p</i> )	0.771	1.464	-1.165 157 3	-100.669 992 1	4.00	27.42
QCISD(T)/6-311+G(2 <i>d,2p</i> )	0.772	1.479	-1.170 822 9	-100.758 156 3	2.98	29.32
QCISD(T)/6-311++G(3 <i>df,3pd</i> )	0.764	1.550	-1.172 534 2	-100.787 377 4	1.86	32.09
Experimental					~2.0 <sup>a</sup>	31.70 <sup>b</sup>

<sup>a</sup>Reference 28.<sup>b</sup>Reference 27.

only 0.11 eV from the experimental value. A slightly better agreement was gained with the larger basis set [6-311++G(3*df,3pd*)]. The calculated E.A. differs by a mere 0.06 eV from the experimental value. It is interesting to point out that the second hybrid DFT method with the P86 correlation functional (Becke3P86) produces energies that are considerably higher than the experimental values. That is also observed with the nonlocal DFT methods (Table II). To obtain satisfactory results with the *ab initio* methods, very large basis sets and an extensive electron correlation is necessary. To our surprise, the best computed E.A. was achieved by the MP2 *ab initio* method. Other methods that include higher correlation treatment like QCISD(T) with extended basis sets like 6-311++G(3*df,3pd*) produce worse E.A. than BLYP or MP2 calculations.

There are many systems where electron correlation is essential for an accurate prediction. One that attracts significant attention is the hydrogen fluoride. Clearly, noncorrelated methods like HF and LSDA cannot handle this system (Table II) and all DFT methods that include electron correlation produce better results. The *ab initio* methods that incorporate electron correlation (MPn and QCISD) show significant basis set dependence. Thus the calculated H–F bond energy is increased by about 4 kcal/mol going from 6-31+G(*d,p*) and 6-311++G(2*d,2p*) to 6-311++G(3*df,3pd*). This basis set dependence is considerably lower for the DFT methods. Here again, a satisfied bond distance and H–F bond energy are computed with the Becke3LYP hybrid method, particularly with the Becke3LYP/6-311++G(3*df,3pd*) model. The

bond distance is 0.005 Å longer and H–F bond energy is 1.24 kcal/mol higher than the experimental values.<sup>26</sup> An excellent H–F bond energy was computed with the BLYP nonlocal DFT methods regardless of the basis sets, but the predicted bond distance is too long (Table I). The DFT methods that have P86 nonlocal correctional (Becke3P86 and BP86) produce too long H–F bonds and too high H–F energies. As mentioned above, all *ab initio* methods are basis set sensitive and will be discussed accordingly. The best results were obtained with MP2/6-311+G(2*d,2p*) and QCISD(T)/6-311++G(3*df,3pd*). Again, by using smaller or larger basis sets, the obtained results are worse than that obtained by the Becke3LYP methods. Nevertheless, it can be stated that the *ab initio* methods with electron correlation and large basis set are necessary for an accurate prediction of the H–F properties. Similar predictions can be obtained by using the Becke3LYP hybrid DFT method (Table II).

We next turn to the computation of classical barrier height and exothermicity of the  $F+H_2 \rightarrow HF+H$  reaction (Table III). The computed heat of the reaction with LSDA is overestimated by around 17 kcal/mol. Again, for almost an identical value, the ROHF underestimates the exothermicity of the reaction that is experimentally determined to be 31.7 kcal/mol.<sup>27</sup> Every other DFT method (hybrid and nonlocal) generates heat of the reaction that is a major improvement over both ROHF and MP2 *ab initio* calculations. Surprisingly, the MP2/6-311++G(3*df,3pd*) computes exothermicity that is 9.55 kcal/mol higher than the experimental value. The hybrid Becke3LYP/6-311++G(3*df,3pd*) and

TABLE IV. The bending potential (kcal/mol) in the transition state region for  $F+H_2 \rightarrow HF+H$  calculated by using 6-311++G(3df,3pd) basis set.  $E_I$ =BHandH;  $E_{II}$ =BHandHLYP;  $E_{III}$ =Becke3LYP;  $E_{IV}$ =Becke3P86;  $E_V$ =BLYP;  $E_{VI}$ =BP86.

aHHF(°)	$E_I$	$E_{II}$	$E_{III}$	$E_{IV}$	$E_V$	$E_{VI}$
180	0.000	0.000	0.000	0.000	0.000	0.000
175	-0.006	0.000	0.000	-0.002	0.001	0.000
170	-0.023	0.000	-0.003	-0.008	0.002	-0.004
165	-0.054	-0.001	-0.008	-0.019	0.002	-0.011
160	-0.099	-0.005	-0.017	-0.038	0.000	-0.023
155	-0.159	-0.011	-0.035	-0.066	-0.006	-0.042
150	-0.236	-0.019	-0.057	-0.104	-0.016	-0.070
145	-0.327	-0.028	-0.112	-0.151	-0.030	-0.105
140	-0.431	-0.034	-0.144	-0.206	-0.048	-0.148
135	-0.546	-0.035	-0.178	-0.268	-0.065	-0.195
130	-0.670	-0.027	-0.211	-0.334	-0.083	-0.247
125	-0.801	-0.006	-0.243	-0.421	-0.099	-0.304
120	-0.935	-0.032	-0.271	-0.492	-0.112	-0.363
115	-1.063	0.095	-0.289	-0.560	-0.120	-0.424
110	-1.190	0.196	-0.289	-0.616	-0.114	-0.477
105	-1.290	0.348	-0.257	-0.650	-0.082	-0.514
100	-1.260	0.567	-0.184	-0.652	-0.016	-0.528
95	-1.382	0.866	-0.061	-0.617	0.088	-0.517
90	-1.355	1.256	0.116	-0.539	0.233	-0.474
85	-1.271	1.749	0.360	-0.409	-0.435	-0.395

Becke3P86/6-311++G(3df,3pd) DFT models computes an exothermicity of 29.82 and 31.83 kcal/mol, respectively. The obtained values are very close to the QCISD(T) calculations with using 6-311+G(2d,2p) and 6-311++G(3df,3pd) basis sets (Table III).

There is a considerable problem using the DFT method to search and optimize transition state structures for the  $F+H_2 \rightarrow HF+H$  reaction. For example, our attempt to find and optimize the transition state structure with the local spin density approximation (LSDA) was unsuccessful, even if an already optimized transition state structure with any of the *ab initio* and DFT methods presented here was used as a beginning structure. In contrast to the *ab initio* methods, the procedure is straight forward. Because the QCISD(T) *ab initio* method predicts a linear transition state structure, all other calculations were performed with restricting the H–H–F angle to 180° (Table III). The computed bond distances with the *ab initio* and DFT methods are quite different. For example, all DFT methods predict a longer H–F bond (2.8–3.0 Å), contrary to the *ab initio* calculations: ROH (1.18), MP2 (~1.4 Å), and QCISD(T) (~1.5 Å). ROHF calculations that estimate the activation barrier to be almost 30 times higher than the best theoretical estimate employing a linear transition state (~2.0 kcal/mol).<sup>28</sup> All of the DFT calculations (hybrid and nonlocal) estimate the activation energy to be barely above 0 kcal/mol (Table III), which is closer to the previously estimated barrier.<sup>28</sup> On the other hand, the MP2 calculations generate higher energy. To obtain ~2.0 kcal/mol of activation energy, the computation with QCISD(T) and the large basis set, such as 6-311++G(3df,3pd) is required.

Another important question in the  $F+H_2 \rightarrow HF+H$  problem is whether the transition state structure is linear or bent (Table IV). Assuming that the bond distances are obtained with the highest theory level, the QCISD(T)/6-311++G(3df,3pd) is also the most accurate. The single point

DFT calculations on this geometry with variation of the F–H–H angle was performed. The potential energy surface for all calculations is very shallow, indicating the reason why the DFT methods have convergence problems. The angle for minimum energy varies from method to method; however, for the Becke3LYP and Becke3P86, it is between 100°–115°. This approach was previously employed by Scuseria<sup>24</sup> on the linear transition state geometry obtained by CCSD(T) and [5s5p3d2f1g/4s3p2d1f] basis sets. This calculation generates transition state structures ( $r_{HF}=2.913$  and  $r_{HH}=1.445$  Å) that are substantially different than our *ab initio* and DFT calculations. Full optimization of the transition state structures (Table V) indicates a deviation from linearity. Only the ROHF methods predict an almost linear transition structure. The shallow depth of the potential around the transition structures is perfectly demonstrated with almost identical activation energies calculated for linear (Table III) and bent (Table V) transition state structures.

## CONCLUSION

Considering the examples that are difficult to solve by *ab initio* methods, it was demonstrated that the hybrid DFT methods, particularly Becke3LYP, produce geometries, energies, and electron affinities that are better than RHF, MP2, MP3, and even MP4 calculations. In most of the studies, the obtained results can be compared to the QCISD(T) values. Although hybrid DFT methods show lower sensitivity toward chosen basis set, it was demonstrated that the calculation with lower basis sets, 6-31+G(d,p), produce satisfactory results that are in excellent agreement with 6-311++G(2d,2p), and with 6-311++G(3df,3pd). We suggest the calculations with Becke3LYP/6-311+G(2d,2p) to be a theoretical model that should be accepted as the standard. The nonlocal DFT methods similar to the MPn *ab initio*

TABLE V. Geometry of the transition state structure and the barrier height (kcal/mol) for  $F+H_2 \rightarrow HF+H$  calculated by using 6-31+G(d,p) basis set.

Method	$r_{HH}(\text{\AA})$	$r_{HF}(\text{\AA})$	$\alpha_{HHF}(\text{^\circ})$	$E(\text{hartree})$	$\Delta E$
ROHF	0.831	1.176	179.22	-100.4534337	29.03
Becke3LYP	0.743	2.727	152.20	-100.9089671	0.10
Becke3P86	0.744	2.735	158.03	-101.0950270	0.28
BLYP	0.747	2.726	160.85	-100.8885822	0.19
BP86	0.751	2.938	167.44	-100.8978184	0.43
MP2	0.773	1.394	162.07	-100.6459091	6.63

methods, tend to overestimate electron correlations and produce longer bonds and lower energies. The question of linear or bent transition state structures for fluorine radical displacement of the hydrogen radical is addressed. While ROHF and QCISD(T) prefer linear or nearly linear transition state structures, the hybrid and nonlocal DFT methods prefer a bent transition state structure with a FHH angle of  $152^\circ$ – $167^\circ$ . On the basis of the presented results, the Becke3LYP/6-311+G(3df,3pd) theoretical model should produce the same quality of results as do most of the sophisticated quantum chemistry techniques. Due to modest computational cost, Becke3LYP can be applicable to large molecular systems. This should be especially applicable for the study of the decomposition of the energetic molecules with many polar bonds and possible radical degradation pathways.

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