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Electronic Supporting Information

for

The Bader Energy Density: A new topological tool into the framework of Bader's Theory used to explain the instability of PH_5

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E.S.I.1 Table of Electronic Energy in a.u. for fluorine systems computed at different levels of theory. Basis set: Aug-cc-pVTZ.

	HF	MP2	QCISD	CCSD
PF_5	-838.3174734	-839.7646813	-839.7639915	-839.7597792
PF_5 (elongated)	-838.2603209	-839.7656592	-839.7650232	-839.7608302
PF_3	-639.3055895	-640.2226753	-640.2293579	-640.2262218
F_2	-198.7609356	-199.2909071	-199.2950716	-199.2938511

E.S.I.2 Table of Electronic Energy in a.u. for hydrogen systems computed at different levels of theory. Basis set: Aug-cc-pVTZ.

	HF	MP2	QCISD	CCSD
PH_5	-343.5500600	-343.7592943	-343.7941119	-343.7938719
PH_5 (elongated)	-343.5514162	-343.7603523	-343.7951027	-343.7948647
PH_3	-342.4881819	-342.6612882	-342.6893993	-342.6891697
H_2	-1.1330558	-1.1650230	-1.1726355	-1.1726355

E.S.I.3 Table of PF_5 (elongated) source function (SF) atomic percentage contribution calculated into BCPs at different levels of theory. Basis set: Aug-cc-pVTZ.

HF								
BCP	ρ (e/bohr³)	SF%(P_1)	SF%(F_1)	SF%(F_2)	SF%(F_3)	SF%(F_4)	SF%(F_5)	TOT SF%
P-F_{eq1}	0.22984	28.42	53.57	3.71	3.71	5.75	5.75	100.90
P-F_{ax1}	0.11291	9.33	14.20	44.33	4.18	14.20	14.20	100.44
P-F_{ax2}	0.11291	9.25	14.19	4.18	44.34	14.20	14.20	100.35
P-F_{eq2}	0.22984	28.59	5.75	3.71	3.71	53.57	5.75	101.06
P-F_{eq3}	0.22984	28.59	5.74	3.71	3.71	5.75	53.57	101.06
MP2								
BCP	ρ (e/bohr³)	SF%(P_1)	SF%(F_1)	SF%(F_2)	SF%(F_3)	SF%(F_4)	SF%(F_5)	TOT SF%
P-F_{eq1}	0.18422	22.83	50.62	7.26	7.26	5.83	5.83	99.62
P-F_{ax1}	0.17244	21.36	8.59	48.39	4.65	8.59	8.59	100.17
P-F_{ax2}	0.17244	21.36	8.59	4.65	48.39	8.59	8.59	100.17
P-F_{eq2}	0.18422	22.94	5.82	7.26	7.26	50.81	5.83	99.92
P-F_{eq3}	0.18422	22.94	5.82	7.26	7.26	5.83	50.81	99.92
QCISD								
BCP	ρ (e/bohr³)	SF%(P_1)	SF%(F_1)	SF%(F_2)	SF%(F_3)	SF%(F_4)	SF%(F_5)	TOT SF%
P-F_{eq1}	0.18763	23.72	51.02	7.18	7.18	5.78	5.78	100.65
P-F_{ax1}	0.17516	21.53	8.55	48.35	4.61	8.55	8.55	100.14
P-F_{ax2}	0.17516	21.53	8.55	4.61	48.34	8.55	8.55	100.14
P-F_{eq2}	0.18763	23.80	5.78	7.18	7.18	51.03	5.78	100.74
P-F_{eq3}	0.18763	23.80	5.78	7.18	7.18	5.78	51.02	100.74
CCSD								
BCP	ρ (e/bohr³)	SF%(P_1)	SF%(F_1)	SF%(F_2)	SF%(F_3)	SF%(F_4)	SF%(F_5)	TOT SF%
P-F_{eq1}	0.18826	23.75	51.05	7.17	7.17	5.77	5.77	100.68
P-F_{ax1}	0.17565	21.51	8.55	48.38	4.60	8.55	8.55	100.13
P-F_{ax2}	0.17565	21.51	8.54	4.60	48.38	8.55	8.55	100.13
P-F_{eq2}	0.18826	23.83	5.77	7.17	7.17	51.06	5.77	100.77
P-F_{eq3}	0.18826	23.83	5.77	7.17	7.17	5.77	51.06	100.76

E.S.I.4 Table of PH_5 elongated source function (SF) atomic percentage contribution calculated into BCPs at different levels of theory. Basis set: Aug-cc-pVTZ.

HF								
BCP	ρ (e/bohr³)	SF%(P_1)	SF%(H_1)	SF%(H_2)	SF%(H_3)	SF%(H_4)	SF%(H_5)	TOT SF%
P-H_{eq1}	0.17284	29.20	48.39	6.14	6.14	5.20	5.20	100.26
P-H_{ax1}	0.15567	27.03	7.75	45.90	4.05	7.75	7.75	100.24
P-H_{ax2}	0.15567	27.03	7.75	4.05	45.90	7.75	7.75	100.24
P-H_{eq2}	0.17284	29.19	5.20	6.14	6.14	48.40	5.20	100.26
P-H_{eq3}	0.17284	29.19	5.20	6.14	6.14	5.20	48.40	100.26
MP2								
BCP	ρ (e/bohr³)	SF%(P_1)	SF%(H_1)	SF%(H_2)	SF%(H_3)	SF%(H_4)	SF%(H_5)	TOT SF%
P-H_{eq1}	0.1694	30.46	47.24	6.09	6.09	5.05	5.05	99.98
P-H_{ax1}	0.15677	28.98	7.30	45.14	3.93	7.30	7.30	99.95
P-H_{ax2}	0.15677	28.98	7.30	3.93	45.15	7.30	7.30	99.95
P-H_{eq2}	0.1694	30.45	5.05	6.09	6.09	47.25	5.05	99.98
P-H_{eq3}	0.1694	30.45	5.05	6.09	6.09	5.05	47.25	99.98
QCISD								
BCP	ρ (e/bohr³)	SF%(P_1)	SF%(H_1)	SF%(H_2)	SF%(H_3)	SF%(H_4)	SF%(H_5)	TOT SF%
P-H_{eq1}	0.16805	31.93	47.06	6.06	6.06	5.01	5.01	101.15
P-H_{ax1}	0.1561	30.54	7.22	45.02	3.89	7.22	7.22	101.11
P-H_{ax2}	0.1561	30.53	7.22	3.89	45.02	7.22	7.22	101.11
P-H_{eq2}	0.16805	31.90	5.01	6.06	6.06	47.07	5.01	101.12
P-H_{eq3}	0.16805	31.90	5.01	6.06	6.06	5.01	47.07	101.12
CCSD								
BCP	ρ (e/bohr³)	SF%(P_1)	SF%(H_1)	SF%(H_2)	SF%(H_3)	SF%(H_4)	SF%(H_5)	TOT SF%
P-H_{eq1}	0.16812	30.65	47.08	6.07	6.07	5.02	5.02	99.90
P-H_{ax1}	0.15615	29.27	7.22	45.03	3.90	7.22	7.22	99.87
P-H_{ax2}	0.15615	29.27	7.22	3.90	45.03	7.22	7.22	99.87
P-H_{eq2}	0.16812	30.64	5.02	6.07	6.07	47.08	5.02	99.89
P-H_{eq3}	0.16812	30.64	5.02	6.07	6.07	5.02	47.08	99.89

E.S.I.5 Table ofPF_5 source function (SF) atomic percentage contribution calculated into BCPs at different levels of theory. Basis set: Aug-cc-pVTZ.

HF								
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(F_1)	SF%(F_2)	SF%(F_3)	SF%(F_4)	SF%(F_5)	TOT SF%
P-F_{eq1}	0.19019	22.65	51.17	7.52	7.52	5.54	5.54	99.94
P-F_{ax1}	0.19171	22.21	7.76	49.37	4.51	7.76	7.76	99.38
P-F_{ax2}	0.19171	22.21	7.76	4.51	49.38	7.76	7.76	99.37
P-F_{eq2}	0.19019	22.75	5.54	7.52	7.52	51.18	5.54	100.05
P-F_{eq3}	0.19019	22.74	5.54	7.52	7.52	5.54	51.18	100.04
MP2								
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(F_1)	SF%(F_2)	SF%(F_3)	SF%(F_4)	SF%(F_5)	TOT SF%
P-F_{eq1}	0.17850	22.00	50.44	7.81	7.81	5.80	5.80	99.66
P-F_{ax1}	0.18052	21.71	8.01	48.73	4.68	8.01	8.01	99.16
P-F_{ax2}	0.18052	21.72	8.01	4.68	48.73	8.01	8.01	99.16
P-F_{eq2}	0.17850	22.07	5.79	7.81	7.81	50.46	5.80	99.74
P-F_{eq3}	0.17850	22.07	5.79	7.81	7.81	5.80	50.46	99.74
QCISD								
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(F_1)	SF%(F_2)	SF%(F_3)	SF%(F_4)	SF%(F_5)	TOT SF%
P-F_{eq1}	0.18171	22.11	50.67	7.74	7.74	5.75	5.75	99.76
P-F_{ax1}	0.18355	21.75	7.96	48.90	4.64	7.96	7.96	99.18
P-F_{ax2}	0.18355	21.76	7.96	4.65	48.89	7.96	7.96	99.18
P-F_{eq2}	0.18171	22.18	5.75	7.74	7.74	50.67	5.75	99.83
P-F_{eq3}	0.18171	22.19	5.75	7.74	7.74	5.75	50.67	99.84
CCSD								
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(F_1)	SF%(F_2)	SF%(F_3)	SF%(F_4)	SF%(F_5)	TOT SF%
P-F_{eq1}	0.18230	22.13	50.66	7.73	7.73	5.74	5.74	99.73
P-F_{ax1}	0.18413	21.81	7.95	48.90	4.64	7.95	7.96	99.21
P-F_{ax2}	0.18413	21.80	7.95	4.64	48.90	7.95	7.96	99.20
P-F_{eq2}	0.18230	22.21	5.73	7.73	7.73	50.67	5.74	99.81
P-F_{eq3}	0.18230	22.20	5.73	7.73	7.73	5.74	50.67	99.80

E.S.I.6 Table of PH_5 source function (SF) atomic percentage contribution calculated into BCPs at different levels of theory. Basis set: Aug-cc-pVTZ.

HF								
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(H_1)	SF%(H_2)	SF%(H_3)	SF%(H_4)	SF%(H_5)	TOT SF%
P-H_{eq1}	0.16645	28.12	47.84	6.79	6.79	5.12	5.12	99.78
P-H_{ax1}	0.16571	27.66	7.07	46.76	4.15	7.07	7.07	99.79
P-H_{ax2}	0.16571	27.66	7.07	4.15	46.76	7.07	7.07	99.79
P-H_{eq2}	0.16645	28.11	5.12	6.79	6.79	47.88	5.12	99.81
P-H_{eq3}	0.16645	28.11	5.12	6.79	6.79	5.12	47.87	99.81
MP2								
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(H_1)	SF%(H_2)	SF%(H_3)	SF%(H_4)	SF%(H_5)	TOT SF%
P-H_{eq1}	0.16399	30.03	46.70	6.67	6.67	4.95	4.95	99.97
P-H_{ax1}	0.16512	29.74	6.74	45.97	4.04	6.74	6.74	99.97
P-H_{ax2}	0.16512	29.74	6.74	4.04	45.97	6.74	6.74	99.97
P-H_{eq2}	0.16399	30.03	4.95	6.67	6.67	46.70	4.95	99.97
P-H_{eq3}	0.16399	30.03	4.95	6.67	6.67	4.95	46.70	99.97
QCISD								
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(H_1)	SF%(H_2)	SF%(H_3)	SF%(H_4)	SF%(H_5)	TOT SF%
P-H_{eq1}	0.16275	31.64	46.47	6.63	6.63	4.91	4.91	101.20
P-H_{ax1}	0.16416	31.31	6.67	45.84	4.02	6.67	6.67	101.18
P-H_{ax2}	0.16416	31.31	6.67	4.02	45.84	6.67	6.67	101.18
P-H_{eq2}	0.16275	31.62	4.91	6.63	6.63	46.51	4.91	101.21
P-H_{eq3}	0.16275	31.62	4.91	6.63	6.63	4.91	46.51	101.21
CCSD								
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(H_1)	SF%(H_2)	SF%(H_3)	SF%(H_4)	SF%(H_5)	TOT SF%
P-H_{eq1}	0.16282	31.62	46.49	6.64	6.63	4.91	4.91	101.21
P-H_{ax1}	0.1642	31.29	6.68	45.85	4.02	6.68	6.68	101.20
P-H_{ax2}	0.1642	31.29	6.68	4.02	45.85	6.68	6.68	101.20
P-H_{eq2}	0.16282	31.60	4.91	6.64	6.63	46.53	4.91	101.23
P-H_{eq3}	0.16282	31.60	4.91	6.64	6.63	4.91	46.53	101.23

E.S.I.8 Table of PF_3 source function (SF) atomic percentage contribution calculated into BCPs at different levels of theory. Basis set: Aug-cc-pVTZ.

HF						
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(F_1)	SF%(F_2)	SF%(F_3)	TOT SF%
P-F_1	0.17893	34.53	51.10	7.09	7.10	99.82
P-F_2	0.17893	34.85	7.10	51.32	7.10	100.36
P-F_3	0.17893	34.53	7.10	7.09	51.11	99.82
MP2						
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(F_1)	SF%(F_2)	SF%(F_3)	TOT SF%
P-F_1	0.16732	35.89	50.20	7.32	7.32	100.73
P-F_2	0.16732	36.04	7.32	50.42	7.32	101.09
P-F_3	0.16732	35.87	7.32	7.32	50.22	100.73
QCISD						
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(F_1)	SF%(F_2)	SF%(F_3)	TOT SF%
P-F_1	0.17002	34.58	50.49	7.28	7.28	99.63
P-F_2	0.17002	34.83	7.28	50.49	7.28	99.88
P-F_3	0.17002	34.80	7.28	7.28	50.50	99.86
CCSD						
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(F_1)	SF%(F_2)	SF%(F_3)	TOT SF%
P-F_1	0.17077	34.86	50.41	7.27	7.28	99.82
P-F_2	0.17077	35.07	7.28	50.61	7.28	100.23
P-F_3	0.17077	34.86	7.28	7.27	50.40	99.81

E.S.I.9Table of PH_3 source function (SF) atomic percentage contribution calculated into BCPs at different levels of theory. Basis set: Aug-cc-pVTZ.

HF						
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(H_1)	SF%(H_2)	SF%(H_3)	TOT SF%
P-H_1	0.16627	40.37	47.14	6.57	6.57	100.66
P-H_2	0.16627	40.39	6.57	47.14	6.57	100.67
P-H_3	0.16627	40.37	6.57	6.57	47.14	100.66
MP2						
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(H_1)	SF%(H_2)	SF%(H_3)	TOT SF%
P-H_1	0.16325	42.13	45.61	6.43	6.43	100.59
P-H_2	0.16325	42.15	6.43	45.59	6.43	100.59
P-H_3	0.16325	42.13	6.43	6.43	45.61	100.60
QCISD						
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(H_1)	SF%(H_2)	SF%(H_3)	TOT SF%
P-H_1	0.1621	42.41	45.55	6.38	6.38	100.72
P-H_2	0.1621	42.40	6.38	45.54	6.38	100.70
P-H_3	0.1621	42.42	6.38	6.38	45.54	100.72
CCSD						
BCP	ρ (e/bohr^3)	SF%(P_1)	SF%(H_1)	SF%(H_2)	SF%(H_3)	TOT SF%
P-H_1	0.16218	43.49	45.55	6.38	6.38	101.80
P-H_2	0.16218	43.56	6.38	45.53	6.38	101.86
P-H_3	0.16218	43.49	6.38	6.38	45.55	101.80

E.S.I.10Table of delocalization indexes δ(I,J) for the systems involved in the dissociation reactions, investigated at Hartree-Fock HF /Aug-cc-pVTZ.

PH_5 (elongated)														
$\delta(P_1,H_1)$	$\delta(P_1,H_2)$	$\delta(P_1,H_3)$	$\delta(P_1,H_4)$	$\delta(P_1,H_5)$	$\delta(H_1,H_2)$	$\delta(H_1,H_3)$	$\delta(H_1,H_4)$	$\delta(H_1,H_5)$	$\delta(H_2,H_3)$	$\delta(H_2,H_4)$	$\delta(H_2,H_5)$	$\delta(H_3,H_4)$	$\delta(H_3,H_5)$	$\delta(H_4,H_5)$
0.57	0.47	0.47	0.57	0.57	0.15	0.15	0.06	0.06	0.03	0.15	0.15	0.15	0.15	0.06
PF_5														
$\delta(P_1,F_1)$	$\delta(P_1,F_2)$	$\delta(P_1,F_3)$	$\delta(P_1,F_4)$	$\delta(P_1,F_5)$	$\delta(F_1,F_2)$	$\delta(F_1,F_3)$	$\delta(F_1,F_4)$	$\delta(F_1,F_5)$	$\delta(F_2,F_3)$	$\delta(F_2,F_4)$	$\delta(F_2,F_5)$	$\delta(F_3,F_4)$	$\delta(F_3,F_5)$	$\delta(F_4,F_5)$
0.36	0.21	0.21	0.36	0.36	0.16	0.16	0.07	0.07	0.00	0.16	0.16	0.16	0.16	0.07
PH_3 (elongated)														
$\delta(P_1,H_1)$	$\delta(P_1,H_2)$	$\delta(P_1,H_3)$	$\delta(H_1,H_2)$	$\delta(H_1,H_3)$	$\delta(H_2,H_3)$	-	-	-	-	-	-	-	-	-
0.79	0.80	0.79	0.14	0.14	0.14	-	-	-	-	-	-	-	-	-
PF_3														
$\delta(P_1,F_1)$	$\delta(P_1,F_2)$	$\delta(P_1,F_3)$	$\delta(F_1,F_2)$	$\delta(F_1,F_3)$	$\delta(F_2,F_3)$	-	-	-	-	-	-	-	-	-
0.50	0.50	0.50	0.15	0.15	0.15	-	-	-	-	-	-	-	-	-
H_2														
$\delta(H_1,H_2)$	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1.00	-	-	-	-	-	-	-	-	-	-	-	-	-	-
F_2														
δ(F1,F2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-
1.29	-	-	-	-	-	-	-	-	-	-	-	-	-	-

E.S.I.11 Table of F_2source function (SF) atomic percentage contribution calculated into BCPs for each theoretical approach. Basis set: Aug-cc-pVTZ.

HF				
BCP	ρ (e/bohr^3)	SF%(F_1)	SF%(F_2)	TOT SF%
F1-F2	0.37755	49.99	50.00	99.99
MP2				
BCP	ρ (e/bohr^3)	SF%(F_1)	SF%(F_2)	TOT SF%
F1-F2	0.28983	50.00	50.00	100.00
QCISD				
BCP	ρ (e/bohr^3)	SF%(F_1)	SF%(F_2)	TOT SF%
F1-F2	0.29652	49.99	49.99	99.98
CCSD				
BCP	ρ (e/bohr^3)	SF%(F_1)	SF%(F_2)	TOT SF%
F1-F2	0.29782	50.02	50.01	100.03

E.S.I.12 Table of H_2 source function (SF) atomic percentage contribution calculated into BCPs for each theoretical approach. Basis set: Aug-cc-pVTZ.

HF				
BOND	ρ (e/bohr^3)	SF%(H_1)	SF%(H_2)	TOT SF%
H1-H2	0.27451	49.99	49.99	99.97
MP2				
BCP	ρ (e/bohr^3)	SF%(H_1)	SF%(H_2)	TOT SF%
H1-H2	0.27242	50.00	50.00	100.01
QCISD				
BCP	ρ (e/bohr^3)	SF%(H_1)	SF%(H_2)	TOT SF%
H1-H2	0.26783	50.01	50.01	100.02
CCSD				
BCP	ρ (e/bohr^3)	SF%(H_1)	SF%(H_2)	TOT SF%
H1-H2	0.26783	50.01	50.01	100.02

E.S.I.13 Table of elongated PF_5 integrated atomic charge for each theoretical approach. Basis set: Aug-cc-pVTZ.

ATOM	HF	MP2	QCISD	CCSD
P	4.25	4.12	4.16	4.17
F_{eq1}	-0.86	-0.82	-0.83	-0.83
F_{ax1}	-0.84	-0.83	-0.83	-0.84
F_{ax2}	-0.84	-0.83	-0.83	-0.84
F_{eq2}	-0.86	-0.82	-0.83	-0.83
F_{eq3}	-0.86	-0.82	-0.83	-0.83

E.S.I.14 Table of elongated PH_5 integrated atomic charge for each theoretical approach. Basis set: Aug-cc-pVTZ.

ATOM	HF	MP2	QCISD	CCSD
P	3.35	3.11	3.07	3.07
H_{eq1}	-0.64	-0.59	-0.58	-0.58
H_{ax1}	-0.71	-0.67	-0.66	-0.67
H_{ax2}	-0.71	-0.67	-0.66	-0.67
H_{eq2}	-0.64	-0.59	-0.58	-0.58
H_{eq3}	-0.64	-0.59	-0.58	-0.58

E.S.I.15 Table of PF_3 integrated atomic charge for each theoretical approach. Basis set: Aug-cc-pVTZ.

ATOM	HF	MP2	QCISD	CCSD
P	2.64	2.52	2.54	2.55
F_1	-0.88	-0.84	-0.85	-0.85
F_2	-0.88	-0.84	-0.85	-0.85
F_3	-0.88	-0.84	-0.85	-0.85

E.S.I.16 Table of PH_3 integrated atomic charge for each theoretical approach. Basis set: Aug-cc-pVTZ.

ATOM	HF	MP2	QCISD	CCSD
P	1.90	1.70	1.69	1.69
H_1	-0.63	-0.56	-0.56	-0.56
H_2	-0.63	-0.56	-0.56	-0.56
H_3	-0.63	-0.56	-0.56	-0.56

E.S.I.17 Table of F_2 integrated atomic charge for each theoretical approach. Basis set: Aug-cc-pVTZ.*

ATOM	HF	MP2	QCISD	CCSD
F_1	0.00	0.00	0.00	0.00
F_2	0.00	0.00	0.00	0.00

*The results are null for symmetry but were reported for the sake of honesty

E.S.I.18 Table of H_2 integrated atomic charge for each theoretical approach. Basis set: Aug-cc-pVTZ.*

ATOM	HF	MP2	QCISD	CCSD
H_1	0.00	0.00	0.00	0.00
H_2	0.00	0.00	0.00	0.00

*The results are null for symmetry but were reported for the sake of honesty

E.S.I.19 Table of Atomic basin energies (a.u.) for different theoretical approach used for the reaction PF_5 -> PF_3 + F_2

PF_5	HF	MP2	QCISD	CCSD
P	-338.24	-338.42	-338.37	-338.36
F_{eq1}	-100.18	-100.27	-100.28	-100.28
F_{ax1}	-99.73	-100.27	-100.28	-100.28
F_{ax2}	-99.73	-100.27	-100.28	-100.28
F_{eq2}	-100.18	-100.27	-100.28	-100.28
F_{eq3}	-100.18	-100.27	-100.28	-100.28
PF_3	**HF**	**MP2**	**QCISD**	**CCSD**
P	-339.35	-339.62	-339.59	-339.58
F_1	-99.98	-100.20	-100.21	-100.21
F_2	-99.98	-100.20	-100.21	-100.21
F_3	-99.98	-100.20	-100.21	-100.21
F_2	**HF**	**MP2**	**QCISD**	**CCSD**
F_1	-99.38	-99.65	-99.65	-99.65
F_2	-99.38	-99.65	-99.65	-99.65

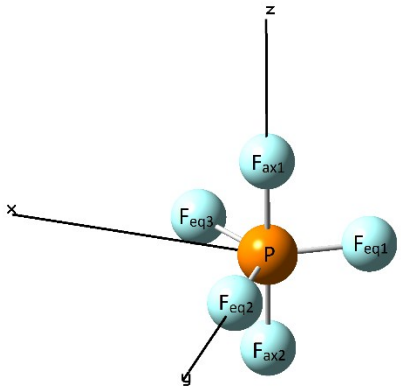
E.S.I.20 Table of Atomic basin energies (a.u) for different theoretical approach used for the reaction PH_5 -> PH_3 + H_2

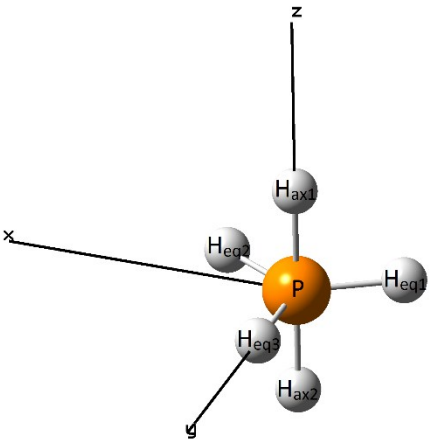
PH_5	HF	MP2	QCISD	CCSD
P	-339.18	-339.45	-339.47	-339.46
H_{eq1}	-0.87	-0.85	-0.86	-0.86
H_{ax1}	-0.88	-0.88	-0.88	-0.88
H_{ax2}	-0.88	-0.88	-0.88	-0.88
H_{eq2}	-0.87	-0.85	-0.86	-0.86
H_{eq3}	-0.87	-0.85	-0.86	-0.86
PH_3	HF	MP2	QCISD	CCSD
P	-340.00	-340.22	-340.23	-340.23
H_1	-0.83	-0.81	-0.82	-0.82
H_2	-0.83	-0.81	-0.82	-0.82
H_3	-0.83	-0.81	-0.82	-0.82
H_2	HF	MP2	QCISD	CCSD
H_1	-0.57	-0.58	-0.59	-0.59
H_2	-0.57	-0.58	-0.59	-0.59

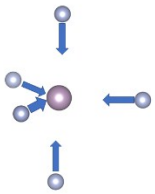
E.S.I.21 Table of bond distances (Å) for the elongated and not of PH_5 and $PF_5$and for PH_3 PF_3 F_2 H_2at each different level of theory

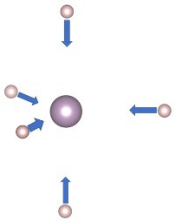
PH_5 (elongated)	HF	MP2	QCISD	CCSD
P-H_{eq}	1.40997	1.41751	1.42252	1.41237
P-H_{ax}	1.47448	1.47504	1.47931	1.47915
PH_5	HF	MP2	QCISD	CCSD
P-H	1.43438	1.43959	1.44446	1.44431
PF_5 (elongated)	HF	MP2	QCISD	CCSD
P-F_{eq}	1.45384	1.55100	1.54428	1.54282
P-F_{ax}	1.80000	1.58958	1.58310	1.58180
PF_5	HF	MP2	QCISD	CCSD
P-F	1.53567	1.56656	1.55993	1.55852
PH_3	HF	MP2	QCISD	CCSD
P-H	1.40781	1.41247	1.41742	1.41724
PF_3	HF	MP2	QCISD	CCSD
P-F	1.54731	1.58209	1.57537	1.57339
H_2	HF	MP2	QCISD	CCSD
H-H	0.73444	0.73744	0.74298	0.74298
F_2	HF	MP2	QCISD	CCSD
F-F	1.32819	1.40137	1.39708	1.39567

E.S.I.22 Table of Eigenvectors of Dipole moment tensor, μ_j, of atomic basin for the elongated PH_5 and PF_5at QCISD/Aug-cc-pVTZ level.









F_{eq1}			F_{ax1}			F_{ax2}			F_{eq2}			F_{eq3}		
μ_x	μ_y	μ_z	μ_x	μ_y	μ_z	μ_x	μ_y	μ_z	μ_x	μ_y	μ_z	μ_x	μ_y	μ_z
0.00	0.60	0.00	0.00	0.00	0.51	0.00	0.00	-0.51	0.52	-0.30	0.00	-0.52	-0.30	0.00
$\lvert\mu\rvert$/a.u.			$\lvert\mu\rvert$/a.u.			$\lvert\mu\rvert$/a.u.			$\lvert\mu\rvert$/a.u.			$\lvert\mu\rvert$/a.u.		
0.60			0.51			0.51			0.60			0.60		

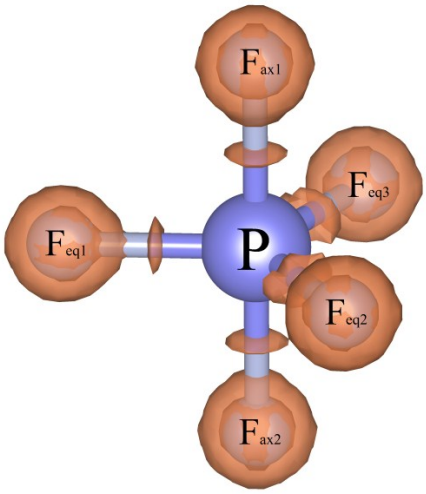
H_{eq1}			H_{ax1}			H_{ax2}			H_{eq2}			H_{eq3}		
μ_x	μ_y	μ_z	μ_x	μ_y	μ_z	μ_x	μ_y	μ_z	μ_x	μ_y	μ_z	μ_x	μ_y	μ_z
0.00	0.36	0.00	0.00	0.00	-0.26	0.00	0.00	0.26	-0.31	-0.18	0.00	0.31	-0.18	0.00
$\lvert\mu\rvert$/a.u.			$\lvert\mu\rvert$/a.u.			$\lvert\mu\rvert$/a.u.			$\lvert\mu\rvert$/a.u.			$\lvert\mu\rvert$/a.u.		
0.36			0.26			0.26			0.36			0.36		

E.S.I.23 "Bader like" calculated values of 3-centre bond indexes for X_{ax}-P-X_{ax}* and 2-centre bond indexes for P-X_{ax}* and P-X_{eq}* within PX_5.

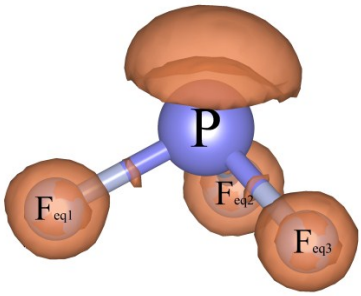
Bond Indexes	Basis Set		
	6-31G**	6-311G**	cc-pVTZ
H_{ax1}-P-H_{ax2}	-0.013	-0.013	-0.011
F_{ax1}-P-F_{ax2}	0.010	-	-
P-H_{ax1}	0.654	0.643	0.636
P-F_{ax1}	0.341	0.434	0.323
P-H_{eq1}	0.804	0.793	0.779
P-H_{eq1}	0.556	0.674	0.549

* Values obtained for P-X_{eq} bonds are all equal to each other by symmetry. Likewise in case of P-X_{ax}.

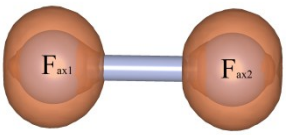
E.S.I.24 Plot of Laplacian of charge density at the null isosurface for all compounds involved into PX_5 dissociation reactions.



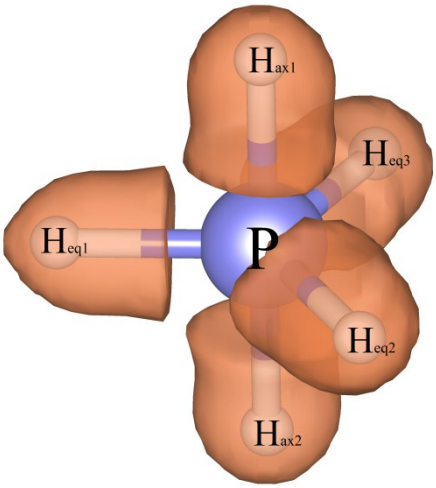
PF_5



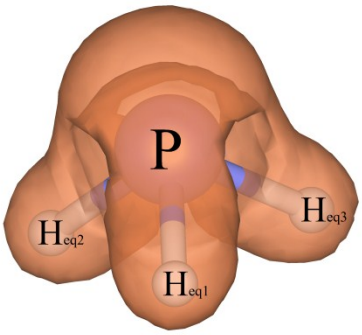
PF_3



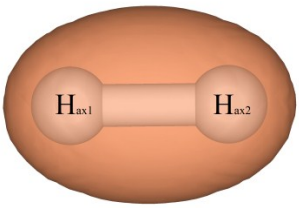
F_2



PH_5



PH_3



H_2

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