Supplementary Information (SI) for Physical Chemistry Chemical Physics.
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Electronic Supplementary Information

Ab initio electronic structures and total internal partition sums of $FeH^{+/2+}$

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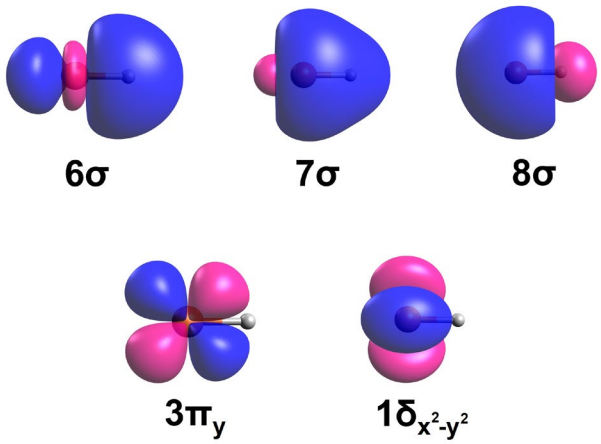

Figure S1. Select stage average CASSCF molecular orbitals of FeH^+ under an isovalue of 0.02 e/Å^3. The Fe (left atom) and H (right atom) of each orbital plot are shown in orange and gray colors, respectively. The 90° and 45° rotations of $3\pi_y$ and $1\delta_{x^2-y^2}$ respectively yield $3\pi_x$ and $1\delta_{xy}$ orbitals. Avogadro visualization software was utilized to plot molecular orbitals.[1, 2] Molecular orbitals of FeH^{2+} are qualitatively similar.

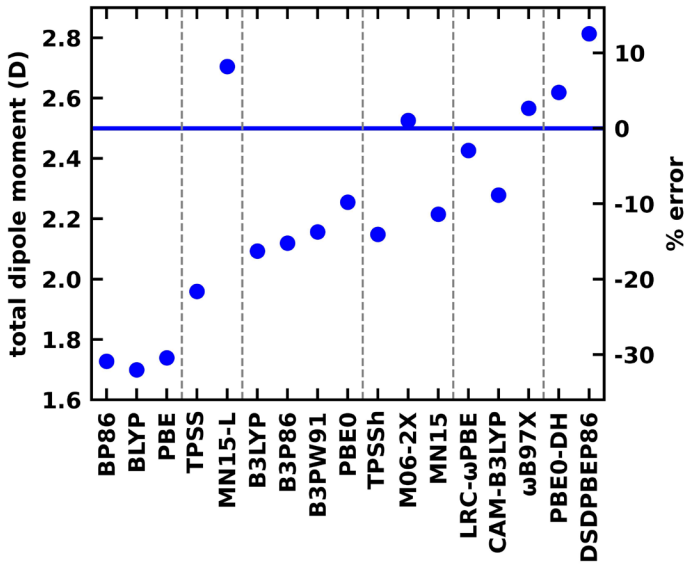

Figure S2. Total μ (D) of FeH^+ ($1^5\Delta$) under various of DFT functionals at the AQZ basis set (blue dots). Each class of density functional is separated with vertical gray dashed lines (i.e., left to right: GGA, MGGA, global GGA hybrid, MGGA hybrid, RSH, and DH). The blue horizontal line represents the AQZ-CCSD(T) total μ of FeH ($a^6\Delta$). The % DFT errors are calculated with respect to the AQZ-CCSD(T) total μ.

Table S1. Total μ (D) of FeH^+ ($1^5\Delta$) under various of DFT functionals at the AQZ basis set and % DFT errors of μ with respect to the AQZ-CCSD(T) μ.

Family of functional	DFA	μ	% DFT error of μ
GGA	BP86	1.73	-30.9
	BLYP	1.70	-32.0
	PBE	1.74	-30.4
MGGA	TPSS	1.96	-21.6
	MN15-L	2.70	8.2
Global GGA Hybrid	B3LYP	2.09	-16.3
	B3P86	2.12	-15.2
	B3PW91	2.16	-13.7
	PBE0	2.25	-9.8
MGGA Hybrid	TPSSh	2.15	-14.1
	M06-2X	2.53	1.0
	MN15	2.21	-11.4
RSH	LRC-ωPBE	2.43	-2.9
	CAM-B3LYP	2.28	-8.9
	ωB97X	2.57	2.6
DH	PBE0-DH	2.62	4.7
	DSDPBEP86	2.81	12.5

Table S2. The FeH^+ total internal partition function sum (TIPS) fit coefficients.

TIPS fit coefficient	N = 17
a_0	71.50708320
a_1	4.80121537
a_2	-2.27804388
a_3	0.07133026
a_4	1.63147380
a_5	-1.06112301
a_6	-3.13026361
a_7	3.63199386
a_8	4.53048612
a_9	-8.22442788
a_{10}	-1.54371893
a_{11}	9.43631754
a_{12}	-4.29681202
a_{13}	-3.12628672
a_{14}	3.79299826
a_{15}	-1.40973241
a_{16}	0.18795683

Table S3. The FeH^{2+} total internal partition function sum (TIPS) fit coefficients.

TIPS fit coefficient	N = 19
a_0	34.63325950
a_1	5.53542111
a_2	-1.53688247
a_3	-1.37361292
a_4	-0.47721383
a_5	0.58839798
a_6	2.34014731
a_7	1.35141182
a_8	-5.99708788
a_9	-2.47014607
a_{10}	11.17570580
a_{11}	-1.82504878
a_{12}	-10.85150190
a_{13}	7.88059971
a_{14}	1.92195008
a_{15}	-4.95239797
a_{16}	2.63275208
a_{17}	-0.63054239
a_{18}	0.05934423

Table S4. MRCI and MRCI+Q absolute energies of FeH^+ (Hartree).

State	Level of theory	Absolute energy
$X^5\Delta$	AQZ-MRCI	-1262.963065
	AQZ-MRCI+Q	-1262.968459
	AQZ-DK-MRCI	-1271.843978
	AQZ-DK-MRCI+Q	-1271.849433
$A^5\Pi$	AQZ-MRCI	-1262.959565
	AQZ-MRCI+Q	-1262.965164
	AQZ-DK-MRCI	-1271.841474
	AQZ-DK-MRCI+Q	-1271.847125
$B^5\Sigma^+$	AQZ-MRCI	-1262.943011
	AQZ-MRCI+Q	-1262.949144
	AQZ-DK-MRCI	-1271.827108
	AQZ-DK-MRCI+Q	-1271.833302
$a^3\Sigma^-$	AQZ-MRCI	-1262.918317
	AQZ-MRCI+Q	-1262.922398
	AQZ-DK-MRCI	-1271.794089
	AQZ-DK-MRCI+Q	-1271.798299
$b^3\Phi$	AQZ-MRCI	-1262.913695
	AQZ-MRCI+Q	-1262.917542
	AQZ-DK-MRCI	-1271.789777
	AQZ-DK-MRCI+Q	-1271.793748
$c^3\Pi$	AQZ-MRCI	-1262.908864
	AQZ-MRCI+Q	-1262.912771
	AQZ-DK-MRCI	-1271.785418
	AQZ-DK-MRCI+Q	-1271.789462
$d^3\Delta$	AQZ-MRCI	-1262.894435
	AQZ-MRCI+Q	-1262.898117
	AQZ-DK-MRCI	-1271.772146
	AQZ-DK-MRCI+Q	-1271.775985
$1^5\Sigma^-$	AQZ-MRCI	-1262.881440
	AQZ-MRCI+Q	-1262.884429
$1^5\Phi$	AQZ-MRCI	-1262.880513
	AQZ-MRCI+Q	-1262.883387
$2^5\Pi$	AQZ-MRCI	-1262.879304
	AQZ-MRCI+Q	-1262.882227
$2^5\Delta$	AQZ-MRCI	-1262.877123
	AQZ-MRCI+Q	-1262.879955
1^3H	AQZ-MRCI	-1262.870627
	AQZ-MRCI+Q	-1262.874930
$2^3\Pi$	AQZ-MRCI	-1262.869245
	AQZ-MRCI+Q	-1262.872765
$1^1\Gamma$	AQZ-MRCI	-1262.866401
	AQZ-MRCI+Q	-1262.870043
$1^1\Sigma^-$	AQZ-MRCI	-1262.865878
	AQZ-MRCI+Q	-1262.869487
$1^3\Gamma$	AQZ-MRCI	-1262.864987
	AQZ-MRCI+Q	-1262.868497
$2^3\Delta$	AQZ-MRCI	-1262.864924
	AQZ-MRCI+Q	-1262.868427
$2^3\Sigma^-$	AQZ-MRCI	-1262.864041
	AQZ-MRCI+Q	-1262.867701
$3^3\Pi$	AQZ-MRCI	-1262.860868
	AQZ-MRCI+Q	-1262.864533
$3^3\Sigma^-$	AQZ-MRCI	-1262.859958
	AQZ-MRCI+Q	-1262.864033
$1^1\Pi$	AQZ-MRCI	-1262.858369
	AQZ-MRCI+Q	-1262.861936
$2^3\Phi$	AQZ-MRCI	-1262.855896

	AQZ-MRCI+Q	-1262.859629
$3^3\Delta$	AQZ-MRCI	-1262.851196
	AQZ-MRCI+Q	-1262.855018
$3^5\Delta$	AQZ-MRCI	-1262.850320
	AQZ-MRCI+Q	-1262.853786
$3^5\Pi$	AQZ-MRCI	-1262.850093
	AQZ-MRCI+Q	-1262.853493
$2^5\Sigma^+$	AQZ-MRCI	-1262.849440
	AQZ-MRCI+Q	-1262.852711
$1^1\Phi$	AQZ-MRCI	-1262.845280
	AQZ-MRCI+Q	-1262.848893

Table S5. Absolute energy (Hartree), adiabatic dissociation energy with respect to the $Fe^+(^6D)+H(^2S)$ fragments D_e (kcal/mol), bond length r_e (Å), excitation energy T_e (cm^{-1}), harmonic vibrational frequency ω_e (cm^{-1}), anharmonicity $\omega_e x_e$ (cm^{-1}), equilibrium rotational constant B_e (cm^{-1}), anharmonic correction to the rotational constant α_e (cm^{-1}), and centrifugal distortion constant $\overline{D}_e$ (cm^{-1}) at the equilibrium distance of the 4 low-lying electronic states of FeH^+ under the CAS(8,7).

State	Level of theory	Absolute energy	D_e	r_e	T_e	ω_e	$\omega_e x_e$	B_e	α_e	$\overline{D}_e$
$X^5\Delta$	AQZ-DK-MRCI	-1271.832705	49.73	1.587	…	1843	39.7	6.773	0.2060	0.000376
	AQZ-DK-MRCI+Q	-1271.844056	53.14	1.578	…	1905	44.9	6.842	0.1939	0.000371
$A^5\Pi$	AQZ-DK-MRCI	-1271.829976	48.02	1.563	599	1827	48.5	6.916	0.2481	0.000399
	AQZ-DK-MRCI+Q	-1271.841371	51.45	1.558	589	1906	66.3	6.999	0.2329	0.000409
$B^5\Sigma^+$	AQZ-DK-MRCI	-1271.816596	39.62	1.630	3536	1640	25.8	6.420	0.2364	0.000382
	AQZ-DK-MRCI+Q	-1271.828277	43.23	1.616	3463	1734	35.3	6.539	0.2548	0.000371
$a^3\Sigma^-$	AQZ-DK-MRCI	-1271.771173	11.12	1.458	13505	2199	36.1	7.981	0.1305	0.000415
	AQZ-DK-MRCI+Q	-1271.785507	16.40	1.443	12850	2257	37.4	8.137	0.1279	0.000392

Table S6. MRCI and MRCI+Q absolute energies of FeH^{2+} (Hartree).

State	Level of theory	Absolute energy
$^4\Pi$	AQZ-MRCI	-1262.336777
	AQZ-MRCI+Q	-1262.337981
	AQZ-DK-MRCI	-1271.212750
	AQZ-DK-MRCI+Q	-1271.213988
$^4\Delta$	AQZ-MRCI	-1262.336163
	AQZ-MRCI+Q	-1262.337271
	AQZ-DK-MRCI	-1271.211928
	AQZ-DK-MRCI+Q	-1271.213062
$^6\Sigma^+$	AQZ-MRCI	-1262.332069
	AQZ-MRCI+Q	-1262.333232
	AQZ-DK-MRCI	-1271.209770
	AQZ-DK-MRCI+Q	-1271.211012
$^6\Delta$	AQZ-MRCI	-1262.330509
	AQZ-MRCI+Q	-1262.331466
	AQZ-DK-MRCI	-1271.206647
	AQZ-DK-MRCI+Q	-1271.207626
$^6\Pi$	AQZ-MRCI	-1262.329312
	AQZ-MRCI+Q	-1262.330293
	AQZ-DK-MRCI	-1271.205575
	AQZ-DK-MRCI+Q	-1271.206589
$^4\Sigma^+$	AQZ-MRCI	-1262.322967
	AQZ-MRCI+Q	-1262.323980
	AQZ-DK-MRCI	-1271.198810
	AQZ-DK-MRCI+Q	-1271.199861

References

[1] M. D. Hanwell *et al.*, J Cheminform **4** (2012) 17.
[2] *Avogadro: an open-source molecular builder and visualization tool*, Version 1.2.0.