Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information for: Extreme NMR shielding in fluoro-nitrogen cations

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Optimized geometries

CCSD(T)-F12b/cc-pVQZ-F12 optimized geometries. Units of Angstrom and degrees. Energies in atomic units (hartrees).

$\mathbf{HNF^+}$

```
CCSD(T)-F12/VQZ-F12  ENERGY=-154.51715792

Cartesian coordinates
 N       0.0000000000      0.0844114665     -0.6779960208
 H       0.0000000000     -0.9130568102     -1.0288827041
 F       0.0000000000     -0.0137916648      0.5544433865

Z-matrix
N
H 1 rNH
F 1 rNF 2 A1

rNH = 1.05738566
rNF = 1.23634572
A1 = 104.82490219
```

$\mathbf{H_2NF^{2+}}$

```
CCSD(T)-F12/VQZ-F12  ENERGY=-154.42521370

Cartesian coordinates
 N       0.0000000000      0.0000000000     -0.6240345715
 F       0.0000000000      0.0000000000      0.5772636214
 H       0.0000000000      0.9890872097     -1.1044416754
 H       0.0000000000     -0.9890872097     -1.1044416754

Z-matrix
N
F 1 rNF
H 1 rNH 2 a1
H 1 rNH 2 a1 3 d180

rNF   =   1.20129819
rNH   =   1.09958378
a1    = 115.90619474
d180 = 180.0
```

$\mathbf{NF^{2+}}$

```
CCSD(T)-F12/VQZ-F12  ENERGY=-152.99508217

Cartesian coordinates
 N       0.0000000000      0.0000000000     -0.6319771217
 F       0.0000000000      0.0000000000      0.4659293705

Z-matrix
N
F 1 rNF

rNF = 1.09790866
```

$\mathbf{N_2F^+}$

```
CCSD(T)-F12/VQZ-F12  ENERGY=-208.65723959

Cartesian coordinates
 N          0.0000000000        0.0000000000       -1.2795424426
 N          0.0000000000        0.0000000000       -0.1745238334
 F          0.0000000000        0.0000000000        1.0720201118

Z-matrix
N
N 1 rNN
X 2 rdum 1 a90
F 2 rNF 3 a90 1 d180

rNN = 1.10501861
rNF = 1.24654395
rdum = 1.0
a90  = 90.0
d180 = 180.0
```

$\mathbf{NF_2^+}$

```
CCSD(T)-F12/VQZ-F12  ENERGY=-253.66767274

Cartesian coordinates
 N       0.0000000000      0.0000000000     -0.5350756265
 F       0.0000000000      1.0056807990      0.1972440467
 F       0.0000000000     -1.0056807990      0.1972440467

Z-matrix
N
F 1 rNF
F 1 rNF 2 A1

rNF = 1.24406028
A1 = 107.87705777
```

HNF_2^{2+}

CCSD(T)-F12/VQZ-F12 ENERGY=-253.53844643

Cartesian coordinates

N	0.0000000000	0.0000000000	0.4275350284
H	0.0000000000	0.0000000000	1.5473158919
F	0.0000000000	1.0351069554	-0.1986471300
F	0.0000000000	-1.0351069554	-0.1986471300

Z-matrix

N

H 1 rNH

F 1 rNF 2 a1

F 1 rNF 2 a1 3 d180

rNH = 1.11978086

rNF = 1.20977291

a1 = 121.17160618

d180 = 180.0

$HNNF^{2+}$

CCSD(T)-F12/VQZ-F12 ENERGY=-208.56054817

Cartesian coordinates

N	0.0000000000	0.0000000000	-1.2056079358
N	0.0000000000	0.0000000000	-0.1173096807
H	0.0000000000	0.0000000000	-2.3070546140
F	0.0000000000	0.0000000000	1.0977282042

Z-matrix

N

X 1 rdum

N 1 rNN 2 a90

X 3 rdum 1 a90 2 d0

H 1 rNH 2 a90 3 d180

F 3 rNF 4 a90 1 d180

rNN = 1.08829826

rNH = 1.10144668

rNF = 1.21503788

rdum = 1.0

a90 = 90.0

d180 = 180.0

d0 = 0.0

$FNNF^{2+}$

CCSD(T)-F12/VQZ-F12 ENERGY=-307.58026622

Cartesian coordinates

N	0.0000000000	0.0000000000	-0.5444296863
N	0.0000000000	0.0000000000	0.5444296863
F	0.0000000000	0.0000000000	-1.7749606383
F	0.0000000000	0.0000000000	1.7749606383

Z-matrix

N

X 1 rdum

N 1 rNN 2 a90

X 3 rdum 1 a90 2 d0

F 1 rNF 2 a90 3 d180

F 3 rNF 4 a90 1 d180

rNN = 1.08885937

rNF = 1.23053095

rdum = 1.0

a90 = 90.0

d180 = 180.0

d0 = 0.0

NH_3F^+

CCSD(T)-F12/VQZ-F12 ENERGY=-155.90582058

Cartesian coordinates

N	0.0000000000	0.0000000000	-0.6913614851
F	0.0000000000	0.0000000000	0.6690373904
H	0.4897408197	0.8482559822	-1.0010348012
H	0.4897408197	-0.8482559822	-1.0010348012
H	-0.9794816393	0.0000000000	-1.0010348012

Z-matrix

N

F 1 rNF

H 1 rNH 2 A1

H 1 rNH 2 A1 3 D120

H 1 rNH 2 A1 4 D120

rNF = 1.36039888

rNH = 1.02726912

A1 = 107.54489214

D120 = 120.0

$NH_2F_2^+$

CCSD(T)-F12/VQZ-F12 ENERGY=-254.98888768

Cartesian coordinates

N	0.0000000000	0.0000000000	-0.5238828584
F	-1.0856876744	0.0000000000	0.2503404140
F	1.0856876744	0.0000000000	0.2503404140
H	0.0000000000	0.8729865391	-1.0785692161
H	0.0000000000	-0.8729865391	-1.0785692161

Z-matrix

N

X 1 rDUM

F 1 rNF 2 AXNF

F 1 rNF 2 AXNF 3 D180

H 1 rNH 2 AXNH 3 D90

H 1 rNH 2 AXNH 3 DM90

rNF = 1.33346894

rNH = 1.03430288

AXNF = 54.50665398

AXNH = 122.43144265

rDUM = 1.0

D180 = 180.0

D90 = 90.0

DM90 = -90.0

NHF_3^+

CCSD(T)-F12/VQZ-F12 ENERGY=-354.08036129

Cartesian coordinates

N	0.0000000000	0.0000000000	0.3450243545
H	0.0000000000	0.0000000000	1.3875910735
F	0.6168713479	-1.0684525163	-0.1093295609
F	-1.2337426959	0.0000000000	-0.1093295609
F	0.6168713479	1.0684525163	-0.1093295609

Z-matrix

N

H 1 rNH

F 1 rNF 2 A1

F 1 rNF 2 A1 3 D120

F 1 rNF 2 A1 4 D120

rNH = 1.04256672

rNF = 1.31474656

A1 = 110.21738155

D120 = 120.0

NF_4^+

CCSD(T)-F12/VQZ-F12 ENERGY=-453.16816733

Cartesian coordinates

N	0.0000000000	0.0000000000	0.0000000000
F	1.0654360405	0.0000000000	0.7533770492
F	-1.0654360405	0.0000000000	0.7533770492
F	0.0000000000	1.0654360405	-0.7533770492
F	0.0000000000	-1.0654360405	-0.7533770492

Z-matrix

N

F 1 RNF

F 1 RNF 2 TDA

F 1 RNF 2 TDA 3 D120

F 1 RNF 2 TDA 4 D120

RNF = 1.30488733

TDA = 109.471220634490692

D120 = 120.0

NF_3^{2+}

CCSD(T)-F12/VQZ-F12 ENERGY=-352.61609865

Cartesian coordinates

N	0.0000000000	0.0000000000	0.0000000000
F	0.6100994513	-1.0567232473	0.0000000000
F	-1.2201989025	0.0000000000	0.0000000000
F	0.6100994513	1.0567232473	0.0000000000

Z-matrix

N

F 1 rNF

F 1 rNF 2 a120

F 1 rNF 2 a120 3 d180

rNF = 1.22019890

a120 = 120.0

d180 = 180.0

$ONHF^+$

CCSD(T)-F12/VQZ-F12 ENERGY=-229.74914950

Cartesian coordinates

N	0.0000000000	0.3913225761	0.1526888397
O	0.0000000000	-0.2384478488	1.1053255819
H	0.0000000000	1.4363348113	0.0811508685
F	0.0000000000	-0.1639008671	-1.0477200685

Z-matrix

N

O 1 RNO

H 1 RNH 2 A1

F 1 RNF 2 A2 3 D180

RNO = 1.14198404

RNH = 1.04745800

RNF = 1.32259390

A1 = 127.38411258

A2 = 121.71016023

D180 = 180.0

ONF_2^+

CCSD(T)-F12/VQZ-F12 ENERGY=-328.83732082

Cartesian coordinates

N	0.0000000000	0.0000000000	0.1566425650
O	0.0000000000	0.0000000000	1.2888274251
F	0.0000000000	1.0581542659	-0.6004323342
F	0.0000000000	-1.0581542659	-0.6004323342

Z-matrix

N

O 1 RNO

F 1 RNF 2 A1

F 1 RNF 2 A1 3 D180

RNO = 1.13218486

RNF = 1.30109679

A1 = 125.58248547

D180 = 180.0

ONF^{2+}

CCSD(T)-F12/VQZ-F12 ENERGY=-228.27767191

Cartesian coordinates

N	0.0000000000	0.0000000000	-0.1073356824
F	0.0000000000	0.0000000000	1.0820153164
O	0.0000000000	0.0000000000	-1.1908661781

Z-matrix

N

X 1 rdum

F 1 rNF 2 a90

O 1 rNO 2 a90 3 d180

rNF = 1.1893510

rNO = 1.0835305

rdum = 1.0

a90 = 90.0

d180 = 180.0

Equilibrium geometry shielding

NMR shielding of N-F cations as a function of basis set and wave function expansion.

Table S1: Calculated equilibrium ^{19}F NMR shielding in NF cations. Units of ppm.

	Basis Set						
Contribution[a]	DZ	TZ	QZ	5Z	6Z	7Z	CBS
N_2F^+							
SCF	106.68	100.79	96.81	95.01	94.47	94.35	94.32
ΔSD	54.94	40.74	40.55				40.42
Δ(T)	-2.01	-0.21	-0.31				-0.38
ΔT	0.18	-0.44					-0.44
ΔQ [b]	0.05						0.05
Sum							133.97
NF_2^+							
SCF	-532.07	-552.05	-564.14	-569.28	-570.81	-571.11	-571.18
ΔSD	125.94	90.60	90.52				90.46
Δ(T)	10.39	12.84	12.42				12.12
ΔT	-5.70	-5.82					-5.82
ΔQ [b]	-0.91						-0.91
Sum							-475.33
NH_3F^+							
SCF	318.74	315.28	313.09	312.35	312.11	312.06	312.05
ΔSD	-1.33	-6.38	-5.98				-5.68
Δ(T)	-2.09	-2.00	-2.14				-2.24
ΔT	-0.42	-0.25					-0.25
ΔQ [b]	-0.44						-0.44
Sum							303.44
$NH_2F_2^+$							
SCF	206.64	200.98	197.78	196.53	196.12	196.04	196.02
ΔSD	-2.24	-8.97	-8.72				-8.55
Δ(T)	-5.36	-5.72	-5.95				-6.12
ΔT	-0.84	-0.75					-0.75
ΔQ [b]	-0.59						-0.59
Sum							180.02

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continued

	Basis Set						
Contribution[a]	DZ	TZ	QZ	5Z	6Z	7Z	CBS
NHF_3^+							
SCF	111.09	104.73	100.64	98.95	98.41	98.30	98.27
ΔSD	-0.88	-10.17	-10.25				-10.31
Δ(T)	-7.76	-8.29	-8.59				-8.81
ΔT [b]	-0.94	-0.87					-0.87
Sum							78.27
NF_4^+							
SCF	31.62	25.57	20.77	18.74	18.08	17.95	17.91
ΔSD	7.94	-4.67	-5.32				-5.79
Δ(T)	-8.22	-8.59	-8.91				-9.15
ΔT [b]	-0.69	-0.66					-0.66
Sum							2.30
$ONHF^+$							
SCF	-145.48	-159.56	-166.93	-170.00	-170.93	-171.11	-171.16
ΔSD	35.94	16.74	17.30				17.71
Δ(T)	-16.34	-17.25	-17.88				-18.35
ΔT	-3.96	-4.08					-4.08
ΔQ [b]	-1.86						-1.86
Sum							-177.73
ONF_2^+							
SCF	-110.77	-121.10	-127.77	-130.61	-131.48	-131.65	-131.69
ΔSD	53.06	33.60	33.21				32.92
Δ(T)	-8.18	-7.30	-7.63				-7.87
ΔT	-1.24	-1.52					-1.52
Sum							-108.17
HNF_2^{2+}							
SCF	-448.94	-473.59	-484.78	-489.45	-490.86	-491.14	-491.21
ΔSD	61.43	33.04	32.78				32.60
Δ(T)	8.32	8.48	7.78				7.26
ΔT	-3.71	-4.04					-4.04
ΔQ [b]	-2.89						-2.89
Sum							-458.27

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continued

	Basis Set						
Contribution[a]	DZ	TZ	QZ	5Z	6Z	7Z	CBS
$HNNF^{2+}$							
SCF	79.86	72.67	68.09	66.16	65.57	65.45	65.41
ΔSD	69.95	55.52	55.31				55.15
Δ(T)	1.10	3.51	3.53				3.54
ΔT	-0.26	-0.96					-0.96
ΔQ [b]	0.68						0.68
Sum							123.83
$FNNF^{2+}$							
SCF	45.69	39.13	34.28	32.16	31.52	31.39	31.36
ΔSD	91.73	75.42	74.97				74.65
Δ(T)	4.01	7.10	7.20				7.26
ΔT	-0.18	-0.95					-0.95
Sum							112.32
NF_3^{2+}							
SCF	-328.45	-344.64	-353.96	-358.01	-359.22	-359.46	-359.52
ΔSD	95.99	69.51	68.64				68.02
Δ(T)	10.42	12.66	12.45				12.30
ΔT	-1.91	-2.69					-2.69
Sum							-281.90
ONF^{2+}							
SCF	-51.73	-60.92	-66.94	-69.41	-70.19	-70.35	-70.39
ΔSD	110.46	92.12	91.91				91.75
Δ(T)	6.17	10.20	10.32				11.89
ΔT	-1.89	-2.98					-2.98
ΔQ [b]	2.38						2.38
Sum							32.65

[a] ACVXZ basis sets and all-electron calculations unless specified. ΔT are dzp (DZ) and tz2p (TZ) results (CBS is tz2p value), while ΔQ are dzp (DZ) results. [b] Frozen-core results.

Table S2: Calculated equilibrium ^{15}N NMR shielding in NF cations. Units of ppm.

	Basis Set						
Contribution[a]	DZ	TZ	QZ	5Z	6Z	7Z	CBS
N_2F^+, N1							
SCF	46.00	30.00	26.50	25.10	24.66	24.58	24.56
ΔSD	31.42	25.17	24.81				24.56
Δ(T)	1.46	2.75	2.83				2.89
ΔT	-0.04	-0.38					-0.38
ΔQ [b]	0.48						0.48
Sum							52.12
N_2F^+, N2							
SCF	-8.24	-23.09	-26.90	-28.56	-29.06	-29.15	-29.17
ΔSD	63.02	53.91	52.95				52.25
Δ(T)	6.16	8.45	8.64				8.78
ΔT	-0.96	-1.50					-1.50
ΔQ [b]	1.78						1.78
Sum							32.14
NF_2^+							
SCF	-712.79	-742.70	-754.89	-760.06	-761.56	-761.83	-761.89
ΔSD	275.93	242.04	240.03				238.57
Δ(T)	49.98	58.36	59.57				60.45
ΔT	-8.87	-10.76					-10.76
ΔQ [b]	3.25						3.25
Sum							-470.38
NH_3F^+							
SCF	157.48	144.21	142.21	141.41	141.15	141.11	141.09
ΔSD	4.00	2.23	1.77				1.43
Δ(T)	-1.24	-1.12	-1.14				-1.16
ΔT	-0.37	-0.25					-0.25
ΔQ [b]	0.06						0.06
Sum							141.01
$NH_2F_2^+$							
SCF	84.49	68.73	65.94	64.83	64.49	64.42	64.41
ΔSD	-2.46	-6.13	-6.84				-7.35
Δ(T)	-4.26	-4.56	-4.67				-4.76
ΔT	-0.55	-0.61					-0.61
ΔQ [b]	-0.27						-0.27
Sum							51.42

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continued

	Basis Set						
Contribution[a]	DZ	TZ	QZ	5Z	6Z	7Z	CBS
NHF_3^+							
SCF	32.27	15.72	12.43	11.08	10.66	10.58	10.57
ΔSD	-5.20	-10.85	-11.66				-12.26
Δ(T)	-5.83	-6.37	-6.56				-6.69
ΔT [b]	-0.23	-0.30					-0.30
Sum							-8.68
NF_4^+							
SCF	-10.59	-27.45	-31.07	-32.64	-33.12	-33.21	-33.23
ΔSD	-3.58	-11.27	-12.07				-12.65
Δ(T)	-5.73	-6.43	-6.64				-6.80
ΔT [b]	0.29	0.20					0.20
Sum							-52.49
$ONHF^+$							
SCF	-82.66	-103.94	-108.33	-110.27	-110.85	-110.96	-110.98
ΔSD	48.83	38.99	38.01				37.30
Δ(T)	0.59	2.50	2.57				2.62
ΔT	-0.47	-0.93					-0.93
ΔQ [b]	0.95						0.95
Sum							-71.05
ONF_2^+							
SCF	-43.43	-64.69	-68.66	-70.45	-70.99	-71.09	-71.11
ΔSD	36.39	28.20	27.67				27.29
Δ(T)	-1.11	0.79	0.85				0.89
ΔT	0.38	-0.09					-0.09
Sum							-43.02
$HNNF^{2+}$, N1							
SCF	97.73	86.26	83.61	82.44	82.10	82.03	82.02
ΔSD	34.71	28.82	28.30				27.92
Δ(T)	3.55	5.03	5.12				5.18
ΔT	-0.39	-0.70					-0.70
ΔQ [b]	0.81						0.81
Sum							115.23

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continued							
	Basis Set						
Contribution[a]	DZ	TZ	QZ	5Z	6Z	7Z	CBS
$HNNF^{2+}$, N2							
SCF	53.88	36.13	32.93	31.59	31.17	31.10	31.08
ΔSD	28.65	23.44	23.10				22.86
Δ(T)	0.83	2.14	2.19				2.23
ΔT	-0.30	-0.67					-0.67
ΔQ [b]	0.57						0.57
Sum							56.08
$FNNF^{2+}$							
SCF	86.77	72.66	69.80	68.59	68.22	68.15	68.14
ΔSD	30.53	25.20	24.81				24.53
Δ(T)	1.91	3.38	3.44				3.49
ΔT	-0.26	-0.66					-0.66
Sum							95.50
NF_3^{2+}							
SCF	-245.99	-270.18	-276.03	-278.87	-279.71	-279.87	-279.90
ΔSD	109.42	94.85	94.16				93.66
Δ(T)	22.51	26.40	26.75				27.01
ΔT	-1.262	-2.47					-2.47
Sum							-161.71
ONF^{2+}							
SCF	-45.03	-63.88	-68.25	-70.10	-70.67	-70.77	-70.79
ΔSD	62.89	55.08	54.62				54.28
Δ(T)	6.99	9.82	10.03				10.18
ΔT	-0.82	-1.55					-1.55
ΔQ [b]	2.00						2.00
Sum							-5.89

[a] ACVXZ basis sets and all-electron calculations unless specified. ΔT are dzp (DZ) and tz2p (TZ) results (CBS is tz2p value), while ΔQ are dzp (DZ) results. [b] Frozen-core results.

Solvent effects

Effect of solvation on calculated chemical shielding of N-F cations. Calculated at the RI-MP2/aug-cc-pwCVTZ (all-electron) and TPSS/pcSseg-3 levels of theory within Orca 5.0.3. Solvent model is CPCM with parameters for water and acetonitrile.The solvent effect is calculated as the difference between gas phase and solvated results, calculated at the CCSD(T)-F12b/cc-pVQZ-F12 optimized geometries used in this work.

Table S3: Solvent effect on shielding constants of N-F cations. Units of ppm

	RI-MP2/aug-cc-pwCVTZ				TPSS/pcSseg-3			
	^{19}F		^{15}N		^{19}F		^{15}N	
Molecule	water	acn	water	acn	water	acn	water	acn
NHF^+	98.25	96.51	-38.12	-37.60	108.59	106.86	41.17	40.55
NNF^+	0.89	1.00	-1.24	-1.21	1.57	1.56	-2.20	-2.16
NF_2^+	8.98	8.82	-6.47	-6.38	16.66	16.40	5.28	5.20
NH_3F^+	31.69	31.10	-9.56	-9.38	34.25	33.68	-8.31	-8.15
$NH_2F_2^+$	17.80	17.50	-6.85	-6.72	21.39	21.04	-6.22	-6.10
NHF_3^+	11.00	10.83	-2.69	-2.64	12.94	12.74	-3.00	-2.94
NF_4^+	1.14	1.12	-0.20	-0.19	1.30	1.28	-0.26	-0.25
$ONHF^+$	30.79	30.28	-4.25	-4.17	35.32	34.74	-8.37	-8.22
ONF_2^+	7.75	7.62	1.96	1.93	7.73	7.61	0.64	0.63
NF^{2+}	1.13	1.12	0.75	0.74	10.50	10.34	4.21	4.14
NH_2F^{2+}	110.94	108.93	-31.28	-30.77	106.78	105.00	-11.73	-11.52
NHF_2^{2+}	32.26	31.68	-19.77	-19.46	44.21	43.49	-7.53	-7.40
NF_3^{2+}	7.61	7.48	-3.80	-3.74	14.26	14.03	1.72	1.70
$HNNF^{2+}$	22.41	22.00	4.58	4.49	25.96	25.50	4.83	4.73
$FNNF^{2+}$	15.43	15.16	1.68	1.65	18.94	18.63	1.43	1.40
ONF^{2+}	6.07	5.96	-0.25	-0.25	7.85	7.73	-0.11	-0.11

DFT results

Table S4: DFT/aug-cc-pVTZ calculated equilibrium geometry shielding constants of HNF^+ and H_2NF^{2+}. Units of ppm. [a]

Method	^{19}F	^{15}N	^{1}H
	HNF^+		
B3LYP	-1883.2	-1795.0	5.2
BP86	-1937.1	-1689.9	5.4
KT2	-1327.3	-1160.1	9.2
PBE0	-2019.0	-1934.5	3.8
CC/CBS	-1394.4	-1283.1	9.3
	H_2NF^{2+}		
B3LYP	-2403.0	-2455.6	-12.2
BP86	-2409.5	-2275.0	-11.0
KT2	-1497.9	-1424.9	-0.2
PBE0	-2692.0	-2758.0	-16.7
CC/CBS	-1044.0	-453.9	12.9

[a] CC/CBS is the coupled-cluster CBS extrapolated value.

Basis sets

Hydrogen aug-cc-pV7Z

Primitives: 13s, 7p, 6d, 5f, 4g, 3h, 2i

Contracted: 8s, 7p, 6d, 5f, 4g, 3h, 2i

includes aug/diffuse functions of 1s, 1p, 1d, 1f, 1g, 1h, 1i

```
$ HYDROGEN
$ S-TYPE FUNCTIONS
   13    8    0
    7190.929446  0.000009    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
       0.000000  0.000000
    1076.486444  0.000068    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
       0.000000  0.000000
     266.962197  0.000312    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
       0.000000  0.000000
      80.908646  0.001227    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
       0.000000  0.000000
      27.603338  0.004274    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
       0.000000  0.000000
      10.128123  0.013908    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
       0.000000  0.000000
       3.801505  0.044520    1.00000000  0.00000000  0.00000000  0.00000000  0.00000000
       0.000000  0.000000
       1.493506  0.097438    0.00000000  1.00000000  0.00000000  0.00000000  0.00000000
       0.000000  0.000000
       0.679975  0.249320    0.00000000  0.00000000  1.00000000  0.00000000  0.00000000
       0.000000  0.000000
       0.274449  0.278658    0.00000000  0.00000000  0.00000000  1.00000000  0.00000000
       0.000000  0.000000
       0.127783  0.166929    0.00000000  0.00000000  0.00000000  0.00000000  1.00000000
       0.000000  0.000000
       0.061164  0.031442    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
       1.000000  0.000000
       0.018167  0.000000    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
       0.000000  1.000000
$ P-TYPE FUNCTIONS
    7    7    0
     14.7287063  1.00000000  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
       0.0000000
       6.2076095  0.00000000  1.00000000  0.00000000  0.00000000  0.00000000  0.00000000
       0.0000000
       2.6162797  0.00000000  0.00000000  1.00000000  0.00000000  0.00000000  0.00000000
       0.0000000
       1.1026659  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000  0.00000000
       0.0000000
       0.4647333  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000
       0.0000000
       0.1958680  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000
       0.0000000
       0.0628034  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
```

```
      1.0000000
$ D-TYPE FUNCTIONS
    6    6    0
       6.312687  1.00000000  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
       2.874992  0.00000000  1.00000000  0.00000000  0.00000000  0.00000000  0.00000000
       1.309360  0.00000000  0.00000000  1.00000000  0.00000000  0.00000000  0.00000000
       0.596323  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000  0.00000000
       0.271584  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000
       0.103144  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000
$ F-TYPE FUNCTIONS
    5    5    0
      6.6492797  1.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      3.1175378  0.00000000  1.00000000  0.00000000  0.00000000  0.00000000
      1.4616684  0.00000000  0.00000000  1.00000000  0.00000000  0.00000000
      0.6853083  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000
      0.2244438  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000
$ G-TYPE FUNCTIONS
    4    4    0
      4.5265189  1.00000000  0.00000000  0.00000000  0.00000000
      2.1475220  0.00000000  1.00000000  0.00000000  0.00000000
      1.0188515  0.00000000  0.00000000  1.00000000  0.00000000
      0.2817031  0.00000000  0.00000000  0.00000000  1.00000000
$ H-TYPE FUNCTIONS
    3    3    0
      3.5953260  1.00000000  0.00000000  0.00000000
      1.4712160  0.00000000  1.00000000  0.00000000
      0.5043276  0.00000000  0.00000000  1.00000000
$ I-TYPE FUNCTIONS
    2    2    0
      3.5686210  1.00000000  0.00000000
      0.8578942  0.00000000  1.00000000
```

Hydrogen aug-cc-pV8Z

Primitives: 15s, 8p, 7d, 6f, 5g, 4h, 3i, 2k

Contracted: 9s, 8p, 7d, 6f, 5g, 4h, 3i, 2k

includes aug/diffuse functions of 1s, 1p, 1d, 1f, 1g, 1h, 1i, 1k

```
$ S-TYPE FUNCTIONS
   15    9    0
  23615.6098119  0.000002    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      0.0000000  0.000000    0.00000000
   3536.5524944  0.000016    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      0.0000000  0.000000    0.00000000
    871.7746818  0.000070    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      0.0000000  0.000000    0.00000000
    278.9755882  0.000249    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      0.0000000  0.000000    0.00000000
     97.4378245  0.000895    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      0.0000000  0.000000    0.00000000
     35.9568780  0.002840    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      0.0000000  0.000000    0.00000000
```

```
     14.2727331  0.008454    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      0.0000000  0.000000    0.00000000
      5.9898527  0.021467    1.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      0.0000000  0.000000    0.00000000
      2.7879534  0.050343    0.00000000  1.00000000  0.00000000  0.00000000  0.00000000
      0.0000000  0.000000    0.00000000
      1.1754980  0.124305    0.00000000  0.00000000  1.00000000  0.00000000  0.00000000
      0.0000000  0.000000    0.00000000
      0.5995840  0.230482    0.00000000  0.00000000  0.00000000  1.00000000  0.00000000
      0.0000000  0.000000    0.00000000
      0.2520867  0.278324    0.00000000  0.00000000  0.00000000  0.00000000  1.00000000
      0.0000000  0.000000    0.00000000
      0.1168822  0.148197    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      1.0000000  0.000000    0.00000000
      0.0564851  0.022470    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      0.0000000  1.000000    0.00000000
      0.0172689  0.000000    0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      0.0000000  0.000000    1.00000000
$ P-TYPE FUNCTIONS
    8    8    0
     19.9350960  1.00000000  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      0.0000000  0.00000000
      9.0576305  0.00000000  1.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      0.0000000  0.00000000
      4.1153888  0.00000000  0.00000000  1.00000000  0.00000000  0.00000000  0.00000000
      0.0000000  0.00000000
      1.8698516  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000  0.00000000
      0.0000000  0.00000000
      0.8495783  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000
      0.0000000  0.00000000
      0.3860110  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000
      0.0000000  0.00000000
      0.1753864  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      1.0000000  0.00000000
      0.0639571  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      0.0000000  1.00000000
$ D-TYPE FUNCTIONS
    7    7    0
      8.9420070  1.00000000  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      0.0000000
      4.3682241  0.00000000  1.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      0.0000000
      2.1339037  0.00000000  0.00000000  1.00000000  0.00000000  0.00000000  0.00000000
      0.0000000
      1.0424248  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000  0.00000000
      0.0000000
      0.5092307  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000
      0.0000000
      0.2487623  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000
      0.0000000
      0.1031437  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      1.0000000
$ F-TYPE FUNCTIONS
    6    6    0
      9.5998430  1.00000000  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      4.8033678  0.00000000  1.00000000  0.00000000  0.00000000  0.00000000  0.00000000
```

```
      2.4034083  0.00000000  0.00000000  1.00000000  0.00000000  0.00000000  0.00000000
      1.2025670  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000  0.00000000
      0.6017152  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000
      0.2131359  0.00000000  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000
$ G-TYPE FUNCTIONS
    5    5    0
      5.7626060  1.00000000  0.00000000  0.00000000  0.00000000  0.00000000
      2.9625557  0.00000000  1.00000000  0.00000000  0.00000000  0.00000000
      1.5230499  0.00000000  0.00000000  1.00000000  0.00000000  0.00000000
      0.7830000  0.00000000  0.00000000  0.00000000  1.00000000  0.00000000
      0.3084796  0.00000000  0.00000000  0.00000000  0.00000000  1.00000000
$ H-TYPE FUNCTIONS
    4    4    0
      4.7736170  1.00000000  0.00000000  0.00000000  0.00000000
      2.5298977  0.00000000  1.00000000  0.00000000  0.00000000
      1.3407825  0.00000000  0.00000000  1.00000000  0.00000000
      0.4545281  0.00000000  0.00000000  0.00000000  1.00000000
$ I-TYPE FUNCTIONS
    3    3    0
      4.9694530  1.00000000  0.00000000  0.00000000
      2.1727890  0.00000000  1.00000000  0.00000000
      0.7082765  0.00000000  0.00000000  1.00000000
$ K-TYPE FUNCTIONS
    2    2    0
      4.162      1.00000000  0.00000000
      1.022      0.00000000  1.00000000
```