Treating sub-valence correlation effects in domain based pair natural orbital coupled cluster calculations: an out-of-the-box approach.

Giovanni Bistoni,[1] Christoph Riplinger,[1] Yury Minenkov,[2] Luigi Cavallo,[2] Alexander A. Auer[1] and Frank Neese[1]*

1) Department of Molecular Theory and Spectroscopy, Max Planck Institute for Chemical Energy Conversion, Stiftstr. 34-36, D-45470 Mülheim an der Ruhr, Germany. E-Mail: Frank.Neese@cec.mpg.de
2) Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, KAUST Catalysis Center, Thuwal 23955-6900, Saudi Arabia. E-mail: Yury.Minenkov@kaust.edu.sa, Luigi.Cavallo@kaust.edu.sa

Table S1. Dependence of the CCSD(T) HDEs and ΔHDEs on the basis set superposition error (BSSE) for a representative subset of the systems studied in this work. See the paper for computational details.

MF_n	BSSE correction included	Core-electrons of M in the correlation treatment	HDE (kcal/mol)	ΔHDE* (kcal/mol)
LiF	No	None	190.1	0.0
	Yes	None	184.9	0.0
	No	$1s^2$	187.9	-2.1
	Yes	$1s^2$	182.7	-2.2
NaF	No	None	159.4	0.0
	Yes	None	154.5	0.0
	No	$1s^22s^22p^6$	154.7	-4.8
	Yes	$1s^22s^22p^6$	149.8	-4.8
CaF_2	No	None	537.3	0.0
	Yes	None	527.5	0.0
	No	$1s^22s^22p^63s^23p^6$	506.6	-30.7
	Yes	$1s^22s^22p^63s^23p^6$	497.2	-30.2
AlF_3	No	None	1436.2	0.0
	Yes	None	1423.0	0.0
	No	$1s^22s^22p^6$	1424.5	-11.6
	Yes	$1s^22s^22p^6$	1411.3	-11.6
InF_3	No	None	1338.2	0.0
	Yes	None	1277.5	0.0
	No	$1s^22s^22p^63s^23p^63d^{10}4s^24p^6$	1335.0	-3.2
	Yes	$1s^22s^22p^63s^23p^63d^{10}4s^24p^6$	1275.1	-2.4

*calculated using as reference the AE calculations with the same basis set. See text for details.

Table S2. Basis set decontraction effect on the CCSD(T) HDEs and ΔHDEs. See the paper for computational details.

MF_n	BSSE correction included	Decontraction** of the basis set	Core-electrons of M in the correlation treatment	HDE (kcal/mol)	ΔHDE* (kcal/mol)
CaF_2	No	No	None	537.3	0.0
	Yes	No	None	527.5	0.0
	No	Yes	None	536.9	0.0
	Yes	Yes	None	527.5	0.0
	No	No	$1s^22s^22p^63s^23p^6$	506.6	-30.7
	Yes	No	$1s^22s^22p^63s^23p^6$	497.2	-30.2
	No	Yes	$1s^22s^22p^63s^23p^6$	506.6	-30.3
	Yes	Yes	$1s^22s^22p^63s^23p^6$	497.2	-30.3
InF_3	No	No	None	1338.2	0.0
	Yes	No	None	1277.5	0.0
	No	Yes	None	1337.7	0.0
	Yes	Yes	None	1277.7	0.0
	No	No	$1s^22s^22p^63s^23p^63d^{10}4s^24p^6$	1335.0	-3.2
	Yes	No	$1s^22s^22p^63s^23p^63d^{10}4s^24p^6$	1275.1	-2.4
	No	Yes	$1s^22s^22p^63s^23p^63d^{10}4s^24p^6$	1334.9	-2.8
	Yes	Yes	$1s^22s^22p^63s^23p^63d^{10}4s^24p^6$	1275.1	-2.6

*calculated using as reference the AE calculations with the same basis set. See text for details.

** The decontracted cc-pwCV5Z (CaF_2) and cc-pwCVTZ-DK (InF_3) basis sets are used in the calculations of HDEs.

Table S3. Δ is the difference between the energy of the monomer (Ca^{2+} or F^-) calculated with the full molecular basis set and the one calculated with the monomer basis set. All electrons were included in the correlation treatment.

Ions CaF_2	Type of basis set	Energy using the monomer basis set (a.u.)	Energy using the molecular basis set at the CaF_2 geometry (a.u.)	Δ (a.u.)	Δ (kcal/mol)
Ca^{2+}	cc-pwCV5Z	-676.7586367	-676.7593611	-0.000724	-0.45
F^-	cc-pwCV5Z	-99.8418056	-99.8496376	-0.007445	-4.67
F^-	aug-cc-pwCV5Z	-99.8518553	-99.8520355	-0.000180	-0.11

Table S4: Calculated homolytic dissociation energies (HOMO-DE) for MF_n compounds at the canonical CCSD(T) level of theory with different FC settings for the metal. UHF/CCSD(T) calculations were carried out for the radical fragments (cc-pwCV5Z basis set). ΔHOMO-DE is the difference between the HOMO-DE calculated for a given FC definition and the one calculated for the same system with all-electron calculations.

MF_n	Core-electrons of M in the correlation treatment	HOMO-DE	ΔHOMO-DE
LiF	None	-138.6	0.0
	$1s^2$	-137.4	-1.2
NaF	None	-114.0	0.0
	$1s^2$	-113.8	-0.2
	$1s^22s^22p^6$	-113.2	-0.9
CaF_2	None	-270.1	0.0
	$1s^22s^22p^6$	-269.1	-1.0
	$1s^22s^22p^63s^23p^6$	-254.9	-15.2

Table S5: Calculated heterolytic dissociation energies (HDE kcal/mol) for MCl_n compounds (MF_n -> M^{n+} +nCl^-) at the canonical CCSD(T) level of theory with different FC settings for the metal. In FC calculations, the $1s^22s^22p^6$ orbitals of Cl where excluded from the correlation treatment in all cases. The computational method is analogous to the one used for the fluorinated species reported in the paper (RI-MP2/cc-pwCV5Z/AutoAux geometries and CCSD(T)/c-pwCV5z energies).

MF_n	Core-electrons of M in the correlation treatment	HDE	ΔHDE
LiCl	None	156.5	0.0
	$1s^2$	154.8	-1.8
NaCl	None	134.8	0.0
	$1s^2$	134.8	0.0
	$1s^22s^22p^6$	131.8	-3.1
$CaCl_2$	None	466.4	0.0
	$1s^22s^22p^6$	465.4	-1.0
	$1s^22s^22p^63s^23p^6$	449.9	-16.5

Table S6. CCSD and DLPNO-CCSD correlation energy contributions to the HDE, calculated using different FC and DLPNO settings. Reduced core electrons were excluded from the correlation treatment in FC calculations. See the paper for computational details and discussion.

Systems	AE DLPNO-CCSD (old DLPNO settings)	AE DLPNO-CCSD (new DLPNO settings)	AE CCSD	FC DLPNO-CCSD	FC-CCSD
LiF	-1.0	-1.0	-1.0	-1.0	-1.0
NaF	-2.1	-2.2	-2.2	-2.2	-2.2
CaF_2	-11.2	-11.6	-11.6	-10.9	-10.9
AlF_3	-6.8	-7.1	-7.2	3.4	3.5
GaF_3	-28.6	-29.5	-29.7	-29.6	-29.8
InF_3	-49.6	-51.7	-52.2	-49.6	-49.8
CuF	-15.8	-16.1	-16.6	-16.1	-16.6
YF_3	-38.9	-39.6	-39.8	-38.6	-38.7
AgF	-17.5	-18.6	-18.9	-18.4	-18.7
HfF_4	-68.4	-71.1	-71.6	-70.3	-70.9
AuF	-25.9	-28.8	-29.4	-28.3	-28.9

XYZ Geometries (Å)

LiF

```
Li  0.00000000000000     0.00000000000000     0.21289429892351
F   0.00000000000000     0.00000000000000     1.78710570107649
```

NaF

```
Na  0.00000000000000     0.00000000000000     0.03749428401565
F   0.00000000000000     0.00000000000000     1.96250571598435
```

AlF_3

```
Al  0.18402301682525    -0.00000000093518    -0.06506049873924
F   -0.11419489155577     0.00000000031170     1.53945600107279
F   1.72268451389203     0.00000000031178    -0.60905510894739
F   -1.05642063916150     0.00000000031170    -1.12558239338617
```

CaF_2

```
Ca  -0.00000002321785     0.00000002329061     0.00000000008580
F   0.00000001160893    -0.00000001164531     2.01178624876996
F   0.00000001160893    -0.00000001164531    -2.01178624885577
```

CuF

```
Cu  0.00000000000000     0.00000000000000     0.13208842529325
F   0.00000000000000     0.00000000000000     1.86791157470675
```

GaF_3

```
Ga  0.18402302928136    -0.00000000052674    -0.06506050988073
F   -0.12864882293101     0.00000000017555     1.61722513527226
```

F	1.79726107385149	0.00000000017564	-0.63542169229459
F	-1.11654328020183	0.00000000017555	-1.17698493309694

YF_3

Y	0.18402500061538	0.00000000000954	-0.06506116326455
F	-0.18039014364898	-0.00000000000319	1.89561144686097
F	2.06421940942626	-0.00000000000316	-0.72980503842384
F	-1.33176226639267	-0.00000000000319	-1.36098724517258

AgF

Ag	0.00000000000000	0.00000000000000	0.02284822703589
F	0.00000000000000	0.00000000000000	1.97715177296411

InF_3

In	0.18402303185281	-0.00000000026768	-0.06506050593439
F	-0.16398842222602	0.00000000008919	1.80736495566479
F	1.97959674706085	0.00000000008929	-0.69988657057281
F	-1.26353935668763	0.00000000008919	-1.30265987915760

HfF_4

Hf	0.00000415993383	-0.48229599832361	-0.00000310794918
F	-0.18646891284278	0.31128657372546	1.69401290444402
F	1.75624809012967	-0.22870874051353	-0.62093729673503
F	-1.20979063482069	0.31126252767900	-1.20035710755200
F	-0.35998270240003	-2.32306136256731	0.12728460779218

AuF

Au	0.00000000000000	0.00000000000000	0.05396779067253
F	0.00000000000000	0.00000000000000	1.94603220932747