Supporting Information for Benchmark relativistic Delta-Coupled-Cluster Calculations of K-edge Core-ionization Energies for Third-Row elements.

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TABLE I. Molecular structure adopted in Delta-CC calculation (Cartesian coordinates in Bohr). The structure have been optained at the SFX2C-1e-CCSD(T)/cc-pCVTZ level.

molecule	atoms	x	y	z	molecule	atoms	x	y	z
	S	0.00000	0.00000	0.10389		S	0.00000	0.00000	0.68555
H_2S	H	0.00000	-1.81882	-1.64782	SO_2	O	0.00000	-2.34803	-0.68517
	H	0.00000	1.81882	-1.64782		O	0.00000	2.34803	-0.68517
	C	0.00000	0.00000	-0.99523		C	0.00000	0.00000	0.00000
OCS	O	0.00000	0.00000	-3.18585	CS_2	S	0.00000	0.00000	-2.94401
	S	0.00000	0.00000	1.96734		S	0.00000	0.00000	2.94401
	P	-0.12884	0.00000	0.00000		P	0.00000	0.00000	-1.38358
	H	1.31992	-2.24392	0.00000		Cl	-3.44173	0.00000	0.40850
PH_3	H	1.31990	1.12198	1.94329	PCl_3	Cl	1.72086	2.98062	0.40850
	H	1.31990	1.12198	-1.94329		Cl	1.72086	-2.98062	0.40850
						P	0.00000	0.00000	0.00000
	P	0.00000	-0.94859	0.00000		F	-2.51486	0.00000	1.45196
	F	2.57368	0.51551	0.00000		F	0.00000	0.00000	-2.90392
PF_3	F	-1.28684	0.51551	2.22887	PF_5	F	2.51486	0.00000	1.45196
	F	-1.28684	0.51551	-2.22887		F	0.00000	-2.97627	0.00000
						F	0.00000	2.97627	0.00000
	Si	0.00000	0.00000	0.00000		Si	0.00000	0.00000	0.00000
	H	0.00000	-2.27733	1.61031		Cl	0.00000	-3.12242	2.20789
SiH_4	H	0.00000	2.27733	1.61031	$SiCl_4$	Cl	0.00000	3.12242	2.20789
	H	2.27733	0.00000	-1.61031		Cl	3.12242	0.00000	-2.20789
	H	-2.27733	0.00000	-1.61031		Cl	-3.12242	0.00000	-2.20789
	P	0.30251	0.00000	0.00000		P	-0.29032	0.00000	0.00000
	O	3.01833	0.00000	0.00000		S	3.24147	0.00000	0.00000
POF_3	F	-1.01145	2.22376	1.28389	PSF_3	F	-1.66056	-1.27885	2.21503
	F	-1.01145	0.00000	-2.56778		F	-1.66056	2.55770	0.00000
	F	-1.01145	-2.22376	1.28389		F	-1.66056	-1.27885	-2.21503
	S	0.00000	0.00000	0.00000					
	F	0.00000	0.00000	2.94888		Cl	0.00000	0.00000	1.89443
	F	0.00000	-2.94888	0.00000	Cl_2	Cl	0.00000	0.00000	-1.89443
SF_6	F	2.94888	0.00000	0.00000					
	F	0.00000	0.00000	-2.94888		Cl	0.00000	0.00000	0.06742
	F	0.00000	2.94888	0.00000	HCl	H	0.00000	0.00000	-2.33914
	F	-2.94888	0.00000	0.00000					

TABLE II. High-level relativistic (HLR) corrections (in eV) to 1s ionization energies of Si, P, S and Cl in atoms and molecules using uncontracted ANO-RCC (ANO-RCC-unc) basis sets.

	Two electron picture change	Spin-orbit coupling	Breit interaction	QED effects	All correction (ΔHLR)
Si*	0.451	-0.002	-0.950	-0.297	-0.798
Si*H$_4$	0.451	-0.002	-0.951	-0.297	-0.798
P*	0.563	-0.002	-1.198	-0.381	-1.019
P*H$_3$	0.562	-0.002	-1.199	-0.381	-1.020
S*	0.692	-0.003	-1.488	-0.481	-1.280
H$_2$**S***	0.691	-0.004	-1.488	-0.481	-1.282
S*O$_2$	0.691	-0.004	-1.490	-0.481	-1.284
Cl*	0.839	-0.005	-1.823	-0.599	-1.588
H**Cl***	0.839	-0.005	-1.822	-0.599	-1.587
Cl$_2^*$	0.839	-0.005	-1.823	-0.599	-1.588