Supporting Information
Theoretical Analysis of NMR Shieldings in XSe and XTe (X = Si, Ge, Sn and Pb): The Spin–Rotation Constant Saga

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Table S1: Comparison of the calculated electronic contributions to C, paramagnetic contributions to σ, shielding spans (Ω) and the perpendicular component of C for nuclei in XSe and XTe (X = Ge, Sn and Pb) (all in ppm); BP86/cv4z using CGO for all calculations.

	NR [a]	SC [b]	DKS [c]	ΔSC [d]	ΔSO [e]	Δrel [f]	Previous[g]	NR[a]	SC[b]	DKS[c]	ΔSC [d]	ΔSO [e]	Δrel [f]	Previous[g]
			Ge							Se				
$C^{el}_{\perp}$	-4035.9	-4201.6	-4444.3	-165.7	-242.7	-408.4	-3913	-4515.4	-4793.8	-4721.7	-278.4	72.1	-206.3	-4175
$\sigma^{para}_{\perp}$	-4035.9	-3982.0	-4267.2	53.9	-285.2	-231.3	-3993	-4515.4	-4526.2	-4489.8	-10.8	36.4	25.6	-4212
$\sigma^{para}_{\parallel}$	0.0	220.3	312.8	220.3	92.5	312.8	0.0	0.0	268.0	347.3	268.0	79.3	347.3	0.0
$\sigma^{dia,iso}$	2829.8	2844.5	2844.5	14.7	0.0	14.7	3134	3071.6	3089.9	3089.9	18.3	0.0	18.3	3439
Ω	3938.4	4105.2	4482.9	166.8	377.7	544.5	3768	4421.4	4700.6	4743.5	279.2	42.9	322.1	4001
$C_{\perp}$	-3926.6	-4092.3	-4335.2	-165.7	-242.9	-408.6	-3694	-4406.9	-4685.3	-4613.2	-278.4	72.1	-206.3	-3967
			Ge							Te				
$C^{el}_{\perp}$	-4609.9	-4798.0	-5305.3	-188.1	-507.3	-695.4	-4636	-7110.2	-8151.7	-7721.9	-1041.5	429.8	-611.7	-7004
$\sigma^{para}_{\perp}$	-4609.9	-4578.8	-5182.3	31.1	-603.5	-572.4	-4710	-7110.2	-7039.6	-6708.7	70.6	330.9	401.5	-6953
$\sigma^{para}_{\parallel}$	0.0	220.3	448.8	220.3	228.5	448.8	0.0	0.0	1113.4	1349.4	1113.4	236.0	1349.4	0.0
$\sigma^{dia,iso}$	2833.9	2848.5	2848.5	14.6	0.0	14.6	3194	5444.2	5521.3	5521.8	77.1	0.5	77.6	6693
Ω	4509.5	4699.1	5531.3	189.6	832.2	1021.8	4514	6999.7	8042.9	7948.1	1043.2	-94.8	948.4	6760
$C_{\perp}$	-4494.4	-4682.5	-5189.8	-188.1	-507.3	-695.4	-4329	-6988.6	-8030.1	-7600.4	-1041.5	429.7	-611.8	-6811
			Sn							Se				
$C^{el}_{\perp}$	-6396.0	-7127.7	-8255.1	-731.7	-1127.4	-1072.7	-7201	-4748.7	-5109.9	-4999.0	-361.2	110.9	-250.3	-4957
$\sigma^{para}_{\perp}$	-6396.0	-6158.8	-7468.7	237.2	-1309.9	-1072.7	-7368	-4748.7	-4842.3	-4821.3	-93.6	21.0	-72.6	-4976
$\sigma^{para}_{\parallel}$	0.0	970.8	1342.7	970.8	371.9	1342.7	0.0	0.0	268.0	444.8	268.0	176.8	444.8	0.0
$\sigma^{dia,iso}$	5169.2	5236.5	5236.8	67.3	0.3	67.6	6203	3078.9	3096.9	3096.9	18.0	0.0	18.0	3327
Ω	6279.6	7013.7	8695.6	734.1	1681.9	2416	7163	4647.4	5009.5	5165.3	362.1	156.0	517.9	4672
$C_{\perp}$	-6271.0	-7002.7	-8130.2	-731.7	-1127.5	-1859.2	-7000	-4629.7	-4990.9	-4880.0	-361.2	110.9	-250.3	-4674
			Sn							Te				
$C^{el}_{\perp}$	-7165.9	-7991.1	-9749.9	-825.2	-1758.8	-2584	-7751	-7287.3	-8476.2	-7814.9	-1188.9	661.3	-527.6	-7304
$\sigma^{para}_{\perp}$	-7165.9	-7023.5	-9099.6	142.4	-2076.1	-1933.7	-7895	-7287.3	-7364.6	-6888.8	-77.3	475.8	398.5	-7329
$\sigma^{para}_{\parallel}$	0.0	970.8	1699.7	970.8	728.9	1699.7	0.0	0.0	1113.4	1522.2	1113.4	408.8	1522.2	0.0
$\sigma^{dia,iso}$	5180.2	5247.2	5247.5	67.0	0.3	67.3	6203	5458.6	5535.5	5535.9	76.9	0.4	77.3	6639
Ω	7036.0	7865.1	10670.4	829.1	2805.3	3634.4	7604	7158.3	8349.8	8282.9	1191.5	-66.9	1124.6	7049
$C_{\perp}$	-7024.3	-7849.6	-9608.4	-825.3	-1758.8	-2584.1	-7461	-7144.3	-8333.2	-7672.0	-1188.9	661.2	-527.7	-7020
			Pb							Se				
$C^{el}_{\perp}$	-10843.2	-15087.1	-26427.2	-4243.9	-11340.1	-15584.0	23431	-4880.2	-5471.3	-5181.3	-591.1	290.0	-301.1	5621
$\sigma^{para}_{\perp}$	-10843.2	-8552.8	-21901.8	2290.4	-13349.0	-11058.6	-23964	-4880.2	-5203.0	-5303.1	-322.8	-100.1	-422.9	-5624
$\sigma^{para}_{\parallel}$	0.0	6540.6	9912.5	6540.6	3371.9	9912.5	0.0	0.0	268.0	935.9	268.0	667.9	935.9	0.0
$\sigma^{dia,iso}$	10156.2	10520.3	10527.0	364.1	6.7	370.8	20688	3086.5	3104.0	3104.0	17.5	0.0	17.5	3619
Ω	10705.4	14956.3	31678.3	4250.9	16722	20972.9	23765	4770.4	5362.1	6130.5	591.7	768.4	1360.1	5143
$C_{\perp}$	-10697.9	-14941.8	-26281.8	-4243.9	-11340	-15583.9	23335	-4749.8	-5341.0	-5051.0	-591.2	290.0	-301.2	5137
			Pb							Te				
$C^{el}_{\perp}$	-12065.5	-16794.0	-30116.5	-4728.5	-13322.5	-18051	25168	-7416.7	-8952.3	-7591.1	-1535.6	1361.2	-174.4	7734
$\sigma^{para}_{\perp}$	-12065.5	-10263.9	-26282.2	1801.6	-16018.3	-14216.7	-25589	-7416.7	-7840.4	-7106.5	-423.7	733.9	310.2	-7736
$\sigma^{para}_{\parallel}$	0.0	6540.5	11692.9	6540.5	5152.4	11692.9	0.0	0.0	1113.4	2362.2	1113.4	1248.8	2362.2	0.0
$\sigma^{dia,iso}$	10176.6	10540.4	10546.8	363.8	6.4	370.2	20743	5475.0	5551.1	5551.5	76.1	0.4	76.5	6862
Ω	11900.0	16640.1	37812.2	4740.1	16640.1	25912.2	25306	7265.6	8804.2	9319.6	1538.6	515.4	2054	7172
$C_{\perp}$	-11889.4	-16618.0	-29940.5	-4728.6	-13322.5	-18051.1	24854	-7249.2	-8784.9	-7423.5	-1535.7	1361.4	-174.3	7283

[a] NR — non–relativistically calculated results using BP86/cv4z.

[b] SC — results calculated without considering spin–orbit coupling using BP86/cv4z.

[c] DKS — full four–component relativistically calculated results using BP86/cv4z.

[d] ΔSC is the scalar relativistic correction (difference between noSO and NR).

[e] ΔSO is the spin–orbit relativistic correction (difference between DKS and noSO).

[f] Δrel is the total relativistic correction (difference between DKS and NR).

[g] In the experimental papers the isotropic values for the shielding contributions were reported, hence they are converted to the corresponding perpendicular components using $\sigma^{para}_{\perp} = 3\sigma^{para}/2$. The SiSe and SiTe values are taken from Ref. [1], GeSe and GeTe values from Ref. [2], SnSe and SnTe values from Ref. [3]; PbSe and PbTe values from Ref. [4].

Table S2: Comparison of the calculated shielding spans (Ω, in ppm) of nuclei in XSe and XTe (X = Ge, Sn and Pb) molecules using different computational levels, the final total shielding spans and experimental values.

		NR[a]	SO-ZORA[a]	DKS[a]	$\Delta\Omega$(rel 1)[b]	$\Delta\Omega$(rel 2)[c]	CCSD(T)[d]	CCSD(T)[e]	Total 1[f]	Total 2[g]	Previous[h]
GeSe	Ge	3938	4358	4477	539	551	3498	3535.5	4037	4049	3768 [i]
	Se	4421	4739	4751	330	318	4311	3928.1	4641	4629	4028 [i]
GeTe	Ge	4510	5228	5533	1023	1040	3957	4054.6	4980	4997	4514 [i]
	Te	7000	8076	7968	968	882	6510	6305.5	7478	7392	6760 [i]
SnSe	Sn	6280	8221	8680	2400	2519	5522	5642.7	7922	8041	7163 [j]
	Se	4647	5163	5198	551	522	4562	4138.0	5113	5084	4672 [j]
SnTe	Sn	7036	9693	10654	3618	3791	6129	6254.7	9747	9920	7604 [j]
	Te	7158	8424	8335	1177	1041	6708	6534.5	7885	7749	7049 [j]
PbSe	Pb	10705	26385	31532	20827	23148	9092	9176.9	29919	32240	23765 [k]
	Se	4770	5868	6173	1403	1467	4705	4389.7	6108	6172	5143 [k]
PbTe	Pb	11900	29639	37612	25712	28200	10014	–	35726	38214	25306 [k]
	Te	7266	9059	9375	2109	2048	6818	–	8927	8866	7172 [k]

[a] calculated using the BP86 functional (see Table **??** for the results using the B3LYP functional).
[b] $\Delta\Omega$(rel 1) is the difference between DKS and NR results using BP86/cv4z (relativistic corrections).
[c] $\Delta\Omega$(rel 2) is the difference between DKS and NR results using B3LYP/cv4z (relativistic corrections).
[d] the unc-DZP-DKH basis set was used.
[e] the unc-ANO-RCC basis set was used.
[f] Total 1 is the sum of the CCSD(T) results and $\Delta\Omega$(rel 1) from BP86/cv4z, absolute values.
[g] Total 2 is the sum of the CCSD(T) results and $\Delta\Omega$(rel 2) from B3LYP/cv4z, absolute values.
[h] Estimated from experimental spin–rotation constants.
[i] Taken from Ref. [2]
[j] Taken from Ref. [3]
[k] Taken from Ref. [4]