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Supplementary material

Electric field gradients in Hg compounds: Molecular orbital (MO) analysis and comparison of 4-component and 2-component (ZORA) methods

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Herein, we compare the performance of Hartree-Fock (HF), BH&H and BP86 functionals at the 4-component level in calculating electron configuration of Hg, charges q of Hg and Cl, polarisation terms (gross populations) (Table 1) and MO contributions to V_{zz} at Hg (Table 2) in $HgCl_2$. On the one hand, the net charges of Hg and Cl are increasing along the series BP86 –> BH&H –> HF. On the other hand, the population of Hg 6p orbitals is decreasing along the series. This causes increasing negative contributions to V_{zz} from the Hg core (mainly Hg 5p) and Hg6p + Cl MOs and total V_{zz} values due to growing polarisation, including a partial cancellation due to decreasing electron donation from occupied Cl orbitals to the formally empty Hg 6p orbitals.

Table S1: Electron configuration of Hg, charge q of Hg and Cl and polarisation terms (gross populations) in $HgCl_2$ obtained by projection analysis at the 4-component level using HF, BH&H and BP86 functionals.

	HF	BH&H	BP86
5*d*	9.858	9.850	9.839
6*s*	0.805	0.941	1.066
6*p*	0.142	0.250	0.342
q Hg	1.194	0.960	0.752
q Cl	-0.530×2	-0.429×2	-0.328×2
polar term	0.134	0.102	0.096

Table S2: MO contributions to V_{zz} at Hg in $HgCl_2$ obtained at the 4-component level using Hartree-Fock (HF), BH&H and BP86 functionals and the UKB condition.

	HF	BH&H	BP86
∑ Hg core:	-3.14	-0.11	2.11
∑ Cl core:	-0.36	-0.36	-0.36
∑ Hg5d + Cl MOs:	2.44	2.64	2.63
∑ Hg6p + Cl MOs:	-11.85	-11.77	-10.46
Total V_{zz}:	-12.91	-9.60	-6.08

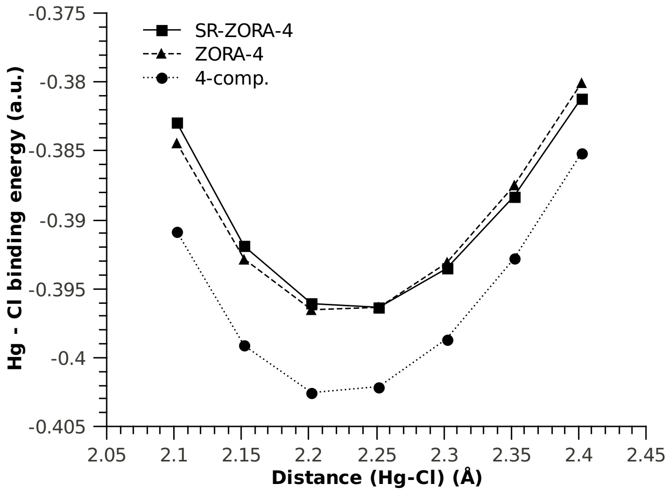


Figure S1: Bond length r(Hg-Cl) dependence of Hg-Cl binding energy calculated with different Hamiltonians at the DFT/BH&H level.

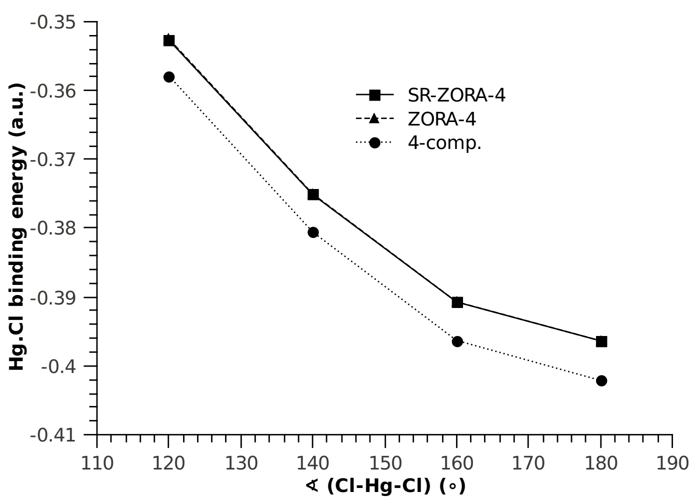


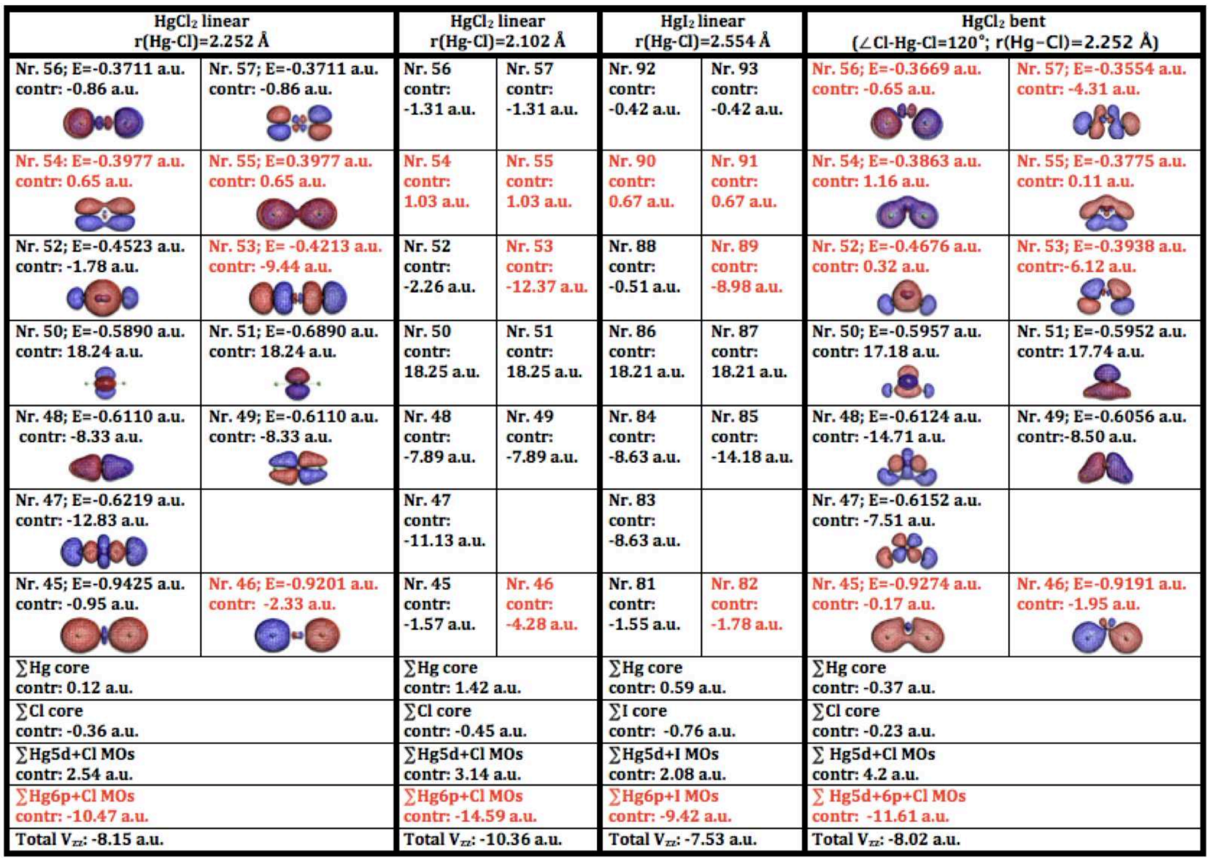
Figure S2: Angle ∠(Cl-Hg-Cl) dependence of Hg-Cl binding energy calculated with different Hamiltonians at the DFT/BH&H level.

HgCl$_2$ linear		
MO Nr. E(a.u.)	j; m$_j$	Contr. to MO
45	Hg 5d 3/2; 1/2	0.0221
-0.9412	Hg 5d 5/2; 1/2	0.0217
	Hg 6s 1/2; 1/2	0.0094
	Cl 3s 1/2; 1/2	0.4061
46	Hg 6p 1/2; 1/2	0.0008
-0.9190	Hg 6p 3/2; 1/2	0.0008
	Cl 3s 1/2; 1/2	0.4746
47	Hg 5d 3/2; 1/2	0.8630
-0.6511	Hg 5d 5/2; 1/2	0.0002
	Hg 6s 1/2; 1/2	0.0002
	Cl 3s 1/2; 1/2	0.0342
	Cl 3p 1/2; 1/2	0.0009
	Cl 3p 3/2; 1/2	0.0252
48	Hg 5d 3/2; -3/2	0.9668
-0.6358	Hg 5d 5/2; -3/2	0.0154
	Cl 3p 3/2; -3/2	0.0032
49	Hg 5d 3/2; 1/2	0.0185
-0.5915	Hg 5d 5/2; 1/2	0.7390
	Hg 6s 1/2; 1/2	0.0003
	Cl 3s 1/2; 1/2	0.0365
	Cl 3p 1/2; 1/2	0.0444
	Cl 3p 3/2; 1/2	0.0171
50	Hg 5d 3/2; -3/2	0.0241
-0.5761	Hg 5d 5/2; -3/2	0.9077
	Cl 3p 3/2; -3/2	0.0152
51 -0.5580	Hg 5d 5/2; 5/2	0.9997
52	Hg 5d 3/2; 1/2	0.0455
-0.4500	Hg 5d 5/2; 1/2	0.1406
	Hg 6s 1/2; 1/2	0.3401
	Cl 3s 1/2; 1/2	0.0176
	Cl 3p 1/2; 1/2	0.0415
	Cl 3p 3/2; 1/2	0.1166
53	Hg 6p 1/2; 1/2	0.0073
-0.4211	Hg 6p 3/2; 1/2	0.0024
	Cl 3s 1/2; 1/2	0.0081
	Cl 3p 1/2; 1/2	0.1511
	Cl 3p 3/2; 1/2	0.3296
54	Hg 6p 1/2; 1/2	0.0101
-0.3990	Hg 6p 3/2; 1/2	0.0029
	Cl 3s 1/2; 1/2	0.00004
	Cl 3p 1/2; 1/2	0.3255
	Cl 3p 3/2; 1/2	0.1310
55	Hg 6p 3/2; -3/2	0.0087
-0.3946	Cl 3p 3/2; -3/2	0.4647
56	Hg 5d 3/2; 1/2	0.0361
-0.3716	Hg 5d 5/2; 1/2	0.0466
	Hg 6s 1/2; 1/2	0.0008
	Cl 3s 1/2; 1/2	0.000008
	Cl 3p 1/2;1/2	0.3264
	Cl 3p 3/2; 1/2	0.1662
57	Hg 5d 3/2; -3/2	0.00112
-0.3666	Hg 5d 5/2; -3/2	0.0894
	Cl 3p 3/2; -3/2	04898

HgCl$_2$ bent (∠(Cl-Hg-Cl)=120°)		
MO Nr. E(a.u.)	j; m$_j$	Contr. to MO
45	Hg 5d 3/2; 1/2	0.0004
-0.9267	Hg 5d 3/2; -3/2	0.0099
	Hg 5d 5/2; 1/2	0.0005
	Hg 5d 5/2; 5/2	0.0082
	Hg 5d 5/2; -3/2	0.0018
	Hg 6s 1/2; 1/2	0.0098
	Hg 6p 1/2; 1/2	0.0002
	Hg 6p 3/2; 1/2	0.0002
	Cl 3s 1/2; 1/2	0.4262
46	Hg 5d 3/2; 1/2	0.0099
-0.9185	Hg 5d 3/2; -3/2	0.0035
	Hg 5d 5/2; 1/2	0.0041
	Hg 5d 5/2; -3/2	0.0082
	Hg 6p 1/2; 1/2	0.0007
	Hg 6p 3/2; 1/2	0.0002
	Hg 6p 3/2; -3/2	0.0005
	Cl 3s 1/2; 1/2	0.4484
47	Hg 5d 3/2; 1/2	0.3876
-0.6476	Hg 5d 3/2; -3/2	0.5045
	Hg 5d 5/2; -3/2	0.0008
	Hg 6s 1/2; 1/2	0.0003
	Cl 3s 1/2; 1/2	0.0270
	Cl 3p 1/2; 1/2	0.0005
	Cl 3p 3/2; 1/2	0.0105
	Cl 3p 3/2; -3/2	0.0083
48 -0.6383	Hg 5d 3/2; 1/2	0.5412
	Hg 5d 3/2; -3/2	0.4170
	Hg 5d 5/2; 1/2	0.0007
	Hg 5d 5/2; 5/2	0.0016
	Hg 5d 5/2; -3/2	0.0025
	Cl 3s 1/2; 1/2	0.0065
	Cl 3p 1/2; 1/2	0.0002
	Cl 3p 3/2; 1/2	0.0002
	Cl 3p 3/2; -3/2	0.0066
49	Hg 5d 3/2; 1/2	0.0050
-0.5863	Hg 5d 3/2; -3/2	0.0014
	Hg 5d 5/2; 1/2	0.3204
	Hg 5d 5/2; 5/2	0.1549
	Hg 5d 5/2; -3/2	0.3298
	Cl 3s 1/2; 1/2	0.0278
	Cl 3p 1/2; 1/2	0.0299
	Cl 3p 3/2; 1/2	0.0062
	Cl 3p 3/2; -3/2	0.0105
50	Hg 5d 3/2; 1/2	0.0107
-0.5765	Hg 5d 3/2; -3/2	0.0003
	Hg 5d 5/2; 1/2	0.0080
	Hg 5d 5/2; 5/2	0.6435
	Hg 5d 5/2; -3/2	0.2302
	Cl 3s 1/2; 1/2	0.0100
	Cl 3p 1/2; 1/2	0.0141
	Cl 3p 3/2; 1/2	0.0112
	Cl 3p 3/2; -3/2	0.0012
51	Hg 5d 5/2; 1/2	0.5901
-0.5652	Hg 5d 5/2; 5/2	0.0525
	Hg 5d 5/2; -3/2	0.3139
	Hg 6s 1/2; 1/2	0.0002
	Cl 3s 1/2; 1/2	0.0025
	Cl 3p 1/2; 1/2	0.0034
	Cl 3p 3/2; 1/2	0.0022
	Cl 3p 3/2; -3/2	0.0052
52	Hg 5d 3/2; -3/2	0.0227
-0.4662	Hg 5d 5/2; 5/2	0.0702
	Hg 5d 5/2; -3/2	0.0139
	Hg 6s 1/2; 1/2	0.2390
	Hg 6p 1/2; 1/2	0.0005
	Hg 6p 3/2; 1/2	0.0002

HgCl$_2$ bent (∠(Cl-Hg-Cl)=120°) (continued)		
MO Nr. E(a.u.)	j; m$_j$	Contr. to MO
	Cl 3s 1/2; 1/2	0.0288
	Cl 3p 1/2; 1/2	0.0723
	Cl 3p 3/2; 1/2	0.0445
	Cl 3p 3/2; -3/2	0.1048
53	Hg 5d 3/2; 1/2	0.0113
-0.3942	Hg 5d 3/2; -3/2	0.0018
	Hg 5d 5/2; 1/2	0.0074
	Hg 5d 5/2; 5/2	0.0003
	Hg 5d 5/2; -3/2	0.0093
	Hg 6s 1/2; 1/2	0.0006
	Hg 6p 1/2; 1/2	0.0152
	Hg 6p 3/2; 1/2	0.0018
	Hg 6p 3/2; -3/2	0.0031
	Cl 3s 1/2; 1/2	0.0035
	Cl 3p 1/2; 1/2	0.1230
	Cl 3p 3/2; 1/2	0.2745
	Cl 3p 3/2; -3/2	0.0545
54	Hg 5d 3/2; 1/2	0.0056
-0.3857	Hg 5d 3/2; -3/2	0.0010
	Hg 5d 5/2; 1/2	0.0003
	Hg 5d 5/2; 5/2	0.0006
	Hg 5d 5/2; -3/2	0.0195
	Hg 6s 1/2; 1/2	0.0027
	Hg 6p 1/2; 1/2	0.0042
	Hg 6p 3/2; 1/2	0.0002
	Hg 6p 3/2; -3/2	0.0073
	Cl 3p 1/2; 1/2	0.2212
	Cl 3p 3/2; 1/2	0.0415
	Cl 3p 3/2; -3/2	0.1912
55	Hg 5d 3/2; 1/2	0.0114
-0.3763	Hg 5d 3/2; -3/2	0.0110
	Hg 5d 5/2; 1/2	0.0328
	Hg 5d 5/2; 5/2	0.0029
	Hg 6s 1/2; 1/2	0.0343
	Hg 6p 1/2; 1/2	0.0022
	Hg 6p 3/2; 1/2	0.0062
	Hg 6p 3/2; -3/2	0.0002
	Cl 3p 1/2; 1/2	0.1168
	Cl 3p 3/2; 1/2	0.3057
	Cl 3p 3/2; -3/2	0.0209
56	Hg 5d 3/2; -3/2	0.0168
-0.3655	Hg 5d 5/2; 1/2	0.0034
	Hg 5d 5/2; 5/2	0.0478
	Hg 5d 5/2; -3/2	0.0032
	Hg 6s 1/2; 1/2	0.0020
	Hg 6p 3/2; 1/2	0.0004
	Cl 3p 1/2; 1/2	0.1362
	Cl 3p 3/2; 1/2	0.0675
	Cl 3p 3/2; -3/2	0.2890
57	Hg 5d 3/2; 1/2	0.0239
-0.3537	Hg 5d 3/2; -3/2	0.0059
	Hg 5d 5/2; 1/2	0.0396
	Hg 5d 5/2; 5/2	0.0002
	Hg 5d 5/2; -3/2	0.0754
	Hg 6p 1/2; 1/2	0.0030
	Hg 6p 3/2; 1/2	0.0008
	Hg 6p 3/2; -3/2	0.0013
	Cl 3p 1/2; 1/2	0.1827
	Cl 3p 3/2; 1/2	0.1017
	Cl 3p 3/2; -3/2	0.2087

Figure S3: AO contributions to MOs obtained for the linear and bent $HgCl_2$ with projection analysis at the 4-component level using the BH&H functional and the RKB condition.



$HgCl_2$ linear r(Hg-Cl)=2.252 Å		$HgCl_2$ linear r(Hg-Cl)=2.102 Å		HgI_2 linear r(Hg-Cl)=2.554 Å		$HgCl_2$ bent (∠Cl-Hg-Cl=120°; r(Hg−Cl)=2.252 Å)	
Nr. 56; E=-0.3711 a.u. contr: -0.86 a.u.	Nr. 57; E=-0.3711 a.u. contr: -0.86 a.u.	Nr. 56 contr: -1.31 a.u.	Nr. 57 contr: -1.31 a.u.	Nr. 92 contr: -0.42 a.u.	Nr. 93 contr: -0.42 a.u.	Nr. 56; E=-0.3669 a.u. contr: -0.65 a.u.	Nr. 57; E=-0.3554 a.u. contr: -4.31 a.u.
Nr. 54: E=-0.3977 a.u. contr: 0.65 a.u.	Nr. 55; E=0.3977 a.u. contr: 0.65 a.u.	Nr. 54 contr: 1.03 a.u.	Nr. 55 contr: 1.03 a.u.	Nr. 90 contr: 0.67 a.u.	Nr. 91 contr: 0.67 a.u.	Nr. 54; E=-0.3863 a.u. contr: 1.16 a.u.	Nr. 55; E=-0.3775 a.u. contr: 0.11 a.u.
Nr. 52; E=-0.4523 a.u. contr: -1.78 a.u.	Nr. 53; E= -0.4213 a.u. contr: -9.44 a.u.	Nr. 52 contr: -2.26 a.u.	Nr. 53 contr: -12.37 a.u.	Nr. 88 contr: -0.51 a.u.	Nr. 89 contr: -8.98 a.u.	Nr. 52; E=-0.4676 a.u. contr: 0.32 a.u.	Nr. 53; E=-0.3938 a.u. contr:-6.12 a.u.
Nr. 50; E=-0.5890 a.u. contr: 18.24 a.u.	Nr. 51; E=-0.6890 a.u. contr: 18.24 a.u.	Nr. 50 contr: 18.25 a.u.	Nr. 51 contr: 18.25 a.u.	Nr. 86 contr: 18.21 a.u.	Nr. 87 contr: 18.21 a.u.	Nr. 50; E=-0.5957 a.u. contr: 17.18 a.u.	Nr. 51; E=-0.5952 a.u. contr: 17.74 a.u.
Nr. 48; E=-0.6110 a.u. contr: -8.33 a.u.	Nr. 49; E=-0.6110 a.u. contr: -8.33 a.u.	Nr. 48 contr: -7.89 a.u.	Nr. 49 contr: -7.89 a.u.	Nr. 84 contr: -8.63 a.u.	Nr. 85 contr: -14.18 a.u.	Nr. 48; E=-0.6124 a.u. contr: -14.71 a.u.	Nr. 49; E=-0.6056 a.u. contr:-8.50 a.u.
Nr. 47; E=-0.6219 a.u. contr: -12.83 a.u.		Nr. 47 contr: -11.13 a.u.		Nr. 83 contr: -8.63 a.u.		Nr. 47; E=-0.6152 a.u. contr: -7.51 a.u.	
Nr. 45; E=-0.9425 a.u. contr: -0.95 a.u.	Nr. 46; E=-0.9201 a.u. contr: -2.33 a.u.	Nr. 45 contr: -1.57 a.u.	Nr. 46 contr: -4.28 a.u.	Nr. 81 contr: -1.55 a.u.	Nr. 82 contr: -1.78 a.u.	Nr. 45; E=-0.9274 a.u. contr: -0.17 a.u.	Nr. 46; E=-0.9191 a.u. contr: -1.95 a.u.
∑Hg core contr: 0.12 a.u.		∑Hg core contr: 1.42 a.u.		∑Hg core contr: 0.59 a.u.		∑Hg core contr: -0.37 a.u.	
∑Cl core contr: -0.36 a.u.		∑Cl core contr: -0.45 a.u.		∑I core contr: -0.76 a.u.		∑Cl core contr: -0.23 a.u.	
∑Hg5d+Cl MOs contr: 2.54 a.u.		∑Hg5d+Cl MOs contr: 3.14 a.u.		∑Hg5d+I MOs contr: 2.08 a.u.		∑ Hg5d+Cl MOs contr: 4.2 a.u.	
∑Hg6p+Cl MOs contr: -10.47 a.u.		∑Hg6p+Cl MOs contr: -14.59 a.u.		∑Hg6p+I MOs contr: -9.42 a.u.		∑ Hg5d+6p+Cl MOs contr: -11.61 a.u.	
Total V_{zz}: -8.15 a.u.		Total V_{zz}: -10.36 a.u.		Total V_{zz}: -7.53 a.u.		Total V_{zz}: -8.02 a.u.	

Figure S4: Energies and a graphical representation of valence MOs in linear and bent $HgCl_2$, HgI_2 (isosurface: 0.015) and their contributions to V_{zz} obtained at the SR-ZORA-4 level using the BH&H functional; red colour corresponds to the MOs with an admixture of Hg 6p and their contributions to V_{zz}.