

# Perturbation Theory Treatment of Spin-Orbit Coupling. II: Coupled Perturbed Kohn Sham Method

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TABLE S1: Extension of Table 2 of the main text using different exchange-correlation functionals and the HF method.

	F <sub>2</sub>	Cl <sub>2</sub>	Br <sub>2</sub>	I <sub>2</sub>
<b>HF</b>				
2c	$-7.10 \times 10^{-05}$	$-2.86 \times 10^{-04}$	$-6.90 \times 10^{-03}$	$-3.75 \times 10^{-02}$
$\Delta_2$	$+1.08 \times 10^{-07}$	$-1.79 \times 10^{-07}$	$-9.26 \times 10^{-05}$	$-5.48 \times 10^{-04}$
$\Delta_3$	$+2.02 \times 10^{-08}$	$-2.31 \times 10^{-08}$	$-2.65 \times 10^{-05}$	$-4.92 \times 10^{-04}$
$\Delta_4$	$+1.71 \times 10^{-08}$	$+3.00 \times 10^{-09}$	$+1.29 \times 10^{-06}$	$+1.65 \times 10^{-04}$
<b>SVWN5</b>				
2c	$-7.03 \times 10^{-05}$	$-2.92 \times 10^{-04}$	$-7.13 \times 10^{-03}$	$-3.83 \times 10^{-02}$
$\Delta_2$	$+7.46 \times 10^{-08}$	$-2.32 \times 10^{-07}$	$-1.12 \times 10^{-04}$	$-1.17 \times 10^{-03}$
$\Delta_3$	$-9.39 \times 10^{-10}$	$-4.06 \times 10^{-08}$	$-3.45 \times 10^{-05}$	$-7.06 \times 10^{-04}$
$\Delta_4$	$-4.68 \times 10^{-10}$	$-7.00 \times 10^{-09}$	$-1.89 \times 10^{-06}$	$+2.19 \times 10^{-04}$
<b>BHandH</b>				
2c	$-7.08 \times 10^{-05}$	$-2.91 \times 10^{-04}$	$-7.05 \times 10^{-03}$	$-3.81 \times 10^{-02}$
$\Delta_2$	$+7.98 \times 10^{-08}$	$-2.37 \times 10^{-07}$	$-1.07 \times 10^{-04}$	$-8.98 \times 10^{-04}$
$\Delta_3$	$-8.66 \times 10^{-10}$	$-3.73 \times 10^{-08}$	$-3.07 \times 10^{-05}$	$-5.98 \times 10^{-04}$
$\Delta_4$	$-4.12 \times 10^{-10}$	$-4.40 \times 10^{-09}$	$+7.10 \times 10^{-07}$	$+2.22 \times 10^{-04}$
<b>PBE</b>				
2c	$-6.98 \times 10^{-05}$	$-2.96 \times 10^{-04}$	$-7.22 \times 10^{-03}$	$-3.83 \times 10^{-02}$
$\Delta_2$	$+7.39 \times 10^{-08}$	$-3.09 \times 10^{-07}$	$-1.27 \times 10^{-04}$	$-1.36 \times 10^{-03}$
$\Delta_3$	$-7.34 \times 10^{-10}$	$-4.24 \times 10^{-08}$	$-3.58 \times 10^{-05}$	$-7.21 \times 10^{-04}$
$\Delta_4$	$-4.47 \times 10^{-10}$	$-7.43 \times 10^{-09}$	$-1.87 \times 10^{-06}$	$+2.33 \times 10^{-04}$

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TABLE S2: Extension of Table 3 of the main text using different exchange-correlation functionals and the HF method.

	Br <sub>2</sub>	I <sub>2</sub>	I <sub>2</sub> <sup>+</sup>	At <sub>2</sub>
HF				
2c	$-3.43 \times 10^{-03}$	$-7.37 \times 10^{-03}$	$-6.94 \times 10^{-03}$	$-7.15 \times 10^{-02}$
$\Delta_2$	$-3.00 \times 10^{-05}$	$-1.60 \times 10^{-04}$	$-1.48 \times 10^{-04}$	$-1.29 \times 10^{-02}$
$\Delta_3$	$+1.34 \times 10^{-06}$	$-3.66 \times 10^{-05}$	$-3.25 \times 10^{-05}$	$-3.18 \times 10^{-03}$
$\Delta_4$	$-5.33 \times 10^{-07}$	$+5.72 \times 10^{-06}$	$+4.64 \times 10^{-06}$	$+7.46 \times 10^{-03}$
SVWN5				
2c	$-3.50 \times 10^{-03}$	$-7.91 \times 10^{-03}$	$-7.45 \times 10^{-03}$	$-7.38 \times 10^{-02}$
$\Delta_2$	$-3.04 \times 10^{-05}$	$-2.32 \times 10^{-04}$	$-2.14 \times 10^{-04}$	$-1.82 \times 10^{-02}$
$\Delta_3$	$+2.43 \times 10^{-07}$	$-5.69 \times 10^{-05}$	$-4.89 \times 10^{-05}$	$-3.66 \times 10^{-03}$
$\Delta_4$	$-7.15 \times 10^{-07}$	$+1.13 \times 10^{-06}$	$+1.41 \times 10^{-06}$	$+1.16 \times 10^{-02}$
BHandH				
2c	$-3.48 \times 10^{-03}$	$-7.66 \times 10^{-03}$	$-7.24 \times 10^{-03}$	$-7.28 \times 10^{-02}$
$\Delta_2$	$-3.06 \times 10^{-05}$	$-2.00 \times 10^{-04}$	$-1.87 \times 10^{-04}$	$-1.56 \times 10^{-02}$
$\Delta_3$	$+8.36 \times 10^{-07}$	$-4.61 \times 10^{-05}$	$-4.06 \times 10^{-05}$	$-3.45 \times 10^{-03}$
$\Delta_4$	$-6.28 \times 10^{-07}$	$+6.06 \times 10^{-06}$	$+5.32 \times 10^{-06}$	$+1.02 \times 10^{-02}$
PBE				
2c	$-3.55 \times 10^{-03}$	$-8.02 \times 10^{-03}$	$-7.56 \times 10^{-03}$	$-7.42 \times 10^{-02}$
$\Delta_2$	$-3.17 \times 10^{-05}$	$-2.56 \times 10^{-04}$	$-2.37 \times 10^{-04}$	$-1.92 \times 10^{-02}$
$\Delta_3$	$+6.88 \times 10^{-08}$	$-5.91 \times 10^{-05}$	$-5.09 \times 10^{-05}$	$-3.54 \times 10^{-03}$
$\Delta_4$	$-7.29 \times 10^{-07}$	$+1.38 \times 10^{-06}$	$+1.65 \times 10^{-06}$	$+1.20 \times 10^{-02}$

TABLE S3: Extension of Table 4 of the main text using different exchange-correlation functionals and the HF method.

	F <sub>2</sub> <sup>-</sup>	Cl <sub>2</sub> <sup>-</sup>	Br <sub>2</sub> <sup>-</sup>	I <sub>2</sub> <sup>-</sup>
HF				
2c	$-6.00 \times 10^{-05}$	$-2.34 \times 10^{-04}$	$-5.56 \times 10^{-03}$	$-3.10 \times 10^{-02}$
$\Delta_2$	$+1.08 \times 10^{-07}$	$+2.46 \times 10^{-07}$	$+4.53 \times 10^{-06}$	$+7.97 \times 10^{-04}$
$\Delta_3$	$+3.37 \times 10^{-10}$	$-8.88 \times 10^{-09}$	$-7.65 \times 10^{-06}$	$-3.67 \times 10^{-05}$
$\Delta_4$	$-6.03 \times 10^{-11}$	$-3.89 \times 10^{-10}$	$-2.38 \times 10^{-07}$	$+3.74 \times 10^{-06}$
SVWN5				
2c	$-6.00 \times 10^{-05}$	$-2.38 \times 10^{-04}$	$-5.68 \times 10^{-03}$	$-3.13 \times 10^{-02}$
$\Delta_2$	$+1.04 \times 10^{-07}$	$+2.84 \times 10^{-07}$	$+1.01 \times 10^{-05}$	$+7.32 \times 10^{-04}$
$\Delta_3$	$+2.80 \times 10^{-10}$	$-9.15 \times 10^{-09}$	$-8.22 \times 10^{-06}$	$-6.72 \times 10^{-05}$
$\Delta_4$	$-1.10 \times 10^{-10}$	$-1.00 \times 10^{-09}$	$-4.96 \times 10^{-07}$	$-1.29 \times 10^{-06}$
BHandH				
2c	$-6.00 \times 10^{-05}$	$-2.37 \times 10^{-04}$	$-5.65 \times 10^{-03}$	$-3.13 \times 10^{-02}$
$\Delta_2$	$+1.06 \times 10^{-07}$	$+2.48 \times 10^{-07}$	$+3.50 \times 10^{-06}$	$+7.11 \times 10^{-04}$
$\Delta_3$	$+3.01 \times 10^{-10}$	$-9.53 \times 10^{-09}$	$-8.40 \times 10^{-06}$	$-6.48 \times 10^{-05}$
$\Delta_4$	$-1.07 \times 10^{-10}$	$-7.20 \times 10^{-10}$	$-1.84 \times 10^{-07}$	$+4.80 \times 10^{-06}$
PBE				
2c	$-5.96 \times 10^{-05}$	$-2.38 \times 10^{-04}$	$-5.68 \times 10^{-03}$	$-3.10 \times 10^{-02}$
$\Delta_2$	$+1.02 \times 10^{-07}$	$+2.58 \times 10^{-07}$	$+5.80 \times 10^{-06}$	$+6.67 \times 10^{-04}$
$\Delta_3$	$+3.09 \times 10^{-10}$	$-9.10 \times 10^{-09}$	$-8.16 \times 10^{-06}$	$-6.63 \times 10^{-05}$
$\Delta_4$	$-1.10 \times 10^{-10}$	$-1.00 \times 10^{-09}$	$-4.83 \times 10^{-07}$	$-1.77 \times 10^{-06}$

TABLE S4: Extension of Table 5 of the main text using different exchange-correlation functionals and the HF method.

	$\text{Br}_2^-$	$\text{I}_2^-$	$\text{I}_2^*$	$\text{At}_2^-$
HF				
2c	$-3.27 \times 10^{-03}$	$-5.96 \times 10^{-03}$	$-5.52 \times 10^{-03}$	$-5.67 \times 10^{-02}$
$\Delta_2$	$-3.43 \times 10^{-05}$	$-2.00 \times 10^{-05}$	$-1.95 \times 10^{-05}$	$-2.54 \times 10^{-03}$
$\Delta_3$	$+3.39 \times 10^{-06}$	$-9.51 \times 10^{-06}$	$-9.99 \times 10^{-06}$	$-1.01 \times 10^{-03}$
$\Delta_4$	$-3.93 \times 10^{-07}$	$+2.30 \times 10^{-07}$	$+5.08 \times 10^{-07}$	$+7.61 \times 10^{-04}$
SVWN5				
2c	$-3.27 \times 10^{-03}$	$-6.25 \times 10^{-03}$	$-5.79 \times 10^{-03}$	$-5.81 \times 10^{-02}$
$\Delta_2$	$-3.10 \times 10^{-05}$	$-2.26 \times 10^{-05}$	$-2.27 \times 10^{-05}$	$-3.11 \times 10^{-03}$
$\Delta_3$	$+3.05 \times 10^{-06}$	$-1.28 \times 10^{-05}$	$-1.19 \times 10^{-05}$	$-1.24 \times 10^{-03}$
$\Delta_4$	$-4.67 \times 10^{-07}$	$-3.70 \times 10^{-07}$	$-1.23 \times 10^{-07}$	$+9.27 \times 10^{-04}$
BHandH				
2c	$-3.28 \times 10^{-03}$	$-6.11 \times 10^{-03}$	$-5.68 \times 10^{-03}$	$-5.74 \times 10^{-02}$
$\Delta_2$	$-3.34 \times 10^{-05}$	$-2.64 \times 10^{-05}$	$-2.65 \times 10^{-05}$	$-3.15 \times 10^{-03}$
$\Delta_3$	$+3.24 \times 10^{-06}$	$-1.17 \times 10^{-05}$	$-1.15 \times 10^{-05}$	$-1.17 \times 10^{-03}$
$\Delta_4$	$-4.37 \times 10^{-07}$	$+2.18 \times 10^{-07}$	$+4.46 \times 10^{-07}$	$+1.07 \times 10^{-03}$
PBE				
2c	$-3.30 \times 10^{-03}$	$-6.25 \times 10^{-03}$	$-5.79 \times 10^{-03}$	$-5.77 \times 10^{-02}$
$\Delta_2$	$-3.20 \times 10^{-05}$	$-2.77 \times 10^{-05}$	$-2.77 \times 10^{-05}$	$-3.24 \times 10^{-03}$
$\Delta_3$	$+3.04 \times 10^{-06}$	$-1.25 \times 10^{-05}$	$-1.17 \times 10^{-05}$	$-1.19 \times 10^{-03}$
$\Delta_4$	$-4.69 \times 10^{-07}$	$-4.08 \times 10^{-07}$	$-1.41 \times 10^{-07}$	$+8.66 \times 10^{-04}$

TABLE S5: Extension of Table 6 of the main text using different exchange-correlation functionals and the HF method.

	HBr	HI	HAt	HTs
HF				
2c	$-1.58 \times 10^{-03}$	$-3.01 \times 10^{-03}$	$-2.78 \times 10^{-02}$	$-7.13 \times 10^{-01}$
$\Delta_2$	$-1.63 \times 10^{-05}$	$-9.81 \times 10^{-06}$	$-7.34 \times 10^{-04}$	$-9.43 \times 10^{-02}$
$\Delta_3$	$+1.66 \times 10^{-06}$	$-4.44 \times 10^{-06}$	$-3.60 \times 10^{-04}$	$-2.59 \times 10^{-02}$
$\Delta_4$	$-1.71 \times 10^{-07}$	$-9.97 \times 10^{-07}$	$-2.82 \times 10^{-05}$	$+8.70 \times 10^{-03}$
SVWN5				
2c	$-1.58 \times 10^{-03}$	$-3.14 \times 10^{-03}$	$-2.81 \times 10^{-02}$	$-7.30 \times 10^{-01}$
$\Delta_2$	$-1.49 \times 10^{-05}$	$-1.02 \times 10^{-05}$	$-7.83 \times 10^{-04}$	$-1.04 \times 10^{-01}$
$\Delta_3$	$+1.55 \times 10^{-06}$	$-5.75 \times 10^{-06}$	$-4.43 \times 10^{-04}$	$-2.78 \times 10^{-02}$
$\Delta_4$	$-2.11 \times 10^{-07}$	$-1.48 \times 10^{-06}$	$-4.39 \times 10^{-05}$	$+1.19 \times 10^{-02}$
BHandH				
2c	$-1.58 \times 10^{-03}$	$-3.07 \times 10^{-03}$	$-2.79 \times 10^{-02}$	$-7.21 \times 10^{-01}$
$\Delta_2$	$-1.59 \times 10^{-05}$	$-1.18 \times 10^{-05}$	$-8.23 \times 10^{-04}$	$-1.01 \times 10^{-01}$
$\Delta_3$	$+1.63 \times 10^{-06}$	$-5.03 \times 10^{-06}$	$-3.97 \times 10^{-04}$	$-2.71 \times 10^{-02}$
$\Delta_4$	$-1.93 \times 10^{-07}$	$-1.18 \times 10^{-06}$	$-2.27 \times 10^{-05}$	$+1.09 \times 10^{-02}$
PBE				
2c	$-1.59 \times 10^{-03}$	$-3.17 \times 10^{-03}$	$-2.82 \times 10^{-02}$	$-7.26 \times 10^{-01}$
$\Delta_2$	$-1.52 \times 10^{-05}$	$-1.39 \times 10^{-05}$	$-9.12 \times 10^{-04}$	$-1.03 \times 10^{-01}$
$\Delta_3$	$+1.52 \times 10^{-06}$	$-5.84 \times 10^{-06}$	$-4.45 \times 10^{-04}$	$-2.68 \times 10^{-02}$
$\Delta_4$	$-2.10 \times 10^{-07}$	$-1.59 \times 10^{-06}$	$-4.51 \times 10^{-05}$	$+1.09 \times 10^{-02}$

TABLE S6: Eigenvalue differences w.r.t. the HOMO for  $I_2$  with the PBE0 functional from Fig. 2(a) of the main text.

1c-SCF	PT1	PT2	2c-SCF
-0.513148	-0.525999	-0.525608	-0.525299
-0.513148	-0.525999	-0.525608	-0.525299
-0.407819	-0.420636	-0.420387	-0.420112
-0.407819	-0.420636	-0.420387	-0.420112
-0.125425	-0.141393	-0.141694	-0.141137
-0.125425	-0.141393	-0.141694	-0.141137
-0.065552	-0.089587	-0.092148	-0.092005
-0.065552	-0.089587	-0.092148	-0.092005
-0.065552	-0.067147	-0.067096	-0.067104
-0.065552	-0.067147	-0.067096	-0.067104
-0.000000	-0.022443	-0.022527	-0.022576
-0.000000	-0.022443	-0.022527	-0.022576
+0.000000	+0.000000	+0.000000	+0.000000
+0.000000	+0.000000	+0.000000	+0.000000
+0.126951	+0.113455	+0.115754	+0.116113
+0.126951	+0.113455	+0.115754	+0.116113

TABLE S7: Eigenvalue differences w.r.t. the HOMO for  $I_2^-$  with the PBE0 functional from Fig. 2(b) of the main text.

1c-SCF	PT1	PT2	2c-SCF
-0.563350	-0.565074	-0.564527	-0.564595
-0.544978	-0.546708	-0.546553	-0.546591
-0.467421	-0.469127	-0.468607	-0.468667
-0.446792	-0.448496	-0.448351	-0.448382
-0.192943	-0.196758	-0.196655	-0.196671
-0.158239	-0.163767	-0.164191	-0.164148
-0.129676	-0.141989	-0.143721	-0.143825
-0.122587	-0.136485	-0.136994	-0.137121
-0.129676	-0.120757	-0.120520	-0.120668
-0.122587	-0.113780	-0.113760	-0.113891
-0.065786	-0.075688	-0.075654	-0.075812
-0.057943	-0.069458	-0.069754	-0.069869
-0.065786	-0.055423	-0.055223	-0.055362
-0.057943	-0.047687	-0.047688	-0.047808
+0.000000	+0.000000	+0.000000	+0.000000
+0.086332	+0.083952	+0.085465	+0.085437
+0.270290	+0.267403	+0.268035	+0.268044
+0.287170	+0.281878	+0.282423	+0.282448
+0.286852	+0.284872	+0.285307	+0.285282
+0.298339	+0.294232	+0.294745	+0.294680

TABLE S8: Eigenvalue differences w.r.t. the HOMO for  $\text{At}_2^-$  with the PBE0 functional from Fig. 2(c) of the main text.

1c-SCF	PT1	PT2	2c-SCF
-0.578183	-0.594227	-0.590357	-0.591258
-0.561658	-0.577722	-0.579613	-0.578002
-0.530091	-0.546100	-0.542502	-0.543199
-0.510985	-0.526982	-0.529271	-0.527421
-0.152507	-0.190482	-0.193023	-0.193379
-0.118080	-0.172591	-0.179861	-0.176976
-0.088414	-0.144992	-0.158496	-0.155694
-0.088414	-0.135665	-0.153326	-0.152933
-0.082022	-0.073156	-0.072659	-0.073681
-0.082022	-0.067030	-0.069911	-0.069424
-0.043612	-0.065257	-0.068348	-0.067876
-0.043612	-0.056044	-0.057615	-0.059106
-0.036479	-0.024592	-0.024350	-0.025256
-0.036479	-0.017667	-0.020669	-0.020092
+0.000000	+0.000000	+0.000000	+0.000000
+0.081017	+0.058327	+0.074912	+0.073553
+0.237079	+0.215255	+0.219025	+0.219951
+0.250950	+0.225325	+0.226627	+0.229034
+0.266295	+0.247641	+0.249533	+0.250480
+0.268515	+0.248806	+0.249861	+0.251287

TABLE S9: Eigenvalue differences w.r.t. the HOMO for HI with the PBE0 functional from Fig. 3(a) of the main text.

1c-SCF	PT1	PT2	2c-SCF
-0.444482	-0.456232	-0.455894	-0.455755
-0.444482	-0.456232	-0.455894	-0.455755
-0.136224	-0.149372	-0.149302	-0.149062
-0.136224	-0.149372	-0.149302	-0.149062
+0.000000	-0.022022	-0.022895	-0.022882
+0.000000	-0.022022	-0.022895	-0.022882
+0.000000	+0.000000	+0.000000	+0.000000
+0.000000	+0.000000	+0.000000	+0.000000
+0.269837	+0.257798	+0.258624	+0.258908
+0.269837	+0.257798	+0.258624	+0.258908

TABLE S10: Eigenvalue differences w.r.t. the HOMO for HAt with the PBE0 functional from Fig. 3(b) of the main text.

1c-SCF	PT1	PT2	2c-SCF
-0.510108	-0.544767	-0.542129	-0.541286
-0.510108	-0.544767	-0.542129	-0.541286
-0.138537	-0.186412	-0.186684	-0.184874
-0.138537	-0.186412	-0.186684	-0.184874
+0.000000	-0.055881	-0.062452	-0.061593
+0.000000	-0.055881	-0.062452	-0.061593
+0.000000	+0.000000	+0.000000	+0.000000
+0.000000	+0.000000	+0.000000	+0.000000
+0.241646	+0.203879	+0.212904	+0.214541
+0.241646	+0.203879	+0.212904	+0.214541

TABLE S11: Eigenvalue differences w.r.t. the HOMO for HTs with the PBE0 functional from Fig. 3(c) of the main text.

1c-SCF	PT1	PT2	2c-SCF
-0.689590	-0.787847	-0.762933	-0.764708
-0.689590	-0.787847	-0.762933	-0.764708
-0.145696	-0.277061	-0.289273	-0.292665
-0.145696	-0.277061	-0.289273	-0.292665
+0.000000	-0.091836	-0.104447	-0.100114
+0.000000	-0.091836	-0.104447	-0.100114
+0.000000	+0.000000	+0.000000	+0.000000
+0.000000	+0.000000	+0.000000	+0.000000
+0.220750	+0.084396	+0.158195	+0.157089
+0.220750	+0.084396	+0.158195	+0.157089
+0.350156	+0.176687	+0.295757	+0.285636
+0.350156	+0.176687	+0.295757	+0.285636
+0.760352	+0.331370	+0.494706	+0.460291
+0.760352	+0.331370	+0.494706	+0.460291