

## SUPPLEMENTAL MATERIAL

### Towards highly accurate calculations of parity violation in chiral molecules: relativistic coupled-cluster theory including QED-effects

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#### ARTICLE HISTORY

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#### 1. Tight exponents optimized by the simplex algorithm

Tight exponents were optimized with respect to the *dyall.nzp* basis sets, where  $n = 2, 3, 4$  for the Se atom, and  $n = 3$  for the other atoms. The same exponents were used in the extended basis sets of the same cardinal number  $n$  (that is, we added tight exponents optimized for 3zp to *acv3z*, *ae3z*, and *aae3z* basis sets). We did not add any exponents to the basis set for Po because the difference between the numerical and the basis set calculations is less than 1 %.

From Tables 1 and 2, we see that the optimized exponents are tighter than what would be expected by an even-tempered extension based on the ratio between from the tightest and the second tightest existing exponents. The tightest optimized  $p$  exponents of Se and Te are of the order of  $10^7$ . It is the similar order to the tightest exponent of Po atom (4.70483094E+07), where the error is less than 1% in the energy-optimized Dyall basis sets. For O and S atoms the values of the tightest  $p$  exponents are smaller than those of heavier elements by one or two orders of magnitude. It reflects the smaller electron density of the small component of the  $p_{1/2}$  orbital in the nuclear region due to the smaller nuclear charges of O and S.

**Table 1.** Existing and optimized additional exponents for the Se atom.

	Se			
	dyall.2zp		dyall.3zp	dyall.4zp
	s	p	p	p
second tightest	4.07068138E+05	1.45355104E+03	2.22428505E+04	4.05936956E+05
tightest	3.44182887E+06	7.41469836E+03	1.44232694E+05	2.75309494E+06
added	5.61955240E+07	8.99908620E+04	1.66730750E+06	3.34542040E+07
		1.50752220E+06	2.70901280E+07	
		2.48962880E+07		

**Table 2.** Existing and optimized additional exponents for O, S, Te and Po atoms of dyall.3zp basis sets.

	O	S		Te	Po
	p	s	p	p	p
	second tightest	4.55312788E+01	6.54988506E+05	4.13696340E+02	1.05425035E+06
tightest	1.94301648E+02	5.31068821E+06	1.87471736E+03	6.85083154E+06	4.70483094E+07
added	2.81261780E+03	1.09937100E+08	1.59956940E+04	5.10788410E+07	
	1.93965960E+05		3.27674800E+05		
			6.34804920E+06		

## 2. Coupled cluster calibration study

### 2.1. Computational details

A computational protocol for coupled cluster calculations of the title molecules was developed based on the calibration study of  $\text{H}_2\text{Se}_2$  reported here. All calculations employed the X2C molecular-mean-field Hamiltonian ( ${}^2DC_M$ ) [1] based on the Dirac-Coulomb Hamiltonian. For technical reasons, MP2 and CCSD expectation values were calculated using the RELCCSD[2, 3] and ExaCorr[4] modules, respectively. We employed Dyal basis sets [5–7] for all elements of the target molecules, after adding tight exponents as discussed in Section 4.1 of the main text and shown in Tables 1 and 2.

### 2.2. Correlated orbitals

Results at the CCSD and MP2 levels are shown in Tables 3 and 4, respectively. From comparison between the Tables, it is seen that the trend of convergence is different at the CCSD and MP2 level. In the case of the CCSD, an error below 1 % is reached only when correlating  $3s3p3d4s4p$ , whereas for MP2  $4s4p$  is enough.

### 2.3. Diffuse functions and truncation of the virtual space

Having decided to correlate  $3s3p3d4s4p$  electrons at the CCSD level, we consider the effect of adding diffuse functions. Table 5 shows the change from the reference value provided by the ae4z basis set. First, the relative error of the ae3z is around two percent, while that of aae3z, which includes diffuse functions, is less than one percent. Experimenting with different energy cutoffs, we see that the effect of virtual truncation using 500 or even 100  $E_h$  is rather small, so we decided to employ the aae3z basis set combined with 100  $E_h$  energy cutoff in the virtual space for the calculation of  $\text{H}_2\text{X}_2$  molecules.

## 3. Comparison with previous works

For convenience, Table 6 gives the HF, MP2 and CC values calculated in previous works and the present work. We summarize only the values calculated using the

**Table 3.** Parity-violating energy  $E_{PV}$  (in  $E_h$ ) of  $H_2Se_2$  calculated at the CCSD level with different number of correlated electrons. The virtual space is not truncated. Change (%) indicates the relative change with respect to the value on the line above ( $100 * ("target" - "target-1") / "target"$ ).

Basis	ae2z		ae3z		ae4z	
Correlated elec.	$E_{PV}$	change (%)	$E_{PV}$	change (%)	$E_{PV}$	change (%)
4p	-2.537E-15		-2.401E-15			
4s4p	-2.472E-15	2.6	-2.300E-15	4.1		
3d4s4p	-2.625E-15	-6.2	-2.464E-15	-7.0	-2.419E-15	
3s3p3d4s4p	-2.666E-15	-1.5	-2.501E-15	-1.5	-2.455E-15	-1.5
2s2p3s3p3d4s4p	-2.688E-15	-0.8	-2.521E-15	-0.8	-2.475E-15	-0.8
all	-2.689E-15	-5E-02	-2.523E-15	-4E-02		

**Table 4.** Parity-violating energy  $E_{PV}$  (in  $E_h$ ) of  $H_2Se_2$  calculated at the MP2 level with different number of correlated electrons. The virtual space is not truncated. Change (%) indicates the relative change with respect to the value on the line above ( $100 * ("target" - "target-1") / "target"$ ).

Basis	acv2z		acv3z	
Correlated elec.	$E_{PV}$	change (%)	$E_{PV}$	change (%)
4p	-2.365E-15		-2.234E-15	
4s4p	-2.323E-15	1.80	-2.191E-15	1.91
3d4s4p	-2.322E-15	0.05	-2.189E-15	0.08

**Table 5.** Parity-violating energy  $E_{PV}$  (in  $E_h$ ) of  $H_2Se_2$  calculated at the CCSD level with 3s3p3d4s4p orbitals correlated, but in different basis sets and truncation of virtual space.  $\Delta(\%)$  indicates the relative error with respect to the ae4x basis.

Basis	virtual cutoff	$E_{PV}$	$\Delta(\%)$
ae2z	none	-2.666E-15	8.59
ae3z	none	-2.501E-15	1.87
aae3z	100 ( $E_h$ )	-2.463E-15	0.33
aae3z	500 ( $E_h$ )	-2.466E-15	0.44
aae3z	none	-2.467E-15	0.49
ae4z	none	-2.455E-15	

geometries that were obtained in Ref. 8.

**Table 6.** Summary of values of  $E_{PV}$  ( $E_h$ ) of  $H_2X_2$  molecules in previous and present works. All values were calculated by using the geometry obtained in Ref. 8 and at the  $45^\circ$  dihedral angle of the P enantiomer. All values are analytical except for those marked “ff”, which refers to the finite-field results.

Molecule	Hamiltonian	Method	Basis set for X	Correlated elec.	Cutoff ( $E_h$ )	$E_{PV}$ ( $E_h$ )	
$H_2O_2$	${}^2DC_M$	CCSD <sup>a</sup>	dyall.aae3z+2p	all	100	-5.917E-19	
		MP2 <sup>a</sup>	dyall.acv3z+2p	2s2p	100	-6.525E-19	
	${}^4DC$	HF <sup>a</sup>	dyall.aae3z+2p				-6.808E-19
		CCSD <sup>b</sup>	cc-pVDZ+3p	all	100	-6.126E-19	
			dyall.ae3z	all	100	-5.323E-19	
			dyall.ae4z	all	100	-5.583E-19	
		HF <sup>b</sup>	cc-pVDZ+3p				-6.790E-19
			dyall.ae3z				-6.051E-19
			dyall.ae4z				-6.376E-19
		CCSD(ff) <sup>c</sup>	cc-pVDZ+3p	all	not mentioned		-6.180E-19
		CCSD(T)(ff) <sup>c</sup>	cc-pVDZ+3p	all	not mentioned		-6.117E-19
		MP2 <sup>d</sup>	cc-pVDZ+3p	all	none		-5.788E-19
	HF <sup>d</sup>	cc-pVDZ+3p				-6.784E-19	
	$H_2S_2$	${}^2DC_M$	CCSD <sup>a</sup>	dyall.aae3z+1s3p	2s2p3s3p	100	-2.166E-17
MP2 <sup>a</sup>			dyall.acv3z+1s3p	3s3p	100	-2.067E-17	
${}^4DC$		HF <sup>a</sup>	dyall.aae3z+1s3p				-2.160E-17
		CCSD <sup>b</sup>	cc-pCVTZ	3s3p	100	-1.821E-17	
			cc-pVDZ+2p	3s3p	100	-2.089E-17	
		HF <sup>b</sup>	cc-pCVTZ				-1.826E-17
			cc-pVDZ+2p				-2.078E-17
		CCSD(ff) <sup>c</sup>	cc-pVDZ+2p <sup>e</sup>	all	not mentioned		-2.165E-17
		CCSD(T)(ff) <sup>c</sup>	cc-pVDZ+2p <sup>e</sup>	all	not mentioned		-2.113E-17
		MP2 <sup>d</sup>	cc-pVDZ+2p	all	none		-2.112E-17
		HF <sup>d</sup>	cc-pVDZ+2p				-2.077E-17
		$H_2Se_2$	${}^2DC_M(U+FG)$	CCSD <sup>a</sup>	dyall.aae3z+2p	3s3p3d4s4p	100
${}^2DC_M(U+PZ)$			dyall.aae3z+2p	3s3p3d4s4p	100	-2.458E-15	
${}^2DC_M$			dyall.aae3z+2p	3s3p3d4s4p	100	-2.463E-15	
${}^4DC$	MP2 <sup>a</sup>		dyall.acv3z+2p	4s4p	100	-2.191E-15	
	HF <sup>a</sup>		dyall.aae3z+2p				-2.301E-15
	CCSD <sup>b</sup>		dyall.cv3z	3d4s4p	40	-2.115E-15	
	HF <sup>b</sup>		dyall.cv3z				-2.139E-15
	MP2 <sup>d</sup>		dyall.v2z+2p	all	none		-2.275E-15
	HF <sup>d</sup>		dyall.v2z+2p				-2.263E-15
$H_2Te_2$	${}^2DC_M(U+FG)$		CCSD <sup>a</sup>	dyall.aae3z+1p	4s4p4d5s5p	100	-3.471E-14
	${}^2DC_M(U+PZ)$		dyall.aae3z+1p	4s4p4d5s5p	100	-3.525E-14	
	${}^2DC_M$		dyall.aae3z+1p	4s4p4d5s5p	100	-3.536E-14	
	${}^4DC$	MP2 <sup>a</sup>	dyall.acv3z+1p	5s5p	100	-3.236E-14	
		HF <sup>a</sup>	dyall.aae3z+1p				-3.403E-14
		CCSD <sup>b</sup>	dyall.cv3z	4d5s5p	40	-3.289E-14	
		HF <sup>b</sup>	dyall.cv3z				-3.317E-14
		MP2 <sup>d</sup>	dyall.v2z+2p	3s3p3d4s4p4d5s5p	100	-3.806E-14	
		HF <sup>d</sup>	dyall.v2z+2p				-3.612E-14

<sup>a</sup>This work

<sup>b</sup>Shee *et al.*[3]

<sup>c</sup>Thyssen *et al.*[9]

<sup>d</sup>van Stralen *et al.* [10]

<sup>e</sup>The authors reported cc-pVDZ+3p, but cc-pVDZ+2p was mentioned in the computational details.

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