1 H_4

Table 1: Wavefunction parameters (δ, η, in degrees) and related quantities for the singlet state of H_4 in 6-311G** basis obtained in geminal-based models for selected geometries. For details, see legend of Fig. 1 in the main body of the paper.

	$\alpha = 85°$				$\alpha = 87°$				$\alpha = 90°$			
	USLG		HP-USLG		USLG		HP-USLG		USLG		HP-USLG	
μ	1	2	1	2	1	2	1	2	1	2	1	2
δ_μ	0	0	16.5	16.5	0	0	17.0	17.0	0	0	17.4	17.4
η_μ	1.16	19.0	1.35	21.3	1.16	26.3	1.38	28.5	1.16	45.0	1.40	45.0
$\mathcal{M}_\mu$			0.839	0.839			0.829	0.829			0.821	0.821

Table 2: Wavefunction parameters (δ, η, in degrees) and related quantities for the triplet state of H_4 in 6-311G** basis obtained in geminal-based models for selected geometries. For details, see legend of Fig. 1 in the main body of the paper.

	$\alpha = 85°$				$\alpha = 87°$				$\alpha = 90°$			
	USLG		HP-USLG		USLG		HP-USLG		USLG		HP-USLG	
μ	1	2	1	2	1	2	1	2	1	2	1	2
δ_μ	4.65	57.4	17.0	73.0	4.01	65.6	17.0	73.0	3.33	71.3	17.0	73.0
η_μ	1.32	24.6	1.38	41.8	1.28	31.9	1.38	43.1	1.25	45.0	1.39	45.0
$\mathcal{M}_\mu$			0.830	−0.830			0.830	−0.830			0.830	−0.830

2 O_2

Table 3: Weight (in total coefficient squared sense) of $\hat{S}^2$-eigenfunctions corresponding to eigenvalue S in geminal-based wavefunctions, obtained for the singlet and triplet states of O_2 in 6-31G basis. For geometry, we refer to Table 4 of the paper.

	singlet			triplet		
	USLG	HP-USLG, before proj.	HP-USLG, after proj.	USLG	HP-USLG, before proj.	HP-USLG, after proj.
$S = 0$	1	0.1040	0.9972	0	0.8951	0
$S = 1$	0	0.8957	0	1	0.1049	1.0000
$S = 2$	0	0.0029	0.0028	0	$3.32 \cdot 10^{-5}$	0
$S = 3$	0	$< 10^{-7}$	0	0	$< 10^{-8}$	$< 10^{-7}$
$\langle \hat{S}^2 \rangle$	0	1.7932	0.0170	2.0000	0.2100	2.0000

3 NH

Table 4: Wavefunction parameters (δ, η in degrees) and related quantities for the singlet and triplet states of NH in cc-pVTZ basis obtained in geminal-based models. Only correlated geminals are tabulated. For geometry, we refer to Table 5 of the paper.

	singlet						triplet					
	USLG			HP-USLG			USLG			HP-USLG		
μ	1	2	3	1	2	3	1	2	3	1	2	3
δ_μ	0	0	0	1.29	9.27	24.25	0	0	90.00	1.30	9.11	66.8
η_μ	0.22	0.79	45.0	0.22	0.93	45.0	0.21	0.79	n.a.	0.22	0.92	45.0
$\mathcal{M}_\mu$				0.999	0.948	0.663				0.999	0.950	−0.689

Table 5: Weight (in total coefficient squared sense) of $\hat{S}^2$-eigenfunctions corresponding to eigenvalue S in geminal-based wavefunctions, obtained for the singlet and triplet states of NH in cc-pVTZ basis. For geometry, we refer to Table 5 of the paper.

	singlet			triplet		
	USLG	HP-USLG, before proj.	HP-USLG, after proj.	USLG	HP-USLG, before proj.	HP-USLG, after proj.
$S=0$	1	0.8108	0.9963	0	0.1587	0
$S=1$	0	0.1862	0	1	0.8269	1.0000
$S=2$	0	0.0030	0.0037	0	0.0144	0
$S=3$	0	$< 10^{-6}$	0	0	$4.38 \cdot 10^{-6}$	$5.3 \cdot 10^{-6}$
$\langle \hat{S}^2 \rangle$	0	0.3903	0.0220	2.0000	1.7401	2.0000

4 O_3

4.1 Four correlated geminals

Table 6: Ground state energy (in E_h) and vertical excitation energy (in eV) of the lowest triplet state of the ozone molecule in cc-pCVDZ basis, obtained by different geminal based models. Number of correlated geminals is 4 in the Ansätze. Further computational details are provided in Table 6 of the paper.

	$^1A_1$	$^3B_2$
USLG	−224.3645	0.977
USLG-PT2	−224.8600	1.506
HP-USLG	−224.3713	0.943
HP-USLG-PT2 1w	−224.8535	2.375
HP-USLG-PT2 2w	−224.8500	1.922
HP-USLG-PT2 3w	−224.8486	1.463

Table 7: Wavefunction parameters for the singlet and triplet states of ozone in cc-pCVDZ basis obtained in geminal-based models. Only correlated geminals are tabulated. Further computational details are provided in Table 6 of the paper.

	singlet							
	USLG				HP-USLG			
μ	1	2	3	4	1	2	3	4
δ_μ	0	0	0	0	4.78	5.35	5.89	21.85
η_μ	0.44	0.82	1.92	28.3	0.48	0.87	1.98	28.5
$\mathcal{M}_\mu$					0.986	0.983	0.979	0.723
	triplet							
	USLG				HP-USLG			
μ	1	2	3	4	1	2	3	4
δ_μ	0	0	0	90.00	4.96	5.22	5.96	66.1
η_μ	0.44	0.82	1.92	n.a.	0.49	0.87	1.99	37.2
$\mathcal{M}_\mu$					0.985	0.983	0.978	-0.672

Table 8: Weight (in total coefficient squared sense) of $\hat{S}^2$-eigenfunctions corresponding to eigenvalue S in geminal-based wavefunctions, obtained for the singlet and triplet states of ozone in cc-pCVDZ basis. Further computational details are provided in Table 6 of the paper.

	singlet			triplet		
	USLG	HP-USLG, before proj.	HP-USLG, after proj.	USLG	HP-USLG, before proj.	HP-USLG, after proj.
$S=0$	1	0.8403	0.9970	0	0.1672	0
$S=1$	0	0.1572	0	1	0.8182	0.9999
$S=2$	0	0.0251	0.0030	0	0.0146	0
$S=3$	0	$1.26 \cdot 10^{-3}$	0	0	$7.69 \cdot 10^{-5}$	$9.34 \cdot 10^{-5}$
$S=4$	0	$< 10^{-7}$	$< 10^{-7}$	0	$< 10^{-6}$	0
$\langle \hat{S}^2 \rangle$	0	0.3295	0.0179	2.0000	1.7246	2.0009

4.2 Six correlated geminals

Table 9: Wavefunction parameters (δ, η in degrees) and related quantities for the singlet and triplet states of ozone in cc-pCVDZ basis obtained in geminal-based models. Only correlated geminals are tabulated. Further computational details are provided in Table 6 of the paper.

	singlet											
	USLG						HP-USLG					
μ	1	2	3	4	5	6	1	2	3	4	5	6
δ_μ	0.19	0.23	0.37	0.39	0.42	4.80	2.73	3.12	4.63	5.32	5.80	22.8
η_μ	0.58	0.47	0.44	0.82	1.92	28.3	0.59	0.49	0.48	0.88	1.98	28.6
$\mathcal{M}_\mu$							0.995	0.994	0.987	0.983	0.980	0.700
	triplet											
	USLG						HP-USLG					
μ	1	2	3	4	5	6	1	2	3	4	5	6
δ_μ	0	0	0	0	0	90.0	2.66	3.07	4.84	5.28	5.93	65.4
η_μ	0.58	0.47	0.44	0.82	1.92	n.a.	0.59	0.49	0.49	0.88	1.99	38.2
$\mathcal{M}_\mu$							0.996	0.994	0.986	0.983	0.979	-0.654

Table 10: Weight (in total coefficient squared sense) of $\hat{S}^2$-eigenfunctions corresponding to eigenvalue S in geminal-based wavefunctions, obtained for the singlet and triplet states of ozone in cc-pCVDZ basis. Further computational details are provided in Table 6 of the paper.

	singlet			triplet		
	USLG	HP-USLG, before proj.	HP-USLG, after proj.	USLG	HP-USLG, before proj.	HP-USLG, after proj.
$S=0$	0.9928	0.8260	0.9962	0	0.1759	0
$S=1$	0.0072	0.1708	0	1	0.8071	0.9999
$S=2$	$< 10^{-6}$	0.0032	0.0038	0	0.0169	0
$S=3$	$< 10^{-10}$	$2.13 \cdot 10^{-5}$	0	0	$1.19 \cdot 10^{-4}$	$1.47 \cdot 10^{-4}$
$S=4$	$< 10^{-15}$	$< 10^{-7}$	$< 10^{-7}$	0	$3.63 \cdot 10^{-8}$	0
$S=5$	$< 10^{-20}$	$< 10^{-10}$	0	0	$< 10^{-9}$	$< 10^{-9}$
$S=6$	$< 10^{-26}$	$< 10^{-13}$	$< 10^{-13}$	0	$< 10^{-12}$	0
$\langle \hat{S}^2 \rangle$	0.0143	0.3609	0.0230	2.0000	1.7169	2.0015

5 *para*-benzyne

Table 11: Wavefunction parameters (δ and η, in degrees) and related quantities for the singlet and triplet states of *para*-benzyne in 6-31G* basis obtained in geminal-based models. Only correlated geminals are tabulated. For details, see the legend of Table 7 in the main body of the paper.

	singlet							
	USLG				HP-USLG			
μ	1	2	3	4	1	2	3	4
δ_μ	6.234	12.63	9.899	41.28	13.45	23.15	20.55	13.65
η_μ	1.76	7.88	8.96	39.3	2.30	8.45	9.70	39.2
$\mathcal{M}_\mu$					0.89	0.69	0.75	0.89
	triplet							
	USLG				HP-USLG			
μ	1	2	3	4	1	2	3	4
δ_μ	0	0	0	90.00	13.37	23.82	20.00	75.72
η_μ	1.45	8.08	7.52	n.a.	2.30	8.96	9.21	42.0
$\mathcal{M}_\mu$					0.83	0.67	0.77	-0.88

Table 12: Weight (in total coefficient squared sense) of $\hat{S}^2$-eigenfunctions corresponding to eigenvalue S in geminal-based wavefunctions, obtained for the singlet and triplet states of *para*-benzyne in 6-31G* basis. For geometries, see the legend of Table 7 in the main body of the paper.

	singlet			triplet		
	USLG	HP-USLG, before proj.	HP-USLG, after proj.	USLG	HP-USLG, before proj.	HP-USLG, after proj.
$S=0$	0.5284	0.6768	0.9583	0	0.1274	0
$S=1$	0.4458	0.2927	0	1	0.6908	0.9834
$S=2$	0.0254	0.0295	0.0417	0	0.1699	0
$S=3$	$4.00\cdot10^{-4}$	$1.08\cdot10^{-3}$	0	0	0.0117	0.0166
$S=4$	$1.66\cdot10^{-6}$	$1.31\cdot10^{-5}$	$1.86\cdot10^{-5}$	0	0.0002	0
$\langle\hat{S}^2\rangle$	1.0488	0.7753	0.2506	2.0000	2.5454	2.1661