

**Supporting Information:**

**Method for Calculating Excited Electronic States**

**Using Density Functionals and Direct Orbital**

**Optimization with Real Space Grid or Plane Wave**

**Basis Set**

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# 1 Ground-state molecular orbitals of $[\text{Fe}(\text{bmip})_2]^{2+}$

Isosurfaces showing the molecular orbitals of the  $[\text{Fe}(\text{bmip})_2]^{2+}$  complex involved in the electronic transitions investigated in the present work. The isosurfaces are represented with gray and orange colors and correspond to isovalues of  $\pm 0.16 \text{ \AA}^{-3/2}$ .

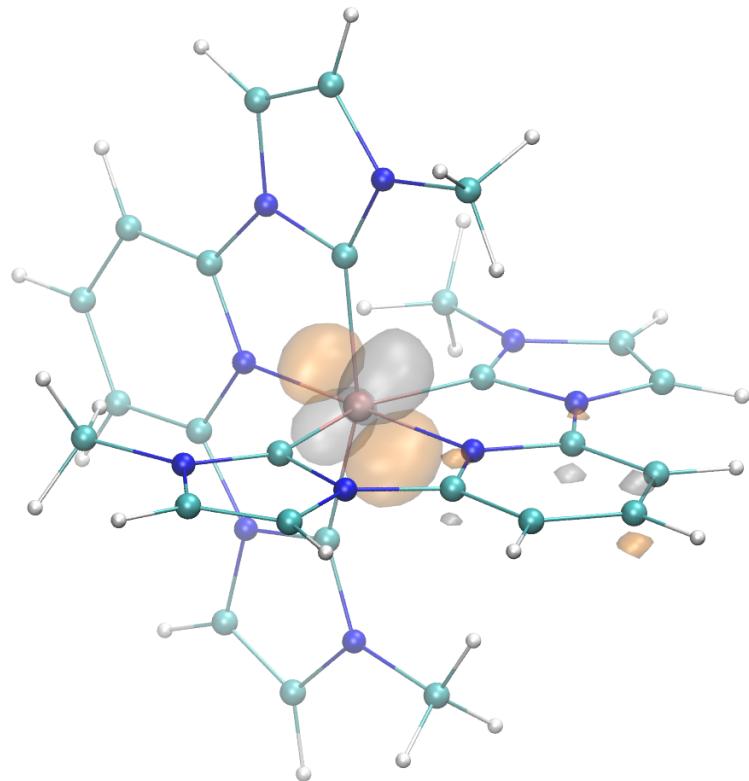


Figure S1: HOMO-1

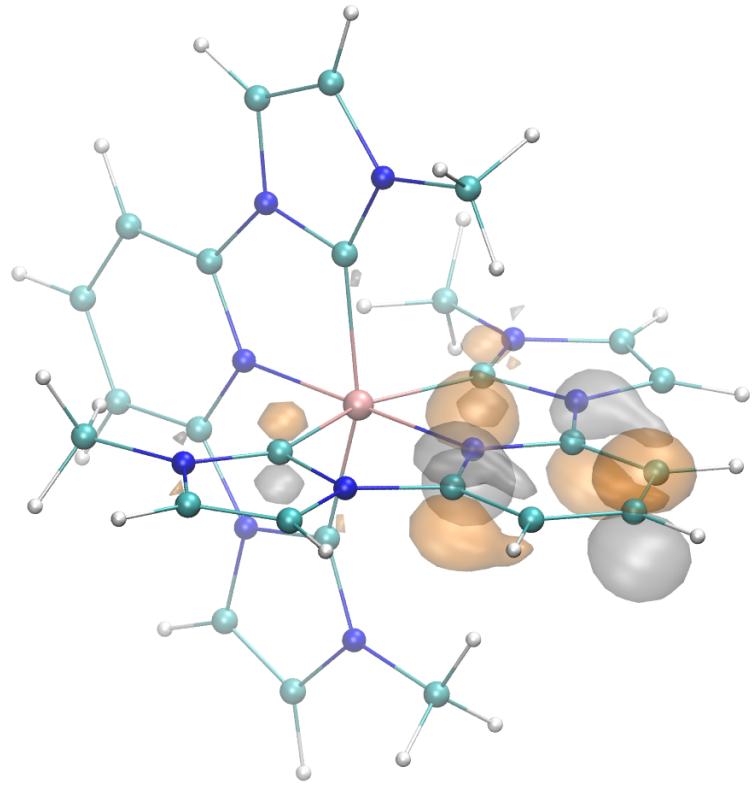


Figure S2: LUMO

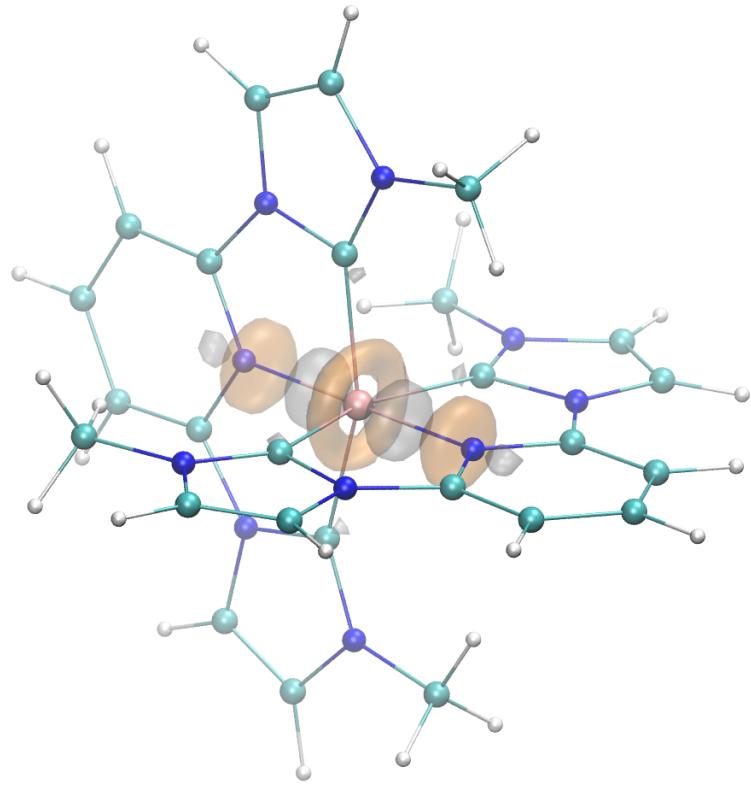


Figure S3: LUMO+4

## 2 Curvature of the ${}^3\text{MC}$ potential energy curve of $[\text{Fe}(\text{bmip})_2]^{2+}$

The potential energy curves of the lowest  ${}^3\text{MC}$  state of  $[\text{Fe}(\text{bmip})_2]^{2+}$  calculated with DO-MOM (BLYP) in the present work and linear response TDDFT (B3LYP\*) from Ref.<sup>S1</sup> are fitted using a fourth order polynomial:

$$E(Q) = -d_e + \frac{k}{2}(Q - r_e)^2 - \alpha(Q - r_e)^3 + \beta(Q - r_e)^4, \quad (1)$$

where  $k$  is the curvature. Below are the results of the fitting of the curve calculated with DO-MOM (BLYP):

$$d_e = -1.934$$

$$k = 1.332 \times 10^{-2}$$

$$r_e = 5.060$$

$$\alpha = 1.265 \times 10^{-4}$$

$$\beta = -1.652 \times 10^{-6}$$

and of the curve calculated with TDDFT (B3LYP\*):

$$d_e = -1.821$$

$$k = 1.263 \times 10^{-2}$$

$$r_e = 5.514$$

$$\alpha = 9.256 \times 10^{-4}$$

$$\beta = 2.461 \times 10^{-7}$$

The fitted curves are shown in Fig. S4 together with the points obtained from the DO-MOM (BLYP) and TDDFT (B3LYP\*) calculations. The curvatures of the fitted curves differ by around 5%. The oscillation period estimated on the basis of TDDFT is 285 fs,<sup>S1</sup> and thus,

we obtain an estimation of an oscillation period on the basis of eDFT as

$$T_{eDFT} = T_{TDDFT} \sqrt{\frac{k_{TDDFT}}{k_{eDFT}}} \approx 280 \text{ (fs)}$$

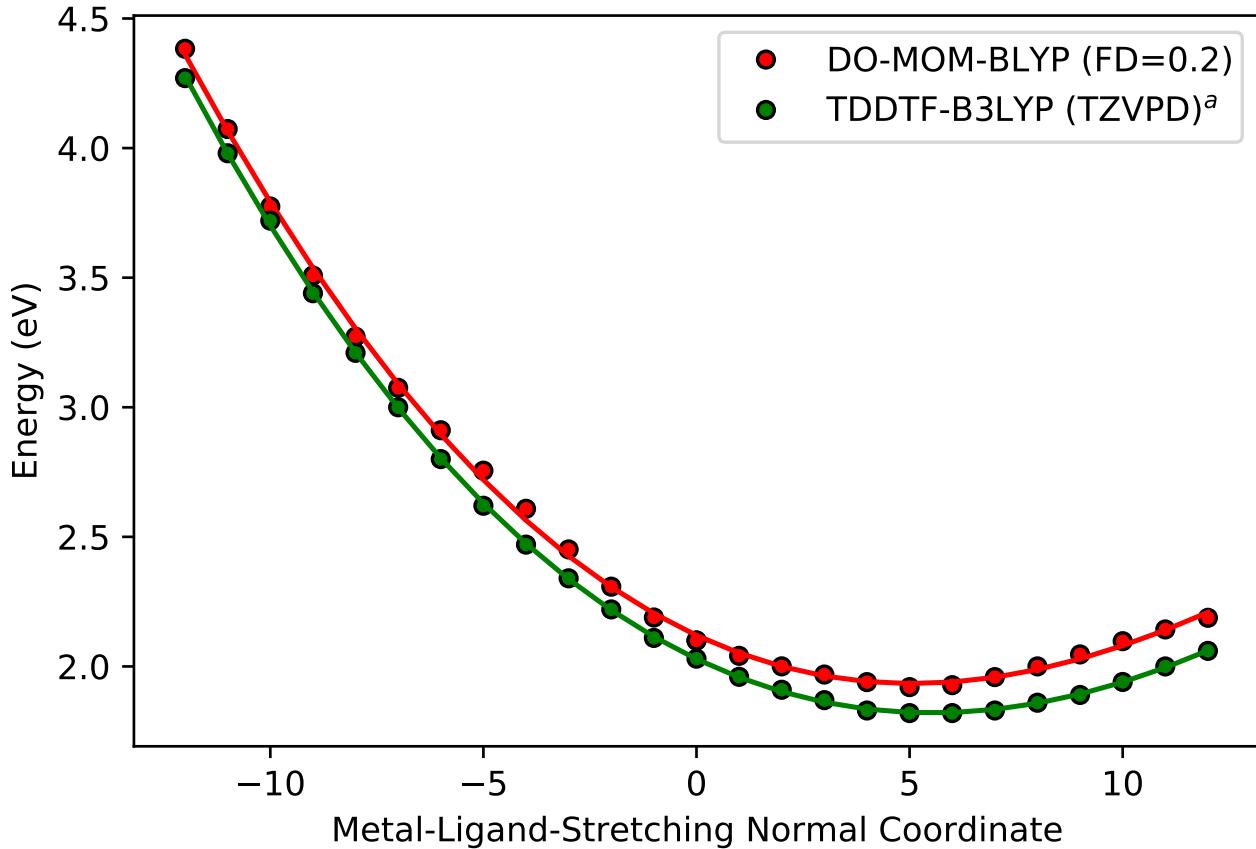


Figure S4: Potential energy curves along a metal-ligand normal coordinate (the breathing mode  $Q_6$  as defined in Ref.<sup>S1</sup>) of the lowest  ${}^3\text{MC}$  state. The DO-MOM (BLYP) calculations were performed using a finite-difference real-space basis set as described in the main text of the article. <sup>a</sup>Calculations from Ref. S1

### 3 Excitation Energy obtained from the Mixed-Spin Determinant

**Table S1: Mixed-Spin States**

species	excitation	PBE <sup>a</sup>	SIC/2 <sup>b</sup>	SIC <sup>b</sup>	TBE <sup>c</sup>	EXP <sup>d</sup>																																										
acetaldehyde	$1^1A'' (n \rightarrow \pi^*; V)$	3.79	3.74	3.69	4.31	4.27																																										
acetylene	$1^1\Delta_u (\pi \rightarrow \pi^*; V)$	6.51	6.81	6.90	7.10	7.2																																										
ammonia	$2^1A_1 (n \rightarrow 3s; R)$	6.30	6.25	6.23	6.66	6.38																																										
carbon monoxide	$1^1\Pi (n \rightarrow \pi^*; V)$	6.70	6.90	7.51	8.48	8.51																																										
diazomethane	$1^1A_2 (\pi \rightarrow \pi^*; V)$	2.85	2.47	2.01	3.13	3.14																																										
ethylene	$1^1B_{3u} (n \rightarrow 3s; R)$ $1^1B_{1u} (\pi \rightarrow \pi^*; V)$	7.07 5.59	7.12 5.90	7.14 6.20	7.43 7.92	7.11 7.6																																										
formaldehyde	$1^1B_2 (n \rightarrow 3s; R)$	6.79	7.04	7.16	7.30	7.11																																										
formamide	$1^1A'' (n \rightarrow \pi^*; V)$	5.26	5.20	5.14	5.63	5.8																																										
hydrogen sulfide	$1^1A_2 (n \rightarrow 4p; R)$	5.51	5.53	5.49	6.10																																											
ketene	$1^1B_1 (\pi \rightarrow 3s; R)$	5.75	5.87	5.95	6.06	5.86																																										
methanimine	$1^1A'' (n \rightarrow \pi^*; V)$	4.43	4.56	4.65	5.21																																											
thioformaldehyde	$1^1A_2 (n \rightarrow \pi^*; V)$ $1^1B_2 (n \rightarrow 4s; R)$ $2^1A_1 (\pi \rightarrow \pi^*; V)$	1.81 5.47 4.36	1.78 5.63 4.67	1.72 5.72 4.97	2.20 5.99 6.34	2.03 5.85 6.2																																										
water	$1^1B_1 (n \rightarrow 3s; R)$ $1^1A_2 (n \rightarrow 3p; R)$ $2^1A_1 (n \rightarrow 3s; R)$	7.28 8.83 9.50	7.27 8.94 9.48	7.24 9.04 9.46	7.70 9.47 9.97	7.41 9.2 9.67																																										
<table border="1" style="width:100%; border-collapse: collapse;"> <tr> <td>ME (TBE)</td> <td>-0.73</td> <td>-0.66</td> <td>-0.59</td> <td></td> <td></td> <td></td> </tr> <tr> <td>ME (EXP)</td> <td>-0.59</td> <td>-0.52</td> <td>-0.49</td> <td></td> <td></td> <td></td> </tr> <tr> <td>MAE (TBE)</td> <td>0.73</td> <td>0.66</td> <td>0.59</td> <td></td> <td></td> <td></td> </tr> <tr> <td>MAE (EXP)</td> <td>0.59</td> <td>0.52</td> <td>0.50</td> <td></td> <td></td> <td></td> </tr> <tr> <td>RMSE (TBE)</td> <td>0.95</td> <td>0.83</td> <td>0.73</td> <td></td> <td></td> <td></td> </tr> <tr> <td>RMSE (EXP)</td> <td>0.88</td> <td>0.76</td> <td>0.68</td> <td></td> <td></td> <td></td> </tr> </table>							ME (TBE)	-0.73	-0.66	-0.59				ME (EXP)	-0.59	-0.52	-0.49				MAE (TBE)	0.73	0.66	0.59				MAE (EXP)	0.59	0.52	0.50				RMSE (TBE)	0.95	0.83	0.73				RMSE (EXP)	0.88	0.76	0.68			
ME (TBE)	-0.73	-0.66	-0.59																																													
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<sup>a</sup> Employing real-valued orbitals; <sup>b</sup> Initial guess for the wave functions is PBE real-valued orbitals followed by complex Rudenberg-Edmiston localization; <sup>c</sup> Corrected theoretical best estimates as given in Ref.<sup>S2</sup>; <sup>d</sup> Listed in Ref. S<sup>2</sup> (see references therein);

## 4 Extended Data For Excitation Energy Including Hybrid Functionals

Calculations with hybrid functionals are performed using the real space grid (RSG) implementation in the GPAW software<sup>S3</sup> with grid spacing and simulation box as described in the main text. Some excitation energies were first compared with all-electron calculation using the ORCA software,<sup>S4,S5</sup> in order to test the validity of the RSG hybrid functional calculations in GPAW. The ORCA calculations made use of a Def2-QZVVPD basis set, no resolution of identity for the calculation of exact exchange, and fifth grid level. For the lowest triplet excitations in diazomethane and thioformaldehyde, the excitation energies given by PBE0 and calculated with ORCA are found to be -2.482 eV and -1.596 eV, respectively, and those calculated with PBE0 and the GPAW software are found to be -2.482 and -1.594 eV, respectively. This indicates that the frozen core approximation and approximations due to the PAW approach have little affect on the low lying excitation energies.

**Table S2: Energy of excitations to triplet states calculated with the DO-MOM method and comparison with theoretical best estimates as well as experimental values. The calculations make use of a generalized gradient approximation Kohn-Sham functional (PBE), with scaled self-interaction correction (SIC/2), with full self-interaction correction (SIC) as well as two hybrid functionals PBE0 with 25% of exact exchange and PBE50 with 50% of exact exchange. The mean error (ME), mean absolute error (MAE) and root mean square error (RMSE) are given with respect to theoretical best estimates and with respect to experimental values at the bottom of the table.**

molecule	excitation	PBE	PBE0	PBE50	SIC/2	SIC	TBE <sup>a</sup>	EXP <sup>b</sup>
acetaldehyde	$1^3A''(n \rightarrow \pi^*; V)$	3.65	3.58	3.45	3.75	3.79	3.98	3.97
acetylene	$1^3\Delta_u(\pi \rightarrow \pi^*; V)$	6.33	6.2	6.07	5.89	6.04	6.40	6.0
ammonia	$2^3A_1(n \rightarrow 3s; R)$	6.16	6.14	6.12	6.10	6.06	6.37	6.02
carbon monoxide	$1^3\Pi(n \rightarrow \pi^*; V)$	5.91	5.88	5.82	5.66	6.28	6.32	
diazomethane	$1^3A_2(\pi \rightarrow \pi^*; V)$	2.76	2.48	2.18	2.38	1.88	2.80	
ethylene	$1^3B_{3u}(n \rightarrow 3s; R)$ $1^3B_{1u}(\pi \rightarrow \pi^*; V)$	7.01 4.46	6.95 4.25	6.89 4.04	7.05 4.63	7.07 4.75	7.28 4.54	6.98 4.36
formaldehyde	$1^3B_2(n \rightarrow 3s; R)$	6.69	6.83	6.91	6.99	7.12	7.14	6.83
formamide	$1^3A''(n \rightarrow \pi^*; V)$	5.14	5.0	4.82	5.23	5.27	5.37	5.2
hydrogen sulfide	$1^3A_2(n \rightarrow 4p; R)$	5.39	5.45	5.49	5.44	5.43	5.74	5.8
ketene	$1^3B_1(\pi \rightarrow 3s; R)$	5.64	5.76	5.87	5.77	5.79	5.85	5.8
methanimine	$1^3A''(n \rightarrow \pi^*; V)$	4.20	4.17	4.10	4.35	4.41	4.64	
thioformaldehyde	$1^3A_2(n \rightarrow \pi^*; V)$ $1^3B_2(n \rightarrow 4s; R)$ $2^3A_1(\pi \rightarrow \pi^*; V)$	1.71 5.31 3.36	1.59 5.47 3.09	1.46 5.61 2.81	1.81 5.54 3.33	1.88 5.67 3.28	1.94 5.76 3.44	3.28
water molecule	$1^3B_1(n \rightarrow 3s; R)$ $1^3A_2(n \rightarrow 3p; R)$ $2^3A_1(n \rightarrow 3s; R)$	7.10 8.75 9.28	7.02 8.74 9.24	6.94 8.72 9.2	7.09 8.87 9.25	7.08 8.97 9.23	7.33 9.30 9.59	7.2 8.9 9.46
ME (TBE)								
ME (EXP)								
MAE (TBE)								
MAE (EXP)								
RMSE (TBE)								
RMSE (EXP)								

<sup>a</sup>Theoretical best estimates as given in Ref.<sup>S2</sup> <sup>b</sup>Experimental values listed in Ref.<sup>S2</sup> (see references therein).

**Table S3: Energy of excitations to singlet states (spin purified) calculated with the DO-MOM method and comparison with theoretical best estimates as well as experimental values. The calculations make use of a generalized gradient approximation Kohn-Sham functional (PBE), with scaled self-interaction correction (SIC/2), with full self-interaction correction (SIC) as well as two hybrid functionals PBE0 with 25% of exact exchange and PBE50 with 50% of exact exchange. The mean error (ME), mean absolute error (MAE) and root mean square error (RMSE) are given with respect to theoretical best estimates and with respect to experimental values at the bottom of the table.**

molecule	excitation	PBE	PBE0	PBE50	SIC/2	SIC	TBE <sup>a</sup>	EXP <sup>b</sup>
acetaldehyde	$1^1A''(n \rightarrow \pi^*; V)$	3.94	3.85	3.70	3.74	3.59	4.31	4.27
acetylene	$1^1\Delta_u(\pi \rightarrow \pi^*; V)$	6.69	6.59	6.47	7.72	7.76	7.10	7.2
ammonia	$2^1A_1(n \rightarrow 3s; R)$	6.44	6.42	6.41	6.40	6.37	6.66	6.38
carbon monoxide	$1^1\Pi(n \rightarrow \pi^*; V)$	7.48	7.83	8.17	7.96	9.36	8.48	8.51
diazomethane	$1^1A_2(\pi \rightarrow \pi^*; V)$	2.94	2.66	2.36	2.56	2.14	3.13	3.14
ethylene	$1^1B_{3u}(n \rightarrow 3s; R)$ $1^1B_{1u}(\pi \rightarrow \pi^*; V)$	7.14 6.72	7.41 7.07	6.99 8.09	7.18 7.17	7.2 7.64	7.43 7.92	7.11 7.6
formaldehyde	$1^1B_2(n \rightarrow 3s; R)$	6.89	6.98	7.01	7.10	7.30	7.11	
formamide	$1^1A''(n \rightarrow \pi^*; V)$	5.38	5.21	5.0	5.17	5.01	5.63	5.8
hydrogen sulfide	$1^1A_2(n \rightarrow 4p; R)$	5.63	5.67	5.69	5.63	5.55	6.10	
ketene	$1^1B_1(\pi \rightarrow 3s; R)$	5.87	5.97	6.06	5.97	6.11	6.06	5.86
methanimine	$1^1A''(n \rightarrow \pi^*; V)$	4.65	4.68	4.65	4.77	4.89	5.21	
thioformaldehyde	$1^1A_2(n \rightarrow \pi^*; V)$ $1^1B_2(n \rightarrow 4s; R)$ $2^1A_1(\pi \rightarrow \pi^*; V)$	1.91 5.64 5.36	1.77 5.76 6.07	1.61 5.84 6.77	1.74 5.72 6.02	1.57 5.77 6.66	2.20 5.99 6.34	2.03 5.85 6.2
water molecule	$1^1B_1(n \rightarrow 3s; R)$ $1^1A_2(n \rightarrow 3p; R)$ $2^1A_1(n \rightarrow 3s; R)$	7.46 8.91 9.73	7.38 8.89 9.75	7.31 8.88 9.78	7.46 9.02 9.71	7.41 9.11 9.69	7.70 9.47 9.97	7.41 9.2 9.67
		ME (TBE)	-0.46	-0.38	-0.33	-0.33	-0.21	
		ME (EXP)	-0.30	-0.22	-0.17	-0.17	-0.06	
		MAE (TBE)	0.46	0.38	0.40	0.40	0.44	
		MAE (EXP)	0.33	0.32	0.39	0.27	0.36	
		RMSE (TBE)	0.54	0.43	0.45	0.43	0.51	
		RMSE (EXP)	0.46	-0.38	0.46	0.35	0.49	

<sup>a</sup>Corrected theoretical best estimates as given in Ref.<sup>S2</sup> <sup>b</sup>Experimental values listed in Ref.<sup>S2</sup> (see references therein).

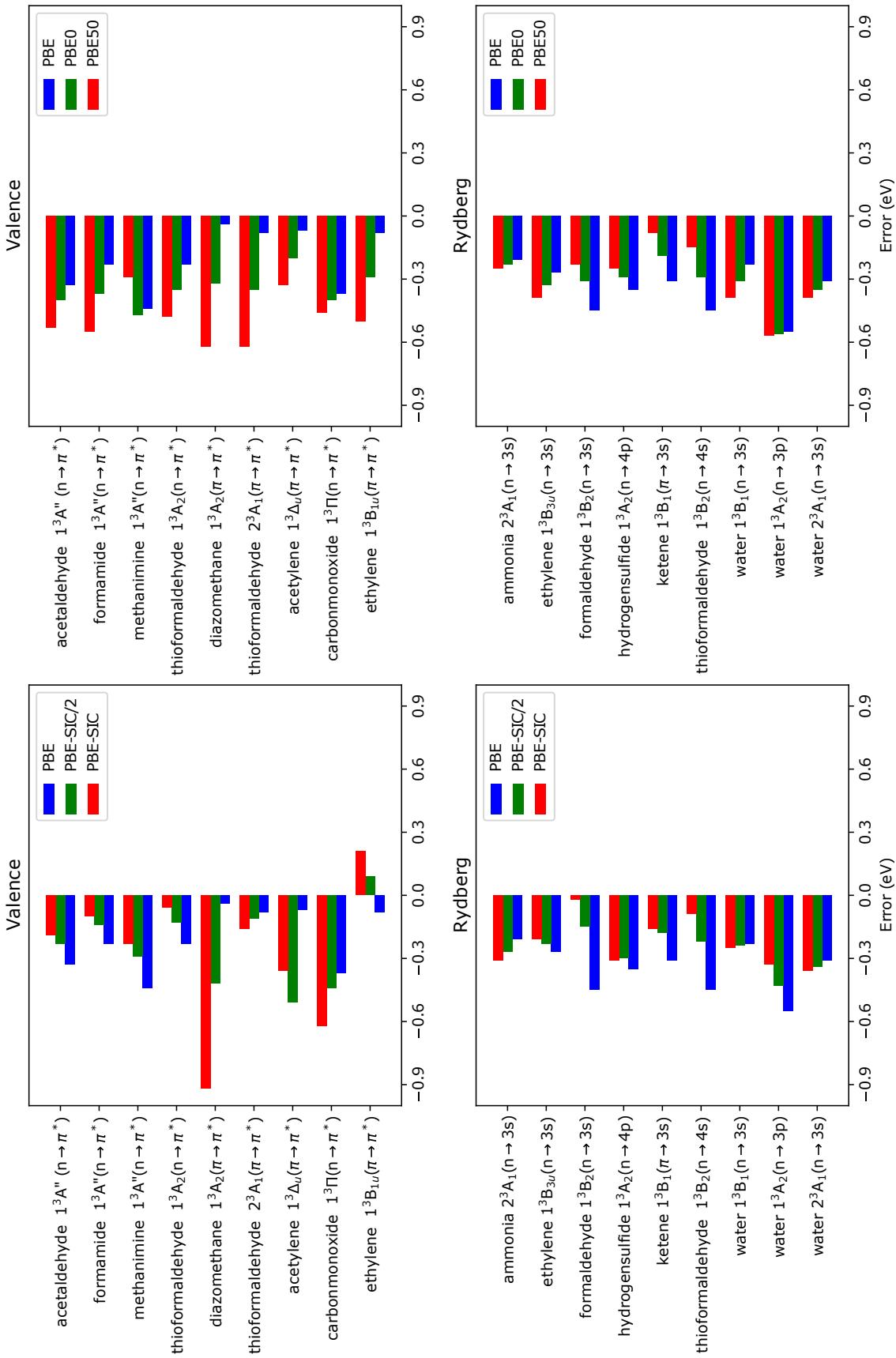


Figure S5: Error bar plot of Table S2

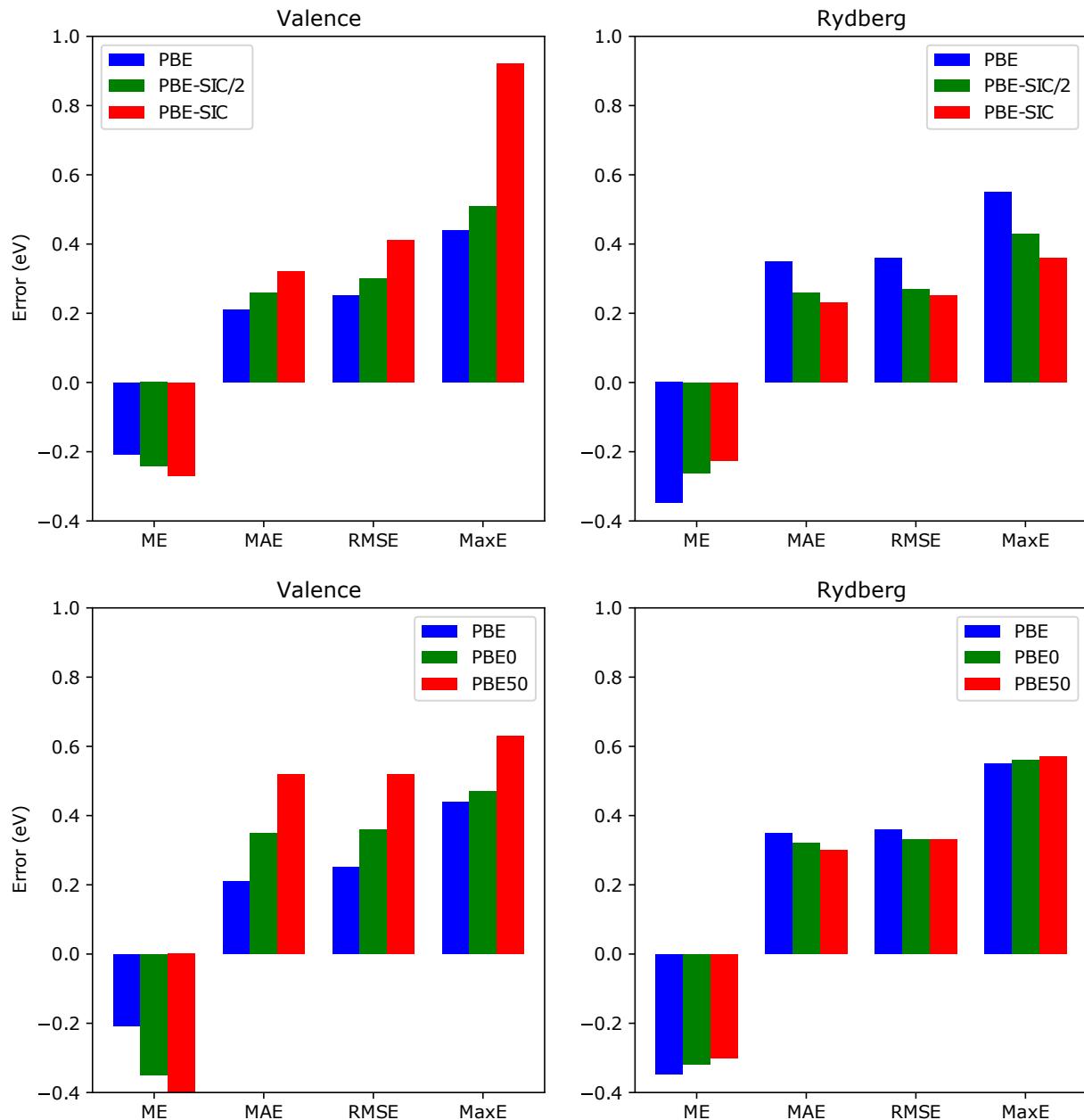


Figure S6: Error bar plot of Table S2

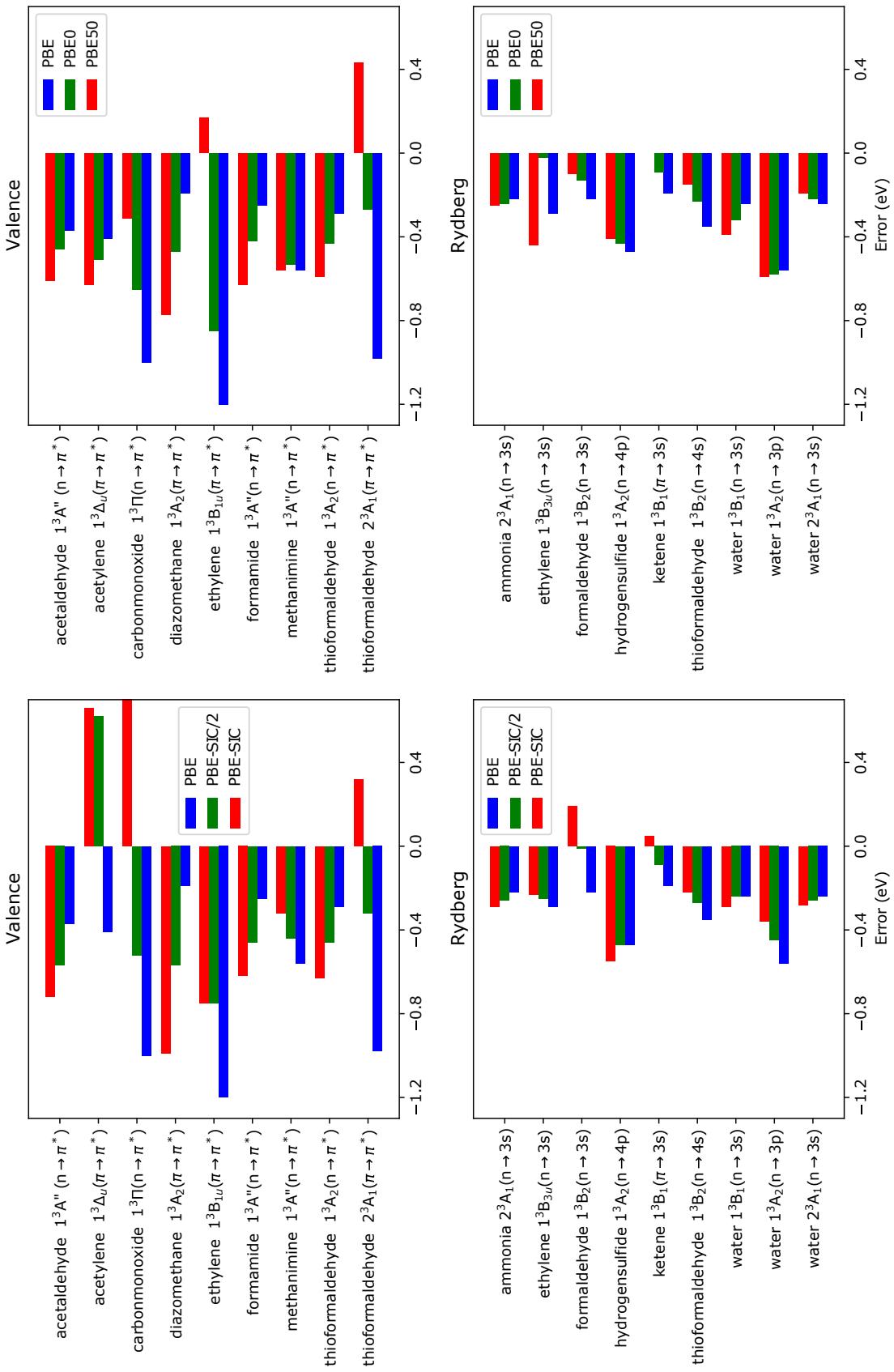


Figure S7: Error bar plot from Table S3

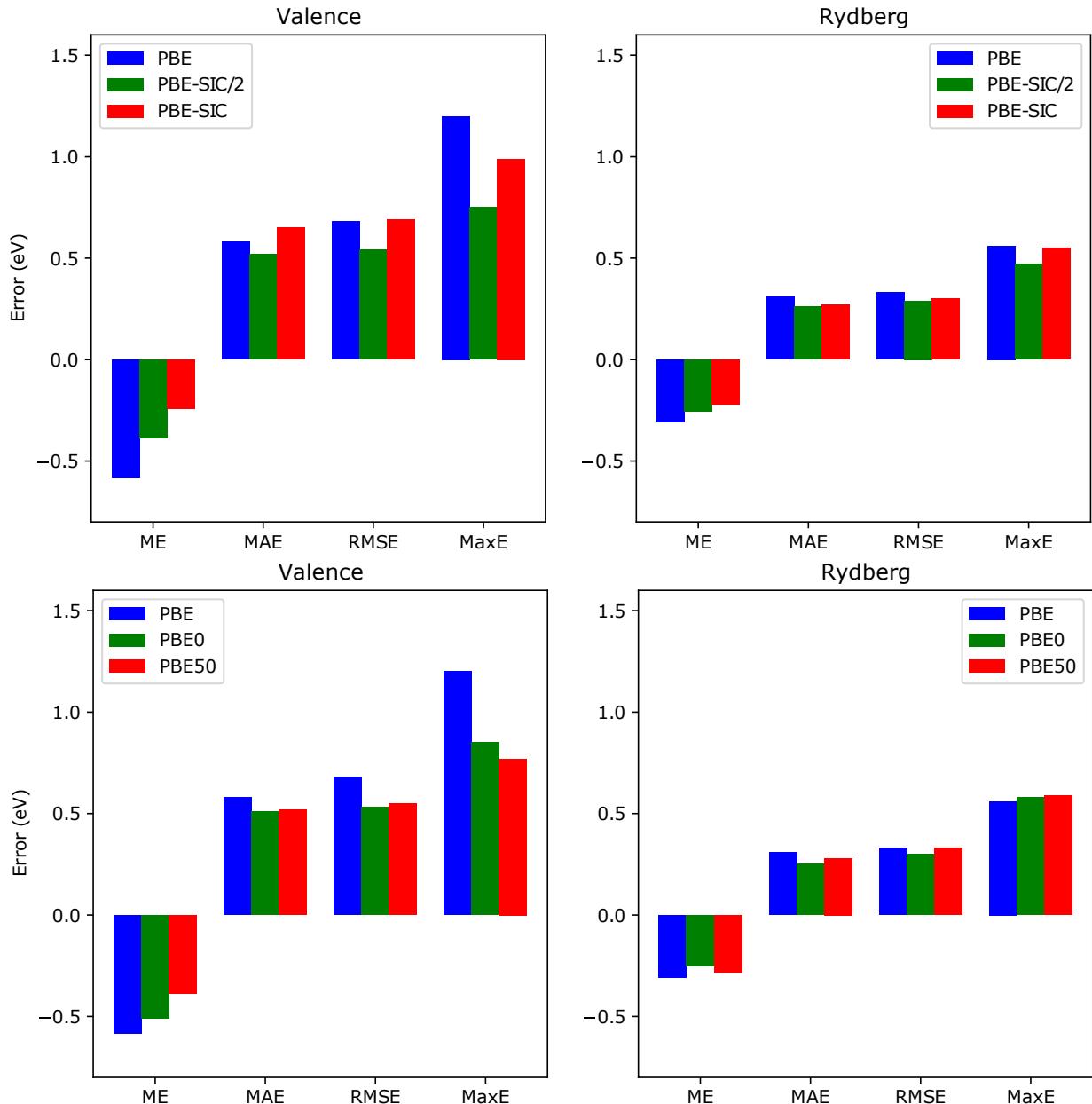


Figure S8: Error bar plot from Table S3

## 5 The Perdew Zunger Self-Interaction Correction Restricted to Real Orbitals (rSIC)

**Table S4:** Excitation energies evaluated with the PBE-rSIC/2 functional

species	excitation	Mixed Spin	Triplet	Singlet
acetaldehyde	$1^1A''(n \rightarrow \pi^*; V)$	3.71	3.73	3.69
acetylene	$1^1\Delta_u(\pi \rightarrow \pi^*; V)$	6.56	5.60	7.52
ammonia	$2^1A_1(n \rightarrow 3s; R)$	6.15	6.01	6.29
carbon monoxide	$1^1\Pi(n \rightarrow \pi^*; V)$	6.94	5.79	8.09
diazomethane	$1^1A_2(\pi \rightarrow \pi^*; V)$	2.26	2.15	2.36
ethylene	$1^1B_{3u}(n \rightarrow 3s; R)$ $1^1B_{1u}(\pi \rightarrow \pi^*; V)$	6.87 5.90	6.80 4.62	6.93 7.19
formaldehyde	$1^1B_2(n \rightarrow 3s; R)$	6.90	6.85	6.96
formamide	$1^1A''(n \rightarrow \pi^*; V)$	5.01	5.06	4.96
hydrogen sulfide	$1^1A_2(n \rightarrow 4p; R)$	5.46	5.42	5.49
ketene	$1^1B_1(\pi \rightarrow 3s; R)$	5.73	5.24	6.22
methanimine	$1^1A''(n \rightarrow \pi^*; V)$	4.66	4.39	4.92
thioformaldehyde	$1^1A_2(n \rightarrow \pi^*; V)$ $1^1B_2(n \rightarrow 4s; R)$ $2^1A_1(\pi \rightarrow \pi^*; V)$	1.75 5.60 4.72	1.80 5.51 3.15	1.69 5.69 6.29
water	$1^1B_1(n \rightarrow 3s; R)$ $1^1A_2(n \rightarrow 3p; R)$ $2^1A_1(n \rightarrow 3s; R)$	7.00 8.69 9.43	6.84 8.63 9.21	7.16 8.76 9.66
ME (TBE <sup>a</sup> )				
ME (EXP <sup>b</sup> )				
MAE (TBE <sup>a</sup> )				
MAE (EXP <sup>a</sup> )				
RMSE (TBE <sup>a</sup> )				
RMSE (EXP <sup>a</sup> )				

<sup>a</sup> Deviation from corrected theoretical best estimates as given in Ref.;<sup>S2</sup> <sup>b</sup> Deviation from experimental values collected in Ref.<sup>S2</sup> (see references therein);

## 6 Ground-State SIC Complex Orbitals of the Water Monomer

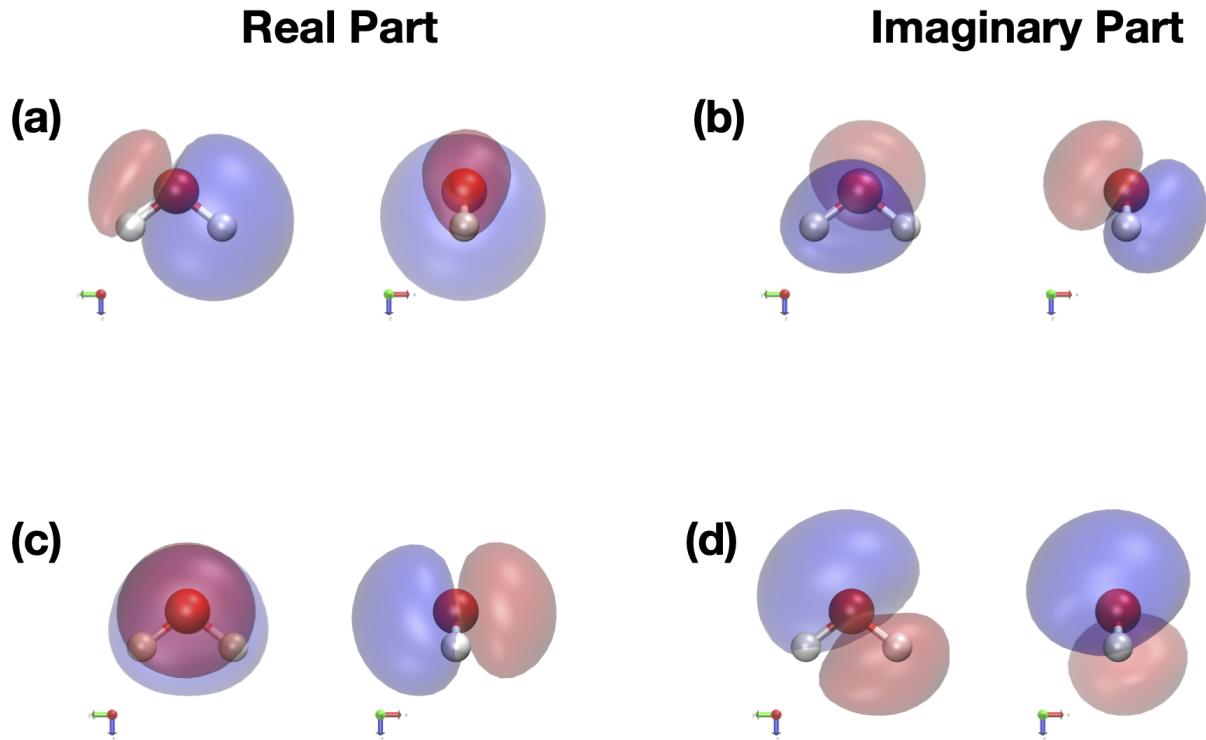


Figure S9: Real and imaginary parts of optimal ground-state SIC complex orbitals of the water monomer. The isosurfaces are represented with blue and red colors and correspond to isovalues of  $\pm 0.05 \text{ \AA}^{-3/2}$ . There are two degenerate pairs and only one orbital of each degenerate pair is shown. One optimal orbital ( $\text{GS}_1$  as denoted in Table 3 of the main text) is made of real part (a) and imaginary part (b). The other optimal orbital ( $\text{GS}_2$  as denoted in Table 3 of the main text) is made of real part (c) and imaginary part (d). Each figure (a), (b), (c), and (d) contains its own isosurfaces from two different views as shown by the axis in insets.

## References

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- (S5) Neese, F. Software update: the ORCA program system, version 4.0. *WIREs Computational Molecular Science* **2018**, *8*, e1327.