Electronic Supplementary Material (ESI) for Faraday Discussions.

Supporting Information: Variational calculations of excited states via direct optimization of the orbitals in DFT

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1 Data of the convergence tests on small molecules

Table S1: Excitation energies in eV and number of iterations (no. it.) for the excited states of the benchmark set of small molecules. NC indicates that the calculation did not converge within the given tolerance and maximum number of iterations.

		SCF-MOM		DO-MOM			
				L-BFGS		Powell	
molecule	state	no. it.	ΔE	no. it.	ΔE	no. it.	ΔE
hydrogenchloride	$1^1\Pi(\pi \rightarrow$n; CT)	NC	NC	37	7.334	NC	NC
water	1^1B_1(n→3s; R)	20	7.288	11	7.288	13	7.288
	1^1A_2(n→3p; R)	28	8.875	11	8.875	15	8.875
	2^1A_1(n→3s; R)	20	9.568	12	9.568	15	9.568
hydrogensulfide	1^1B_1(n→4s; R)	19	5.806	10	5.806	12	5.806
	1^1A_2(n→4p; R)	17	5.644	10	5.644	11	5.644
ammonia	2^1A_1(n→3s; R)	24	6.310	12	6.310	14	6.310
	1^1E(n→3p; R)	96	7.740	32	7.769	23	7.769
	3^1A_1(n→3p; R)	20	8.949	27	8.949	16	8.949
	4^1A_1(n→4s; R)	NC	NC	38	9.871	220	9.861
carbonmonoxide	$1^1\Pi$(n→ π^*; V)	NC	NC	31	6.715	NC	NC
	$1^1\Delta(\pi \rightarrow \pi^*$; V)	NC	NC	NC	NC	NC	NC
	$2^1\Sigma^+$(n→3s; R)	36	10.563	14	10.563	54	10.563
	$3^1\Sigma^+$(n→3p; R)	28	11.103	13	11.103	27	11.103
	$2^1\Pi$(n→3p; R)	NC	NC	36	11.206	NC	NC
dinitrogen	$1^1\Pi_g$(n→ π^*; V)	NC	NC	33	8.008	NC	NC
	$1^1\Delta_u(\pi \rightarrow \pi^*$; V)	NC	NC	180	9.582	NC	NC
	$2^1\Sigma_g^+$(n→n; R)	23	12.613	12	12.613	18	12.613
	$1^1\Pi_u$(n→ π; R)	NC	NC	23	13.079	NC	NC
	$1^1\Sigma_u^+$(n→n; R)	NC	NC	9	12.832	11	12.832
	$2^1\Pi_u(\pi \rightarrow$n; R)	NC	NC	36	14.126	NC	NC
acetylene	$1^1\Delta_u(\pi \rightarrow \pi^*$; V)	NC	NC	33	6.566	NC	NC
thioformaldehyde	1^1A_2(n→ π^*; V)	16	1.868	11	1.868	13	1.868
	1^1B_2(n→4s; R)	24	5.547	13	5.547	27	5.547
	$2^1A_1(\pi \rightarrow \pi^*$; V)	32	4.400	18	4.400	15	4.400
formaldehyde	1^1A_2(n→ π^*; V)	17	3.419	11	3.419	13	3.419
	1^1B_2(n→3s; R)	23	6.810	13	6.810	25	6.810
	2^1B_2(n→3p; R)	25	7.664	15	7.664	23	7.664
	2^1A_1(n→3p; R)	22	7.644	12	7.644	18	7.644
	2^1A_2(n→3p; R)	NC	NC	14	8.224	23	8.224
	1^1B_1(n→ π^*; V)	19	8.325	12	8.325	15	8.325
	$3^1A_1(\pi \rightarrow \pi^*$; V)	29	7.376	17	7.376	13	7.376
methanimine	1^1A"(n→ π^*; V)	17	4.485	13	4.485	14	4.485
ethylene	$1^1B_{1u}(\pi \rightarrow \pi^*$; V)	17	5.602	9	5.602	9	5.602
	1^1B_{3u}(n→3s; R)	23	7.100	11	7.100	23	7.100
	1^1B_{1g}(n→3p; R)	NC	NC	20	7.708	NC	NC
ketene	$1^1A_2(\pi \rightarrow \pi^*$; V)	18	3.630	13	3.630	20	3.630
	$1^1B_1(\pi \rightarrow$3s; R)	NC	NC	13	5.776	23	5.776
	$2^1A_2(\pi \rightarrow$3p; R)	22	6.877	19	6.877	34	6.877
diazomethane	$1^1A_2(\pi \rightarrow \pi^*$; V)	18	2.873	13	2.873	17	2.873

	$2^1A_1(\pi \rightarrow \pi^*$; V)	22	5.442	13	5.442	25	5.442
	$1^1B_1(\pi \rightarrow$3s; R)	17	4.656	13	4.656	18	4.656
cyclopropene	$1^1B_2(\pi \rightarrow \pi^*$; V)	16	4.999	12	4.999	13	4.999
	1^1B_1(n$\rightarrow \pi^*$; V)	20	6.149	12	6.149	13	6.149
nitrosomethane	1^1A"(n$\rightarrow \pi^*$; V)	17	1.239	13	1.239	15	1.239
	2^1A'(n$\rightarrow$3s/3p; V)	26	5.855	20	5.855	25	5.855
formamide	1^1A"(n$\rightarrow \pi^*$; V)	17	5.321	16	5.321	66	5.321
	2^1A'(n$\rightarrow$3s; R)	NC	NC	27	6.496	57	6.496
	$3^1A'(\pi \rightarrow \pi^*$; V)	17	6.029	16	6.029	36	6.029
	4^1A'(n$\rightarrow$3p; R)	NC	NC	31	6.924	33	6.924
acetaldehyde	1^1A"($n \rightarrow \pi^*$; V)	17	3.813	13	3.813	14	3.813
streptocyaninec1	$1^1B_2(\pi \rightarrow \pi^*$; V)	16	5.635	12	5.635	13	5.635