Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Partition of electronic excitation energies: the IQA/EOM-CCSD method

Alberto Fernández-Alarcón,[a,b] José Luis Casalz-Sainz,[b] José Manuel Guevara-Vela,[b] Aurora Costales,[b] Evelio Francisco[b] Ángel Martín Pendás,[b] Tomás Rocha Rinza[a*]

[a]Institute of Chemistry, National Autonomous University of Mexico, 04510 Mexico City, Mexico.
[b]Departament of Analytical and Physical Chemistry, University of Oviedo, E-33006, Oviedo, Spain.

1 XYZ coordinates

1.1 Nitrogen

Table 1: xyz coordinates, in (Å), for the nitrogen molecule computed with the CCSD/Sadlej-plus approximation as implemented in the Psi4 program.

	x	y	z
N	0.000	0.000	−0.557
N	0.000	0.000	0.557

1.2 Carbon monoxide

Table 2: xyz coordinates, in Å, for the carbon monoxide molecule computed with the CCSD/Sadlej-pVTZ approximation as implemented in the Psi4 program.

	x	y	z
C	0.000	0.000	0.648
O	0.000	0.000	−0.486

1.3 Water

Table 3: xyz coordinates, in Å, for the water molecule as reported in reference [39] in the main body of the paper.

	x	y	z
O	0.000	0.000	0.118
H	0.000	0.758	−0.473
H	0.000	−0.758	−0.473

1.4 Ethylene

Table 4: xyz coordinates, in Å, for the ethylene as reported in reference [42] in the main body of the paper.

	x	y	z
C	0.000	0.000	0.670
C	0.000	0.000	−0.670
H	0.000	0.926	1.235
H	0.000	−0.926	1.235
H	0.000	0.926	−1.235
H	0.000	−0.926	−1.235

1.5 Methane

Table 5: xyz coordinates, in Å, for the methane molecule computed with the MP2/aug-cc-pVTZ approximation as implemented in the Psi4 program.

	x	y	z
C	0.000	0.000	0.000
H	0.885	0.000	0.626
H	0.000	−0.885	−0.626
H	0.000	0.885	−0.626
H	−0.885	0.000	0.626

2 QTAIM analysis and IQA partition for the ground and excited states

2.1 Nitrogen

Table 6: QTAIM charges and delocalisation indexes as well as the IQA energy partition of the ground state and the examined excited states of the N_2 molecule. Atomic units are used throughout.

	GS	$1\,^1\Pi_g$	$1\,^1\Sigma_u^-$	$1\,^1\Delta_u$	$1\,^1\Pi_u$	$2\,^1\Pi_u$
DI(N, N)	2.073	1.948	1.927	1.974	2.352	2.304
q^{N}	0.000	0.000	0.000	0.000	0.002	0.001
$E_{\mathrm{class}}^{\mathrm{N,N}}$	0.243	0.275	0.270	0.271	0.439	0.341
$E_{\mathrm{xc}}^{\mathrm{N,N}}$	−0.719	−0.660	−0.656	−0.671	−0.793	−0.698
$E_{\mathrm{net}}^{\mathrm{N}}$	−54.407	−54.277	−54.263	−54.249	−54.234	−54.218

2.1 Carbon monoxide

Table 7: QTAIM charges and delocalisation indexes as well as the IQA energy partition of the ground state and the examined excited states of the CO molecule. Atomic units are used throughout.

	GS	$1\,^1\Pi$	$1\,^1\Sigma^-$	$2\,^1\Sigma^+$
DI(C, O)	1.426	1.622	1.181	1.171
q^{C}	1.187	0.898	0.745	0.769
q^{O}	1.188	−0.897	−0.745	−0.769
$E_{\mathrm{class}}^{\mathrm{C,O}}$	−1.244	−0.712	−0.686	−0.706
$E_{\mathrm{xc}}^{\mathrm{C,O}}$	−0.441	−0.495	−0.368	−0.366
$E_{\mathrm{net}}^{\mathrm{C}}$	−36.962	−37.010	−37.169	−37.151
$E_{\mathrm{net}}^{\mathrm{O}}$	−74.428	−74.539	−74.483	−74.479

Table 8: Continuation of Table 7.

	$3\,^1\Sigma^+$	$2\,^1\Sigma^-$	$4\,^1\Sigma^+$	$3\,^1\Sigma^-$
DI(C, O)	1.952	1.789	1.450	1.373
q^{C}	1.189	1.004	1.290	1.340
q^{O}	−1.181	−0.993	−1.290	−1.340
$E^{\mathrm{C,O}}_{\mathrm{class}}$	−1.064	−1.046	−1.031	−1.043
$E^{\mathrm{C,O}}_{\mathrm{xc}}$	−0.492	−0.503	−0.380	−0.371
$E^{\mathrm{C}}_{\mathrm{net}}$	−36.634	−36.569	−36.745	−36.747
$E^{\mathrm{O}}_{\mathrm{net}}$	−74.394	−74.453	−74.388	−74.381

2.3 Water

Table 9: QTAIM charges and delocalisation indexes as well as the IQA energy partition of the ground state and the examined excited states of the H_2O molecule. Atomic units are used throughout.

	GS	$1\,^1\mathrm{B}_2$	$1\,^1\mathrm{A}_2$	$1\,^1\mathrm{A}_1$	$1\,^1\mathrm{B}_1$
DI(O, H)	0.603	0.634	0.477	0.619	0.458
DI(H, H)	0.021	0.148	0.391	0.096	0.374
q^{O}	−1.159	−0.878	−0.560	−1.052	−0.686
q^{H}	0.580	0.439	0.280	0.526	0.343
$E^{\mathrm{H,H}}_{\mathrm{class}}$	0.137	0.127	0.113	0.153	0.135
$E^{\mathrm{H,H}}_{\mathrm{xc}}$	−0.003	−0.011	−0.022	−0.007	−0.021
$E^{\mathrm{O,H}}_{\mathrm{class}}$	−0.315	−0.235	−0.188	−0.296	−0.236
$E^{\mathrm{O,H}}_{\mathrm{xc}}$	−0.193	−0.164	−0.145	−0.150	−0.130
$E^{\mathrm{O}}_{\mathrm{net}}$	−74.800	−74.754	−74.805	−74.672	−74.744
$E^{\mathrm{H}}_{\mathrm{net}}$	−0.297	−0.284	−0.280	−0.247	−0.245

Table 10: Continuation of Table 9.

	$2\,^1A_2$	$2\,^1B_2$	$2\,^1B_1$	$3\,^1B_1$	$2\,^1A_1$
DI(O, H)	0.642	0.418	0.505	0.552	0.577
DI(H, H)	0.072	0.010	0.013	0.144	0.048
q^{O}	−0.968	−1.487	−1.367	−1.091	−1.224
q^{H}	0.484	0.744	0.682	0.545	0.612
$E^{\mathrm{H,H}}_{\mathrm{class}}$	0.115	0.208	0.184	0.164	0.184
$E^{\mathrm{H,H}}_{\mathrm{xc}}$	−0.008	−0.001	−0.002	−0.012	−0.003
$E^{\mathrm{O,H}}_{\mathrm{class}}$	−0.181	−0.398	−0.362	−0.259	−0.360
$E^{\mathrm{O,H}}_{\mathrm{xc}}$	−0.172	−0.132	−0.152	−0.130	−0.141
$E^{\mathrm{O}}_{\mathrm{net}}$	−74.706	−74.519	−74.491	−74.712	−74.492
$E^{\mathrm{H}}_{\mathrm{net}}$	−0.269	−0.207	−0.220	−0.215	−0.196

2.4 Ethylene

Table 11: QTAIM charges and delocalisation indexes as well as the IQA energy partition of the ground state and the examined excited states of the C_2H_4 molecule. The labelling of the atoms is shown in Figure 1 in the body of the manuscript. Atomic units are used throughout.

	GS	$1\,^1B_{1u}$	$1\,^1B_{3g}$	$1\,^1B_{3u}$	$1\,^1B_{2g}$	$2\,^1B_{1u}$
DI(C_1, C_2)	1.335	1.468	1.268	1.690	1.268	1.294
DI(C_1, H_3)	0.802	0.810	0.755	0.777	0.787	0.795
DI(C_1, H_5)	0.059	0.077	0.040	0.103	0.049	0.068
DI(H_3, H_4)	0.050	0.039	0.130	0.044	0.114	0.084
DI(H_3, H_5)	0.024	0.031	0.123	0.033	0.096	0.082
DI(H_3, H_5)	0.019	0.020	0.096	0.027	0.079	0.067
q^{H}	0.046	0.141	−0.007	0.096	0.021	0.042
q^{C}	−0.091	−0.280	0.020	−0.191	−0.033	−0.077
E^{C_1,C_2}_{class}	0.064	0.076	0.070	0.072	0.071	0.073
E^{C_1,C_2}_{xc}	−0.433	−0.422	−0.414	−0.456	−0.412	−0.415
$E^{C_1H_3}_{class}$	0.038	0.029	0.034	0.033	0.034	0.032
E^{C_1,H_3}_{xc}	−0.258	−0.249	−0.242	−0.251	−0.246	−0.246
E^{C_1,H_5}_{class}	0.002	0.004	0.008	0.003	0.008	0.007
E^{C_1,H_5}_{xc}	−0.007	−0.007	−0.005	−0.010	−0.005	−0.007
E^{H_3,H_4}_{class}	0.004	0.014	0.010	0.009	0.012	0.011
E^{H_3,H_4}_{xc}	−0.006	−0.004	−0.008	−0.005	−0.010	−0.007
E^{H_3,H_5}_{class}	0.001	0.007	0.005	0.004	0.005	0.005
E^{H_3,H_5}_{xc}	−0.002	−0.004	−0.010	−0.003	−0.005	−0.007
E^{H_3,H_6}_{class}	0.001	0.006	0.003	0.003	0.004	0.003
E^{H_3,H_6}_{xc}	−0.001	−0.001	−0.004	−0.002	−0.003	−0.003
E^{C}_{net}	−37.612	−37.533	−37.560	−37.499	−37.561	−37.558
E^{H}_{net}	−0.466	−0.438	−0.443	−0.448	−0.443	−0.446

2.5 Methane

Table 12: Average of QTAIM charges and delocalisation indexes as well as the IQA energy partition of the investigated electronic systems of CH_4. Atomic units are used throughout.

	GS		$1\,^1T_2$		$1\,^1A_2$
$\langle \mathrm{DI(C,\ H)} \rangle$	0.798	0.760	0.760	0.760	0.772
$\langle \mathrm{DI(H,\ H)} \rangle$	0.054	0.102	0.100	0.100	0.121
$\langle q^{\mathrm{C}} \rangle$	−0.083	−0.420	−0.418	−0.418	−0.415
$\langle q^{\mathrm{H}} \rangle$	0.021	0.105	0.104	0.104	0.103
$\langle E^{\mathrm{C,H}}_{\mathrm{class}} \rangle$	0.037	0.014	0.015	0.015	0.018
$\langle E^{\mathrm{C,H}}_{\mathrm{xc}} \rangle$	−0.256	−0.226	−0.226	−0.226	−0.226
$\langle E^{\mathrm{H,H}}_{\mathrm{class}} \rangle$	0.003	0.020	0.019	0.019	0.021
$\langle E^{\mathrm{H,H}}_{\mathrm{xc}} \rangle$	−0.007	−0.009	−0.008	−0.008	−0.010
$E^{\mathrm{C}}_{\mathrm{net}}$	−37.614	−37.570	−37.570	−37.570	−37.567
$\langle E^{\mathrm{H}}_{\mathrm{net}} \rangle$	−0.469	−0.413	−0.413	−0.413	−0.405

Table 13: Continuation of Table 12

	$1\,^1E$			$2\,^1T_2$	
$\langle \mathrm{DI(C,\ H)} \rangle$	0.791	0.788	0.793	0.771	0.771
$\langle \mathrm{DI(H,\ H)} \rangle$	0.089	0.090	0.040	0.037	0.037
$\langle q^{\mathrm{C}} \rangle$	−0.513	−0.499	−0.982	−1.053	−1.053
$\langle q^{\mathrm{H}} \rangle$	0.128	0.125	0.245	0.262	0.262
$\langle E^{\mathrm{C,H}}_{\mathrm{class}} \rangle$	0.017	0.017	−0.010	−0.013	−0.013
$\langle E^{\mathrm{C,H}\rangle}_{\mathrm{xc}}$	−0.229	−0.228	−0.228	−0.227	−0.227
$\langle E^{\mathrm{H,H}}_{\mathrm{class}} \rangle$	0.019	0.019	0.029	0.029	0.029
$\langle E^{\mathrm{H,H}}_{\mathrm{xc}} \rangle$	−0.008	−0.008	−0.005	−0.005	−0.005
$E^{\mathrm{C}}_{\mathrm{net}}$	−37.532	−37.533	−37.484	−37.474	−37.474
$\langle E^{\mathrm{H}}_{\mathrm{net}} \rangle$	−0.402	−0.402	−0.401	−0.403	−0.403

2.6 Helium dimer

Table 14: IQA partition of the excitation energy (E_{h}) of GS, in net as well as classical and exchange-corelation interatomic components, as a function of distance (Å) between the helium atoms in the excimer formation. We also present the changes in the delocalisation index (au) for each point.

Distance Å	DI(He, He)	$E_{\mathrm{class}}^{\mathrm{He,He}}$	$E_{\mathrm{xc}}^{\mathrm{He,He}}$	E_{net}	E	E_{MRCC}
0.800	0.409	0.07	−0.14	−2.69	−5.45	−5.45
1.047	0.245	0.02	−0.08	−2.80	−5.65	−5.65
1.072	0.234	0.01	−0.07	−2.80	−5.67	−5.67
1.200	0.185	0.01	−0.05	−2.83	−5.71	−5.71
1.400	0.130	0.00	−0.03	−2.86	−5.75	−5.75
1.600	0.092	0.00	−0.02	−2.87	−5.77	−5.77
1.800	0.063	0.00	−0.01	−2.88	−5.77	−5.77
2.000	0.043	0.00	−0.01	−2.88	−5.78	−5.78
2.970	0.004	0.00	0.00	−2.89	−5.78	−5.78
3.000	0.004	0.00	0.00	−2.89	−5.78	−5.78
4.000	0.000	0.00	0.00	−2.89	−5.78	−5.78
5.000	0.000	0.00	0.00	−2.89	−5.78	−5.78