

Supporting Information for "Excited-state geometry optimization of small molecules with Many-Body Green's Functions Theory"

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S1. ACETONE C_s SYMMETRY

TABLE S1. Optimized bond lengths (in Å), angles and dihedrals (in degrees) of the $n \rightarrow \pi^*$ excited state ($1^1A''$) of acetone in C_s symmetry. Results from the different GW -BSE variants are obtained with the cc-pVTZ basis and the PBE0 hybrid functional in the underlying DFT calculation. Deviations Δ_i with respect to the CASPT2 reference are given in parentheses.

	C=O		C-C		$\theta(C-C-C)$		$\Theta(H-C-C-O)$	
G_0W_0 -BSE/full/FAA	1.327	(-0.023)	1.495	(-0.001)	113.63	(+0.88)	49.83	(-2.42)
ev GW -BSE/full/FAA	1.302	(-0.048)	1.504	(+0.008)	114.58	(+1.83)	50.09	(-2.16)
G_0W_0 -BSE/TDA/FAA	1.321	(-0.029)	1.492	(-0.004)	114.16	(+1.41)	49.99	(-2.26)
ev GW -BSE/TDA/FAA	1.303	(-0.047)	1.502	(+0.006)	114.61	(+1.86)	49.68	(-2.67)
G_0W_0 -BSE/full/PPM	1.327	(-0.023)	1.494	(-0.002)	113.87	(+1.12)	49.75	(-2.50)
ev GW -BSE/full/PPM	1.308	(-0.042)	1.497	(+0.001)	114.27	(+1.52)	49.65	(-2.60)
G_0W_0 -BSE/TDA/PPM	1.321	(-0.029)	1.490	(-0.006)	114.44	(+1.69)	49.04	(-3.21)
ev GW -BSE/TDA/PPM	1.308	(-0.042)	1.496	(+0.000)	114.43	(+1.68)	49.33	(-2.92)
CASPT2 ^a	1.350		1.496		112.75		52.25	
CC2 ^a	1.404	(+0.054)	1.477	(-0.019)	112.63	(-0.12)	55.37	(+3.12)
VMC ^{ab}	1.344	(-0.006)	1.489	(-0.007)	112.52	(-0.23)	52.16	(-0.09)
TDDFT/PBE0 ^a	1.301	(-0.049)	1.493	(-0.003)	114.91	(+2.16)	51.50	(-0.75)
TDDFT/CAM-B3LYP ^a	1.295	(-0.055)	1.504	(+0.008)	114.84	(+2.09)	51.38	(-0.87)
TDDFT/M06-2X ^a	1.288	(-0.062)	1.516	(+0.020)	114.90	(+2.15)	50.10	(-2.15)

^a from Ref. 1

^b with pseudopotentials and a pVDZ type basis of H and pVTZ type basis for C and O

S2. ACETONE C_{2v} SYMMETRY

TABLE S2. Optimized bond lengths (in Å) and angles (in degrees) of the $n \rightarrow \pi^*$ excited state (1^1A_2) of acetone in C_{2v} symmetry. Results from the different GW -BSE variants are obtained with the cc-pVTZ basis and the PBE0 hybrid functional in the underlying DFT calculation.

	C=O	C-C	$\theta(C-C-C)$
G_0W_0 -BSE/full/FAA	1.341	1.484	117.54
ev GW -BSE/full/FAA	1.319	1.490	118.32
G_0W_0 -BSE/TDA/FAA	1.340	1.482	117.43
ev GW -BSE/TDA/FAA	1.319	1.491	118.51
G_0W_0 -BSE/full/PPM	1.339	1.485	117.50
ev GW -BSE/full/PPM	1.324	1.486	118.20
G_0W_0 -BSE/TDA/PPM	1.337	1.486	117.73
ev GW -BSE/TDA/PPM	1.323	1.487	118.29
CASPT2 ^a	1.360	1.487	116.86
CC2 ^a	1.422	1.473	116.24
VMC ^{ab}	1.348	1.481	118.99
TDDFT/PBE0 ^a	1.314	1.487	118.12
TDDFT/CAM-B3LYP ^a	1.307	1.494	118.26
TDDFT/M06-2X ^a	1.299	1.503	118.86

^a from Ref. 1

^b with pseudopotentials and a pVDZ type basis of H and pVTZ type basis for C and O

S3. *s*-CIS ACROLEIN

TABLE S3. Optimized bond lengths (in Å) and angles (in degrees) of the $n \rightarrow \pi^*$ excited state ($1^1A''$) of *s*-cis acrolein. Results from the different *GW*-BSE variants are obtained with the cc-pVTZ basis and the PBE0 hybrid functional in the underlying DFT calculation.

	C=O	C–C	C=C	$\theta(\text{C–C–C})$	$\theta(\text{C–C–O})$
G_0W_0 -BSE/full/FAA	1.321	1.374	1.379	124.39	123.94
ev <i>GW</i> -BSE/full/FAA	1.299	1.399	1.362	124.94	124.66
G_0W_0 -BSE/TDA/FAA	1.313	1.381	1.375	124.41	125.00
ev <i>GW</i> -BSE/TDA/FAA	1.298	1.399	1.362	124.74	124.63
G_0W_0 -BSE/full/PPM	1.313	1.378	1.379	124.24	124.42
ev <i>GW</i> -BSE/full/PPM	1.303	1.398	1.363	124.63	124.14
G_0W_0 -BSE/TDA/PPM	1.311	1.377	1.381	123.93	124.73
ev <i>GW</i> -BSE/TDA/PPM	1.301	1.398	1.363	124.42	124.15
CASPT2 ^a	1.333	1.378	1.391	124.53	123.84
CC2 ^a	1.374	1.372	1.380	121.42	124.00
VMC ^{a,b}	1.320	1.373	1.386	124.46	125.16
TDDFT/PBE0 ^a	1.274	1.386	1.369	123.96	131.06
TDDFT/CAM-B3LYP ^a	1.278	1.403	1.356	124.64	125.83
TDDFT/M06-2X ^a	1.277	1.418	1.350	124.09	126.62

^a from Ref. 1

^b with pseudopotentials and a pVDZ type basis of H and pVTZ type basis for C and O

S4. *s*-TRANS ACROLEINTABLE S4. Optimized bond lengths (in Å) and angles (in degrees) of the $n \rightarrow \pi^*$ excited state (1^1A_2) of *s*-trans acrolein. Results from the different *GW*-BSE variants are obtained with the cc-pVTZ basis and the PBE0 hybrid functional in the underlying DFT calculation.

	C=O	C–C	C=C	$\theta(\text{C–C–C})$	$\theta(\text{C–C–O})$
G_0W_0 -BSE/full/FAA	1.315	1.377	1.382	123.90	125.39
ev <i>GW</i> -BSE/full/FAA	1.301	1.361	1.399	124.15	125.21
G_0W_0 -BSE/TDA/FAA	1.312	1.376	1.382	124.50	125.68
ev <i>GW</i> -BSE/TDA/FAA	1.300	1.363	1.398	123.94	125.58
G_0W_0 -BSE/full/PPM	1.315	1.379	1.378	123.33	125.76
ev <i>GW</i> -BSE/full/PPM	1.306	1.364	1.396	123.88	124.77
G_0W_0 -BSE/TDA/PPM	1.311	1.382	1.378	123.02	125.78
ev <i>GW</i> -BSE/TDA/PPM	1.305	1.365	1.396	123.77	124.78
CASPT2 ^a	1.336	1.377	1.392	123.26	124.54
CC2 ^a	1.368	1.370	1.383	122.14	127.15
VMC ^{ab}	1.327	1.368	1.383	122.57	125.82
TDDFT/PBE0 ^a	1.272	1.384	1.369	123.96	131.06
TDDFT/CAM-B3LYP ^a	1.278	1.404	1.353	124.30	127.70
TDDFT/M06-2X ^a	1.300	1.418	1.349	124.09	126.62

^a from Ref. 1^b with pseudopotentials and a pVDZ type basis of H and pVTZ type basis for C and O

S5. METHYLENECYCLOPROPENE

TABLE S5. Optimized bond lengths (in Å) and angles (in degrees) of the $\pi \rightarrow \pi^*$ excited state (1^1B_2) of methylenecyclopropene. Results from the different *GW*-BSE variants are obtained with the cc-pVTZ basis and the PBE0 hybrid functional in the underlying DFT calculation.

	C ₁ =C ₂	C ₁ –C ₃	C ₄ =C ₃	$\theta(\text{C}_2=\text{C}_1-\text{C}_3)$	$\theta(\text{C}_1-\text{C}_3=\text{C}_4)$
G_0W_0 -BSE/full/FAA	1.455	1.340	1.524	146.31	55.69
ev <i>GW</i> -BSE/full/FAA	1.436	1.349	1.504	146.39	56.13
G_0W_0 -BSE/TDA/FAA	1.462	1.350	1.492	146.57	56.22
ev <i>GW</i> -BSE/TDA/FAA	1.445	1.348	1.488	146.51	56.51
G_0W_0 -BSE/full/PPM	1.448	1.349	1.513	146.26	55.72
ev <i>GW</i> -BSE/full/PPM	1.433	1.350	1.450	146.45	56.26
G_0W_0 -BSE/TDA/PPM	1.455	1.348	1.485	146.55	56.58
ev <i>GW</i> -BSE/TDA/PPM	1.440	1.350	1.484	146.56	56.61
CASPT2 ^a	1.461	1.360	1.496	146.64	56.64
CC2 ^a	1.457	1.349	1.512	145.90	55.90
VMC ^{ab}	1.456	1.351	1.483	146.66	56.66
TDDFT/PBE0 ^a	1.432	1.349	1.485	146.62	56.62
TDDFT/CAM-B3LYP ^a	1.419	1.344	1.486	146.43	56.43
TDDFT/M06-2X ^a	1.424	1.347	1.483	146.62	56.61

^a from Ref. 1^b with pseudopotentials and a pVDZ type basis of H and pVTZ type basis for C

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- [1] R. Guareschi and C. Filippi, Ground- and excited-state geometry optimization of small organic molecules with quantum Monte Carlo, [Journal of Chemical Theory and Computation](#) **9**, 5513 (2013).