

# Supporting information: An efficient implementation of semiempirical quantum-chemical orthogonalization-corrected methods for excited state dynamics

Jie Liu and Walter Thiel

Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany

(Dated: March 23, 2018)

## I. EFFICIENCY OF THE OMX/CIS METHOD

TABLE 1: Total CPU computation times (in seconds) for single-point energy and gradient calculations with the OM2/CIS and OM2/CIS(GUGA) implementations. NA: number of atoms;  $N_{occ}$ : number of occupied orbitals;  $N_{vir}$ : number of unoccupied orbitals;  $N_{dim}$ : memory scaling (in 8 bytes) for OM2/CIS;  $t_e$  and  $t'_e$ : CPU time (in seconds) for a single-point energy calculation with OM2/CIS and OM2/CIS(GUGA), respectively;  $t_g$  and  $t'_g$ : CPU time (in seconds) for a single-point gradient calculation with OM2/CIS and OM2/CIS(GUGA), respectively.

Molecule	NA	$N_{occ}$	$N_{vir}$	$N_{dim}$	$t_e$	$t'_e$	$t_g$	$t'_g$
A	15	25	20	1000	0.07	0.15	0.13	1.44
GC	29	49	37	3626	0.49	0.78	0.90	67.35
Coronene	36	54	54	5832	0.25	1.19	1.03	263.70
GGG	48	84	63	10584	1.55	9.70	3.10	1481.40
GCGC	58	98	74	14504	2.31	22.62	4.88	4141.06
C2C2PD	72	108	108	23328	3.17	33.98	6.49	
PHE	87	120	102	24480	3.16	63.39	7.61	
C3GC	101	166	154	51128	5.32		13.41	

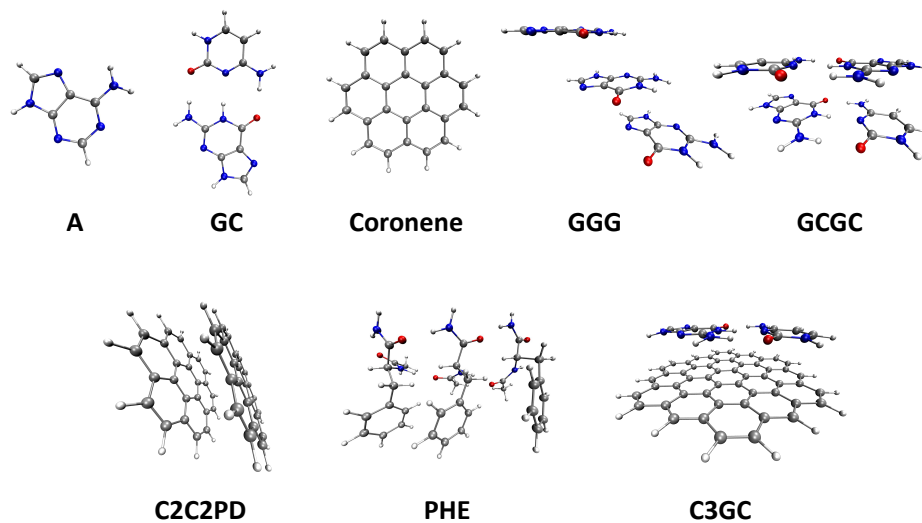


FIG. 1: Structures of molecules used to benchmark the computational efficiency of the OMX/CIS methods. Color code: carbon atoms in silver, hydrogen atoms in white, nitrogen atoms in blue, and oxygen atoms in red. A: adenine; GC: guanine-cytosine base pair; GGG: guanine trimer; GCGC: dimer of guanine-cytosine base pair; C2C2PD; coronene dimer; PHE: trimer of phenylalanine residues; C3GC: guanine-cytosine base pair ··· circumcoronene.

## II. VALIDATION OF IMPLEMENTATION FOR THE OMX/CIS METHOD

TABLE 2: Cartesian coordinates (in Angstrom) of adenine.

	x	y	z
N	-0.646900	-1.804940	-0.000000
C	0.676750	-2.044210	-0.000000
N	1.673050	-1.143680	-0.000000
C	1.382810	0.173970	-0.000000
C	0.014770	0.591020	-0.000000
C	-0.939840	-0.493370	-0.000000
N	-2.175620	0.116140	-0.000000
C	-1.946500	1.492110	-0.000000
N	-0.646040	1.789050	-0.000000
N	2.401040	1.074850	-0.000000
H	0.986130	-3.116100	-0.000000
H	2.223150	2.052870	-0.000000
H	3.345980	0.766660	-0.000000
H	-3.066620	-0.354470	-0.000000
H	-2.754780	2.224660	-0.000000

TABLE 3: Vertical excitation energies (in eV) of the 10 lowest-lying singlet excited states for adenine with the OM2/CIS and OM2/CIS(GUGA) methods.

	OM2/CIS	OM2/CIS(GUGA)
S <sub>1</sub>	4.526507	4.526507
S <sub>2</sub>	4.558948	4.558948
S <sub>3</sub>	4.829995	4.829995
S <sub>4</sub>	5.013998	5.013998
S <sub>5</sub>	5.416253	5.416253
S <sub>6</sub>	5.693989	5.693989
S <sub>7</sub>	5.917236	5.917236
S <sub>8</sub>	5.947062	5.947062
S <sub>9</sub>	6.166503	6.166503
S <sub>10</sub>	6.193376	6.193376

TABLE 4: Cartesian gradient (in kcal/(mol\*Angstrom)) of the first singlet excited state of adenine with the OM2/CIS and OM2/CIS(GUGA) methods.

	OM2/CIS			OM2/CIS(GUGA)		
	x	y	z	x	y	z
N	21.46458	-58.83276	-0.00000	21.46409	-58.83242	0.00000
C	-54.39109	89.29225	0.00000	-54.39047	89.29256	-0.00000
N	31.54196	-63.02210	-0.00000	31.54185	-63.02279	-0.00000
C	-50.78760	46.90426	0.00000	-50.78800	46.90480	0.00000
C	31.88126	-26.85928	-0.00000	31.88142	-26.85928	-0.00000
C	39.24373	20.47327	0.00000	39.24393	20.47272	0.00000
N	-12.96277	9.05804	-0.00000	-12.96286	9.05811	-0.00000
C	0.37136	-22.89218	0.00000	0.37136	-22.89211	-0.00000
N	-2.61074	20.86545	-0.00000	-2.61084	20.86542	0.00000
N	-3.12670	-13.36801	0.00000	-3.12672	-13.36804	-0.00000
H	1.57656	-4.08327	-0.00000	1.57663	-4.08335	0.00000
H	0.42984	0.01294	-0.00000	0.42993	0.01292	-0.00000
H	-0.44505	0.54991	0.00000	-0.44503	0.54996	-0.00000
H	-0.45855	0.53586	0.00000	-0.45855	0.53586	0.00000
H	-1.72678	1.36561	-0.00000	-1.72674	1.36563	0.00000

TABLE 5: Cartesian derivative couplings (in  $\text{\AA}^{-1}$ ) between the second and first singlet excited state of adenine with the OM2/CIS and OM2/CIS(GUGA) methods.

	OM2/CIS			OM2/CIS(GUGA)		
	x	y	z	x	y	z
N	-0.00000	-0.00000	20.24816	0.00000	-0.00001	20.24783
C	-0.00000	0.00000	-27.96971	-0.00001	0.00001	-27.96916
N	0.00000	-0.00000	25.25950	0.00002	-0.00000	25.25902
C	-0.00000	0.00000	0.50345	-0.00001	-0.00001	0.50346
C	-0.00000	0.00000	3.12812	0.00000	0.00001	3.12816
C	0.00000	-0.00000	-22.75890	-0.00001	0.00000	-22.75858
N	-0.00000	0.00000	11.02408	0.00000	0.00000	11.02386
C	-0.00000	-0.00000	-10.69958	-0.00001	-0.00000	-10.69932
N	0.00000	0.00000	9.49227	0.00001	-0.00001	9.49197
N	-0.00000	-0.00000	-3.99401	0.00000	0.00000	-3.99393
H	0.00000	-0.00000	1.11668	-0.00000	0.00000	1.11667
H	-0.00000	0.00000	1.43881	-0.00000	-0.00000	1.43872
H	0.00000	-0.00000	-6.15023	-0.00000	-0.00000	-6.15007
H	-0.00000	0.00000	-1.62441	-0.00000	-0.00000	-1.62436
H	-0.00000	0.00000	0.84967	0.00000	0.00000	0.84963

## III. EXCITED-STATE DYNAMICS OF 2,3,4-PPE

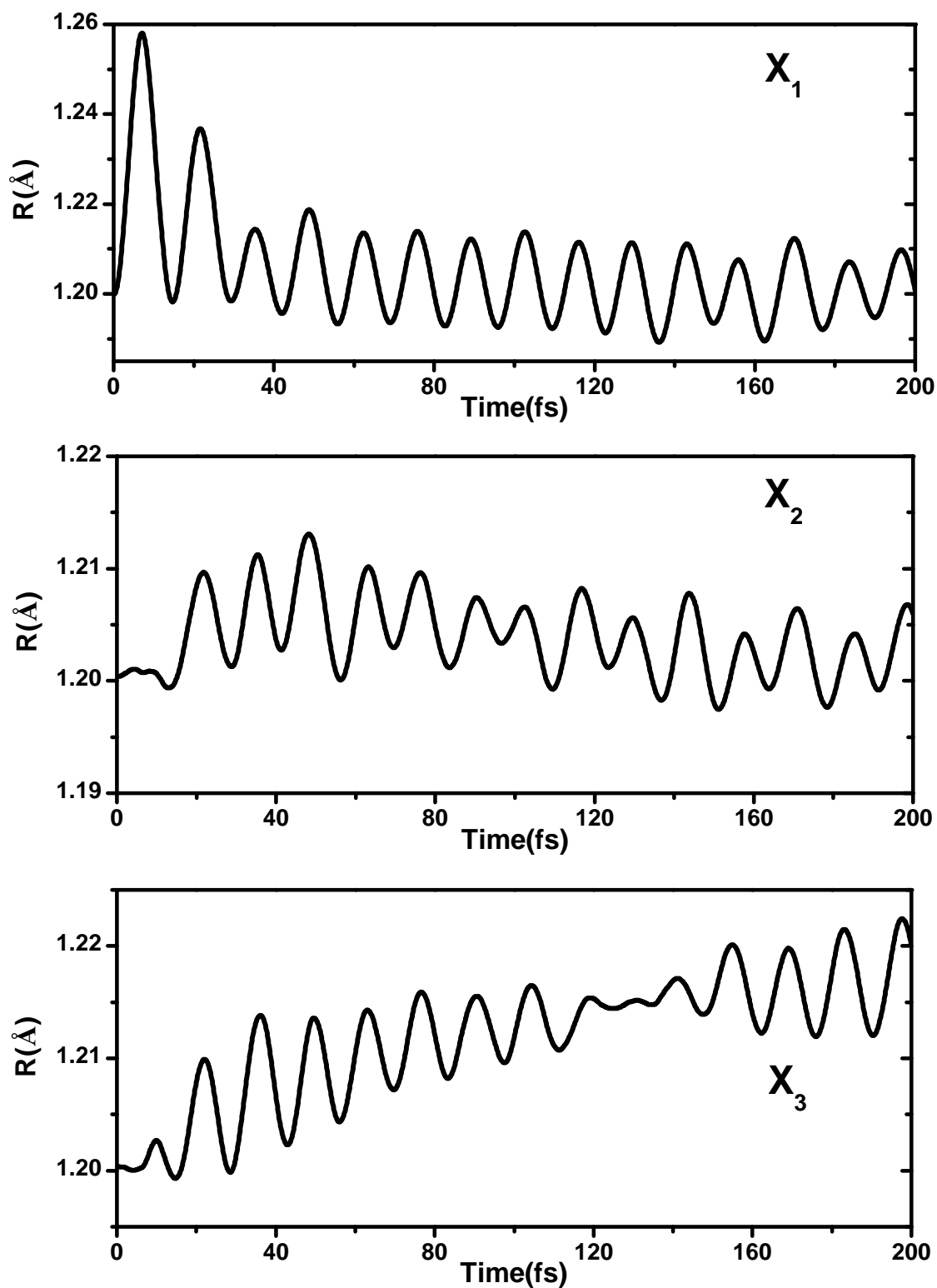


FIG. 2: Lengths of specified ethynylene bonds (see main text) as a function of time obtained from an average over all trajectories: AM1 results.

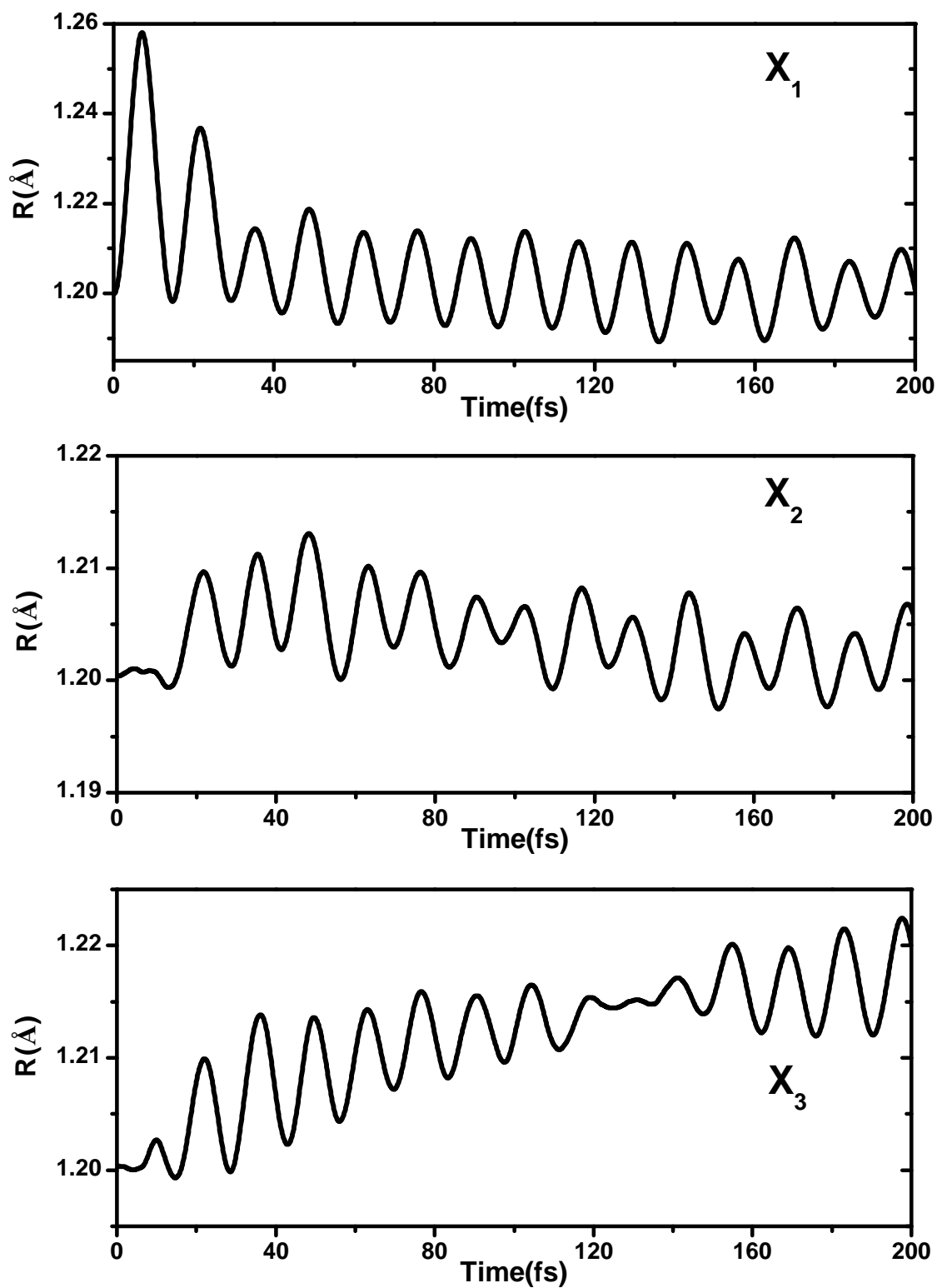


FIG. 3: Lengths of specified ethynylene bonds (see main text) as a function of time obtained from an average over all trajectories: PM3 results.