

Supporting information: Analytic gradient and derivative couplings for the spin-flip extended configuration interaction singles method: Theory, implementation, and application to proton transfer

Jie Liu, Axel Koslowski and Walter Thiel

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

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I. COMPUTATION TIMES

In Table 1, we show CPU computation times for a single-point gradient calculation with the OM2/CIS and OM2/SF-XCIS methods. The total CPU time is decomposed into three parts: the self-consistent field (SCF) part, vertical excitation (VE) energy part, and the gradient part. In the CIS method, the ground state is obtained from the restricted Hartree-Fock method. In the SF-XCIS method, the reference state is computed with the restricted open-shell Hartree-Fock method. The convergence criteria are set to 10^{-10} eV for the energy and to 10^{-10} for the diagonal elements of the density matrix. For the largest test molecule $C_{50}H_{52}$, the total CPU time for SF-XCIS is ~ 16 times of that for CIS. More than half of the total CPU time in SF-XCIS is spent in the SCF calculation. The CPU time for the excited-state part (energy and gradient) in SF-XCIS is ~ 8 times higher than in the case of CIS.

TABLE 1: CPU computation times (in seconds) for single-point gradient calculations with the OM2/CIS and OM2/SF-XCIS methods. The carbon chain length of the polyene test molecules ranges from 6 to 50. VE labels the vertical excitation energy calculation.

Molecule	CIS				SF-XCIS			
	SCF	VE	Gradient	Total	SCF	VE	Gradient	Total
C_6H_8	0.003	0.056	0.016	0.077	0.005	0.403	0.041	0.450
$C_{10}H_{12}$	0.013	0.237	0.058	0.310	0.013	1.308	0.176	1.497
$C_{14}H_{16}$	0.014	0.755	0.136	0.906	0.040	1.825	0.475	2.341
$C_{18}H_{20}$	0.045	2.462	0.249	2.760	0.088	3.804	1.071	4.965
$C_{24}H_{26}$	0.044	0.956	0.476	1.479	0.297	4.413	2.662	7.373
$C_{30}H_{32}$	0.065	1.493	0.873	2.435	1.774	7.779	5.940	15.497
$C_{40}H_{42}$	0.132	2.906	1.901	4.942	16.075	16.528	16.615	49.222
$C_{50}H_{52}$	0.298	5.193	3.525	9.018	71.292	30.721	38.644	140.659

II. VALIDATION OF THE OMX/SF-XCIS IMPLEMENTATION

Here we present the validation of our current implementation of the SF-XCIS method through detailed comparisons with SF-XCIS results obtained with the general MRCI implementation in the MNDO package. This is possible because the SF-XCIS method is equivalent to a multireference CIS treatment in which three configuration state functions are chosen as references, namely the triplet SCF configuration with two singly occupied orbitals and the two closed-shell configurations derived therefrom (i.e., all singlet configurations that can be generated from the HOMO and LUMO of the closed-shell ground state). Hereafter, we will label the SF-XCIS method implemented with the MRCI scheme as MR-CIS(3).

First, we ran the standard benchmark of 104 vertical singlet excitation energies in 28 organic molecules using both the SF-XCIS and MR-CIS(3) implementations and got identical results as expected (see Table I of the main paper). For a more detailed check, we then computed the excitation energies, excited-state gradients, and derivative couplings of adenine (see Table 2 for the coordinates), again using both the SF-XCIS and MR-CIS(3) implementations. In addition, we also compared the analytic SF-XCIS gradient of adenine with finite-difference results. The results are shown in Tables 3-5. The excellent agreement between the results from different treatments further demonstrates the correctness of our implementation of the SF-XCIS 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/SF-XCIS and OM2/MR-CIS(3) methods.

	OM2/SF-XCIS	OM2/MR-CIS(3)
S ₁	0.000000	0.000000
S ₂	4.506222	4.506222
S ₃	4.772248	4.772248
S ₄	4.851654	4.851654
S ₅	5.410528	5.410528
S ₆	5.598901	5.598901
S ₇	5.890911	5.890911
S ₈	5.967332	5.967332
S ₉	6.030129	6.030129
S ₁₀	6.215359	6.215359

TABLE 4: Cartesian gradient (in kcal/(mol*Angstrom)) of the first singlet excited state of adenine with the OM2/SF-XCIS and OM2/MR-CIS(3). The columns under FD contain finite-difference results obtained with OMx/SF-XCIS.

	OM2/SF-XCIS			OM2/MR-CIS(3)			FD		
	x	y	z	x	y	z	x	y	z
N	56.33326	-47.16037	0.00000	56.33319	-47.16042	-0.00000	56.33435	-47.15900	0.00000
C	-47.22404	21.26648	0.00000	-47.22403	21.26642	0.00000	-47.22465	21.26628	-0.00000
N	-15.05675	7.94323	0.00000	-15.05668	7.94325	0.00000	-15.05721	7.94481	0.00000
C	-22.87866	-4.45121	0.00000	-22.87872	-4.45124	-0.00000	-22.87925	-4.45198	-0.00000
C	30.93210	-58.92383	0.00000	30.93213	-58.92388	-0.00000	30.93272	-58.92346	-0.00000
C	-5.27502	60.27426	0.00000	-5.27499	60.27431	0.00000	-5.27560	60.27302	0.00000
N	17.76282	-5.01355	0.00000	17.76282	-5.01356	-0.00000	17.76324	-5.01267	0.00000
C	29.96373	4.58736	0.00000	29.96369	4.58738	0.00000	29.96491	4.58648	-0.00000
N	-48.78713	19.85338	0.00000	-48.78711	19.85343	0.00000	-48.78833	19.85279	-0.00000
N	9.40059	10.59808	0.00000	9.40063	10.59811	0.00000	9.40069	10.59840	0.00000
H	0.60692	-3.57737	0.00000	0.60691	-3.57736	-0.00000	0.60694	-3.57701	0.00000
H	2.42575	-7.59519	0.00000	2.42576	-7.59518	0.00000	2.42571	-7.59569	0.00000
H	-7.71118	2.03672	0.00000	-7.71118	2.03673	-0.00000	-7.71162	2.03666	-0.00000
H	-0.15539	0.04034	0.00000	-0.15540	0.04034	0.00000	-0.15508	0.04031	0.00000
H	-0.33700	0.12167	0.00000	-0.33701	0.12167	0.00000	-0.33689	0.12159	-0.00000

TABLE 5: Cartesian derivative couplings (in kcal/(mol*Angstrom)) between the second and first singlet excited state of adenine with the OM2/SF-XCIS and OM2/MR-CIS(3) methods.

	OM2/SF-XCIS			OM2/MR-CIS(3)		
	x	y	z	x	y z	
N	0.23642	-0.08489	-0.00000	0.23642	-0.08488	-0.00000
C	-0.41486	-0.33189	0.00000	-0.41485	-0.33189	0.00001
N	0.12745	0.77598	-0.00000	0.12745	0.77596	-0.00002
C	0.10098	-0.73632	-0.00000	0.10098	-0.73630	-0.00001
C	-0.22531	0.03778	-0.00000	-0.22530	0.03778	-0.00000
C	0.18981	0.02860	-0.00000	0.18981	0.02860	0.00001
N	-0.13951	0.40175	0.00000	-0.13950	0.40174	0.00001
C	-0.08955	-0.40363	0.00000	-0.08955	-0.40363	0.00001
N	0.14587	-0.05717	0.00000	0.14587	-0.05716	0.00000
N	0.26259	0.33580	-0.00000	0.26259	0.33579	-0.00001
H	-0.01685	0.03764	-0.00000	-0.01685	0.03764	-0.00000
H	0.01515	-0.03710	0.00000	0.01515	-0.03710	0.00000
H	-0.04700	0.00272	-0.00000	-0.04700	0.00272	-0.00000
H	-0.01872	-0.00700	-0.00000	-0.01872	-0.00700	-0.00000
H	-0.03009	0.02585	-0.00000	-0.03009	0.02585	-0.00000