

Supplementary Material for “Analytic derivative couplings for the spin-flip variants of configuration interaction singles and time-dependent density functional theory”

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Here, we compare our analytic derivative couplings with finite-difference results to validate the formalism. The finite difference formula for derivative coupling to the first order is

$$\langle \Psi_I | \Psi_J^{[x]} \rangle = \frac{\langle \Psi_I | \Psi_J(x + \delta x) \rangle - \langle \Psi_I | \Psi_J(x - \delta x) \rangle}{2\delta x} \quad (\text{S1})$$

Our test system is H₂ with a bond length of $R = 1.1\text{\AA}$. The cc-pVTZ basis set was used for all calculations, and CL-SF-TDDFT calculations use the BH&HLYP functional (50% Hartree-Fock exchange plus 50% Becke exchange¹ with Lee-Yang-Parr correlation²). We denote the latter method as SF-BH&HLYP.

The vertical excitation energies of the lowest six singlet states are shown in Table S1. The S₄ state has HOMO → LUMO double excitation character, so it is missing in the restricted CIS (RCIS) calculation. Derivative couplings between the states S₁ and S₃ are listed in Table S2.

From Table S2, we can see that the finite difference results agree well with the analytic results for all of the three methods, which confirms the validity of our formalism as shown in Eq. (13). In addition, the derivative couplings calculated by Eq. (13) and Eq. (22) are exactly the same as the ones calculated using the formalism introduced in Ref. 3 for spin-conserved CIS, which comes as no surprise since the two formalisms are intrinsically equivalent for spin-conserved CIS.

¹ A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

² C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B **37**, 785 (1988).

³ S. Fatehi, E. Alguire, Y. Shao, and J. E. Subotnik, J. Chem. Phys. **135**, 234105:1 (2011).

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TABLE S1: Vertical excitation energies (in eV) for the lowest singlet states of H₂ using RCIS, SF-CIS, and SF-BH&HLYP in the cc-pVTZ basis set.

State	RCIS	SF-CIS	SF-BH&HLYP
S ₁	10.6756	11.4664	9.7089
S ₂	16.3160	14.8178	13.8764
S ₃	20.7863	19.2544	18.4337
S ₄ ($\sigma^0\sigma^{*2}$)		19.3603	17.7473
S ₅	23.1458	21.1063	20.3281
S ₆	23.1458	21.1063	20.3281

TABLE S2: $\langle \Psi_1 | \Psi_3^{[x]} \rangle$ derivative couplings (in a_0^{-1}) calculated by RCIS, SF-CIS and SF-BH&HLYP. The H₂ molecule is aligned to the z -axis and the derivative couplings vanish in the x and y directions.

Atom	RCIS			SFCIS			SF-BH&HLYP		
	Analytic	FD	ETF	Analytic	FD	ETF	Analytic	FD	ETF
H	-0.088057	-0.088057	-0.003857	-0.104717	-0.104718	-0.078036	-0.092725	-0.092725	-0.053895
H	0.088057	0.088057	0.003857	0.104717	0.104718	0.078036	0.092725	0.092725	0.053895