Supporting Information for

Fast and Accurate Computation of Nonadiabatic Coupling Matrix Elements (NACMEs) using the Truncated Leibniz Formula (TLF) and Mixed-Reference Spin-Flip Time-Dependent Density Functional Theory (MRSF-TDDFT)

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Description of the MRSF Method

Detailed discussion of MRSF-TDDFT can be found else where.[1,2] The main concept is summarized in this section. Derivation of the MRSF-TDDFT methodology[1] is based on the density-matrix formulation of time-dependent Kohn-Sham theory.[3] In MRSF-TDDFT, the zeroth-order MR reduced density matrix (RDM), $\rho_0^{\mathrm{MR}}(x, x')$, is defined by satisfying an idempotence relation,

$$\rho_0^{\mathrm{MR}}(x, x') = \int \rho_0^{\mathrm{MR}}(x, x'')\rho_0^{\mathrm{MR}}(x'', x')dx'', \tag{S1}$$

and its density, $\rho_0^{\mathrm{MR}}(x) = \rho_0^{\mathrm{MR}}(x, x)$, is same as an equiensemble density of $M_S = +1$ and $M_S = -1$ components of a triplet state, *e.g.*,

$$\rho_0^{\mathrm{MR}}(x) = \frac{1}{2}\left\{\rho_0^{M_S=+1}(x) + \rho_0^{M_S=-1}(x)\right\}. \tag{S2}$$

Within the Tamm-Dancoff approximation,[4,5] the use of MR-RDM in the linear-response formalism yields completely decoupled two linear-response equations for singlet and triplet excited states, respectively,[1]

$$\sum_{rs}\left(A_{pq,rs}^{(k)(0)} + A_{pq,rs}'^{(k)}\right)X_{rs}^{(k)} = \Omega_{(k)}X_{pq}^{(k)}, \qquad k = S, T \tag{S3}$$

where $k = S, T$ labels singlet and triplet states, $A_{pq,rs}^{(k)(0)}$ is an orbital Hessian matrix derived by the linear response, and $A_{pq,rs}'^{(k)}$ is a coupling matrix between configurations originating from different components, $M_S = +1$ and $M_S = -1$, of the mixed reference.[1,2] $X_{pq}^{(k)}$ and $\Omega_{(k)}$ are the amplitude vectors and the excitation energies with respect to the reference state, respectively.

It was shown that a linear response of MRSF-TDDFT can be represented as configurations from $M_S = +1$ and -1 references depicted as those with black and red arrows, respectively, in Fig. S1.[1] The configurations with the red arrows are missing in the conventional SF-TDDFT; their absence leads to spin contamination of the response states. These are recovered in MRSF-TDDFT and the spin contamination of the response states is nearly eliminated.[1] Configurations with the blue arrows are originated from both $M_S = +1$ and -1 components of the mixed reference.
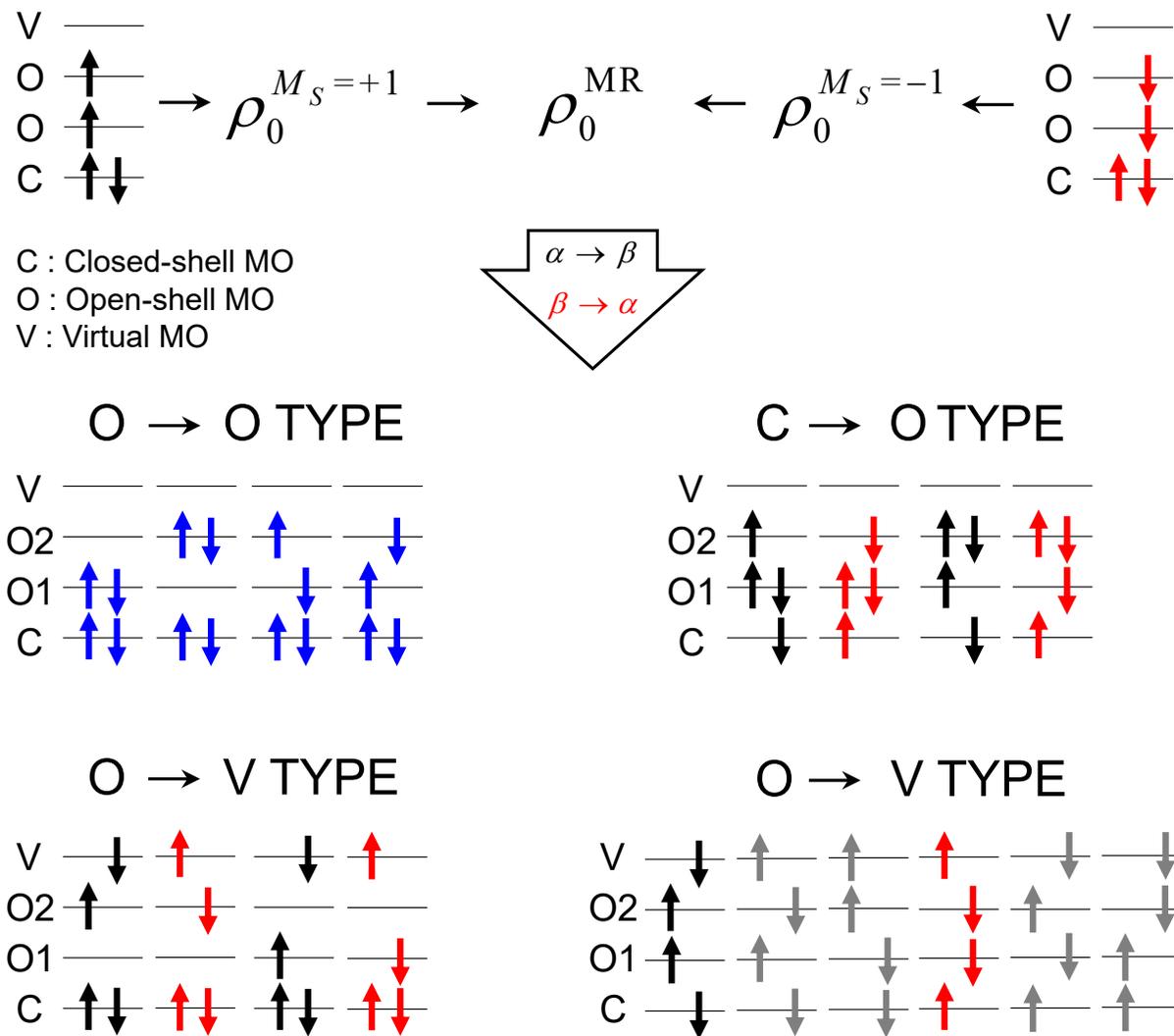
Figure S1: Electronic configurations of the $M_S = +1$ and $M_S = -1$ components of triplet reference in the upper panel and a complete set of configurations for MRSF-TDDFT in the lower panel. Response states are described by configurations represented with blue, black, and red arrows in MRSF-TDDFT, while with blue and black arrows in SF-TDDFT.

Although not all electronic configurations can be recovered by using the MR-RDM, the missing C $\rightarrow$ V configurations (depicted with gray arrows in Fig. S1) represent high-lying excited states and their effect on the lower part of the excitation spectrum is insignificant.[1]
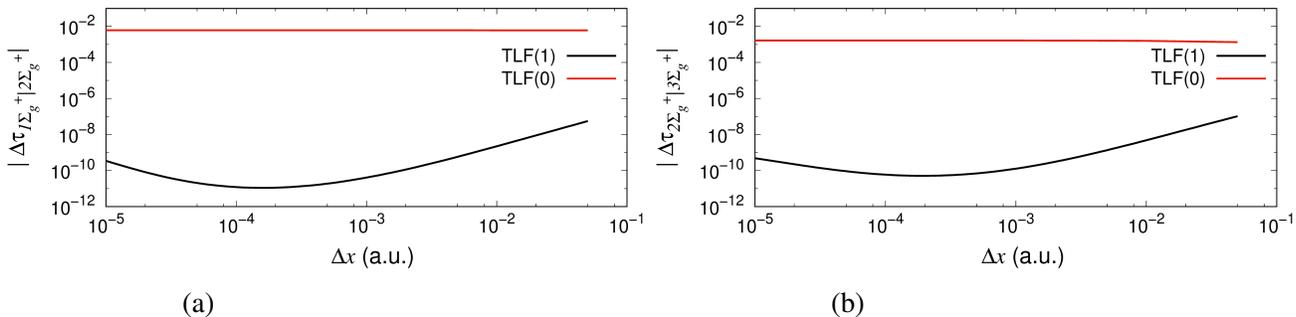
Figure S2: Comparison of the NACME, $|\Delta\tau_{IJ}|$, absolute errors (in a.u.) for the TLF(0) and TLF(1) algorithms for H_2 (a) between $1^1\Sigma_g^+$ and $2^1\Sigma_g^+$ at $R = 4.5$ a.u., (b) between $2^1\Sigma_g^+$ and $3^1\Sigma_g^+$ at $R = 2.8$ a.u. The Δx used here is 10^{-4} a.u. All the data shown were obtained with MRSF-BHHLYP.
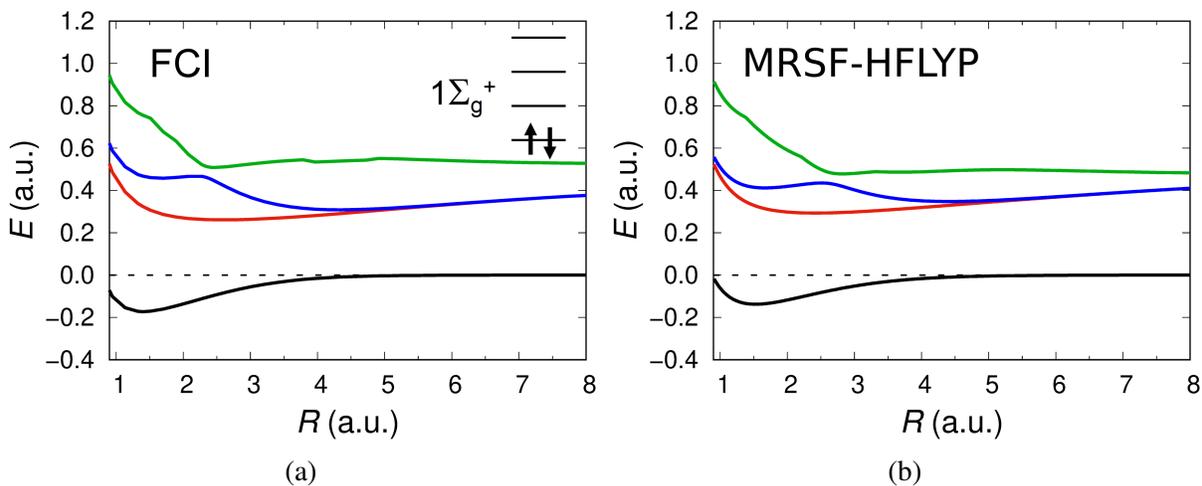

Figure S3: Comparison of the potential energy surfaces for $^1H_2$ dissociation calculated with (a) FCI and (b) MRSF-HFLYP methods. The black, red, blue, and green curves correspond to the S_0, S_1, S_2, and S_3 states, respectively. For the symmetry of the states as well as their configurations, see Figure 2 in the main text. The MRSF energies, ΔE, were calculated as explained in Figure 2 in the main text.

Computational Details

All the LR-TDDFT and the MRSF calculations reported in this work were performed by the locally modified GAMESS-US program package.[6] The accurate H_2 dissociation curves and the NACME curves were calculated by the full configurational interaction (FCI) method implemented in the MOLPRO program package.[7]

The following density functionals were employed: PBE0[8] (0.25), BHHLYP[9] (0.50), STG1X[10] (0.85), and HFLYP[10] (1.00) where the amount of the exact exchange is given in parentheses. The

all-electron cc-pVTZ[11] basis set was employed in for the calculations of H_2. For brevity, the calculations performed with the LR- or MRSF-TDDFT method and the BHHLYP functional will be abbreviated as "LR-BHHLYP" or "MRSF-BHHLYP", respectively. The NACME calculations employed the TLF algorithm of Ref. 12 and geometry displacements (in Cartesian coordinates) of $m \times 10^{-n}$ a.u. with $m = 1, 5$ and $n = 2$–7. The SCF convergence criterion was set to 10^{-6}, the convergence tolerance for Davidson algorithm was set to 10^{-7}. The number of points for the radial and Lebedev grid was 99 and 590, respectively, for DFT, whereas it was 96 and 302, respectively, for TDDFT.

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