Analysis and Visualization of Energy Densities. I. Insights from Real-Time Time-Dependent Density Functional Theory Simulations. Electronic Supplementary Information

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Propagators for RT-TDDFT simulations 1

Different RT-TDDFT Propagation Schemes 1.1

Here a brief summary is provided on several RT-TDDFT propagation schemes implemented in this work.



b) AMUT-k, RKMK-Heun

Figure S1: Different RT-TDDFT propagation schemes tested in the work.

1.1.1 Modified Midpoint Unitary Transformation (MMUT)

The MMUT scheme was proposed by Li *et al* [Phys. Chem. Chem. Phys. 7, 233 (2005)]. Here is the workflow of our implementation.

Algorithm 1 MMUT Scheme

Initialize: Fock Build, $\mathbf{F}_{1} \leftarrow \mathcal{F}(\mathbf{P}_{1})$ for step i = 1 to N do if $i \neq 1$ then Take a series of short Euler steps to reach $\mathbf{P}_{i+\frac{1}{2}}$ else Step 1: Density propagation, $\mathbf{P}_{i+\frac{1}{2}} \leftarrow \exp(i\Delta t\mathbf{F}_{i}) \mathbf{P}_{i-\frac{1}{2}} \exp(-i\Delta t\mathbf{F}_{i})$ end if Step 2: Density propagation, $\mathbf{P}_{i+1} \leftarrow \exp(i\frac{\Delta t}{2}\mathbf{F}_{i}) \mathbf{P}_{i+\frac{1}{2}} \exp(-i\frac{\Delta t}{2}\mathbf{F}_{i})$ Step 3: Fock Build, $\mathbf{F}_{i+1} \leftarrow \mathcal{F}(\mathbf{P}_{i+1})$ end for

1.1.2 Approximate Midpoint Unitary Transformation (AMUT-k)

Below is the workflow of our implementation of AMUT-k schemes. When k=1, it reduces to the Runge-Kutta-Munthe-Kass-Heun (RKMK-Heun) scheme [see Eq. 20 of Casas and Iserles, J. Phys. A: Math. Gen. 39, 5445 (2006).]

Algorithm 2 AMUT-k Scheme

Initialize: Fock Build, $\mathbf{F}_{1} \leftarrow \mathcal{F}(\mathbf{P}_{1})$ for step i = 1 to N do Step 1: Density propagation, $\mathbf{P}_{i+\frac{1}{2}} \leftarrow \exp\left(i\frac{\Delta t}{2}\mathbf{F}_{i}\right)\mathbf{P}_{i}\exp\left(-i\frac{\Delta t}{2}\mathbf{F}_{i}\right)$ for iteration j = 1 to k - 1 do Step 2: Fock Build, $\mathbf{F}_{i+\frac{1}{2}} \leftarrow \mathcal{F}\left(\mathbf{P}_{i+\frac{1}{2}}\right)$ Step 3: Density propagation, $\mathbf{P}_{i+\frac{1}{2}} \leftarrow \exp\left(i\frac{\Delta t}{2}\mathbf{F}_{i+\frac{1}{2}}\right)\mathbf{P}_{i}\exp\left(-i\frac{\Delta t}{2}\mathbf{F}_{i+\frac{1}{2}}\right)$ end for Step 4: Density propagation, $\mathbf{P}_{i+1} \leftarrow \exp\left(i\Delta t\mathbf{F}_{i+\frac{1}{2}}\right)\mathbf{P}_{i}\exp\left(-i\Delta t\mathbf{F}_{i+\frac{1}{2}}\right)$ Step 5: Fock Build, $\mathbf{F}_{i+1} \leftarrow \mathcal{F}(\mathbf{P}_{i+1})$ end for

1.1.3 Exponential Density Predictor-Corrector (EP-PC) and Linear Fock Linear Density Predictor-Corrector (LFLP-PC)

The EP-PC and LFLP-PC schemes were proposed by Zhu and Herbert [J. Chem. Phys. 148, 044117 (2018)]. Here is the workflow of our implementations.

Algorithm 3 EP-PC Scheme

 $\begin{array}{l} \textbf{Initialize:} \\ \textbf{Fock Build, } \mathbf{F}_{1} \leftarrow \mathcal{F}\left(\mathbf{P}_{1}\right) \\ \textbf{for step } i = 1 \text{ to } N \text{ do} \\ \textbf{Step 1: Density propagation, } \mathbf{P}_{i+1}^{p} \leftarrow \exp\left(i\Delta t\mathbf{F}_{i}\right)\mathbf{P}_{i}\exp\left(-i\Delta t\mathbf{F}_{i}\right) \\ \textbf{Step 2: Fock Build, } \mathbf{F}_{i+1}^{p} \leftarrow \mathcal{F}\left(\mathbf{P}_{i+1}^{p}\right) \\ \textbf{Step 3: Linear Fock interpolation, } \mathbf{F}_{i+\frac{1}{2}}^{p} \leftarrow \frac{1}{2}\left(\mathbf{F}_{i} + \mathbf{F}_{i+1}^{p}\right) \\ \textbf{Step 4: Density propagation, } \mathbf{P}_{i+1}^{c} \leftarrow \exp\left(i\Delta t\mathbf{F}_{i+\frac{1}{2}}^{p}\right)\mathbf{P}_{i}\exp\left(-i\Delta t\mathbf{F}_{i+\frac{1}{2}}^{p}\right) \\ \textbf{if } ||\mathbf{P}_{i+1}^{c} - \mathbf{P}_{i+1}^{p}|| > \text{tolerance then} \\ \mathbf{P}_{i+1}^{p} \leftarrow \mathbf{P}_{i+1}^{c} \\ \textbf{go to Step 2} \\ \textbf{end if} \\ \mathbf{P}_{i+1} \leftarrow \mathbf{P}_{i+1}^{c} \\ \textbf{Step 5: Fock Build, } \mathbf{F}_{i+1} \leftarrow \mathcal{F}\left(\mathbf{P}_{i+1}\right) \\ \textbf{end for} \end{array}$

Algorithm 4 LFLP-PC Scheme

$$\begin{split} \textbf{Initialize:} & \text{Fock Build, } \mathbf{F}_{1} \leftarrow \mathcal{F}\left(\mathbf{P}_{1}\right) \\ \mathbf{F}_{\frac{1}{2}} \leftarrow \mathbf{F}_{1} \\ \textbf{for step } i = 1 \text{ to } N \text{ do} \\ & \text{Step 1: Linear Fock extrapolation, } \mathbf{F}_{i+\frac{1}{2}}^{\mathrm{p}} \leftarrow 2\mathbf{F}_{i} - \mathbf{F}_{i-\frac{1}{2}} \\ & \text{Step 2: Density propagation, } \mathbf{P}_{i+1} \leftarrow \exp\left(i\Delta t\mathbf{F}_{i+\frac{1}{2}}^{\mathrm{p}}\right)\mathbf{P}_{i}\exp\left(-i\Delta t\mathbf{F}_{i+\frac{1}{2}}^{\mathrm{p}}\right) \\ & \text{Step 3: Linear Density interpolation, } \mathbf{P}_{i+\frac{1}{2}} \leftarrow \frac{1}{2}\left(\mathbf{P}_{i} + \mathbf{P}_{i+1}\right) \\ & \text{Step 4: Fock Build, } \mathbf{F}_{i+\frac{1}{2}}^{\mathrm{c}} \leftarrow \mathcal{F}\left(\mathbf{P}_{i+\frac{1}{2}}\right) \\ & \text{if } ||\mathbf{F}_{i+\frac{1}{2}}^{\mathrm{c}} - \mathbf{F}_{i+\frac{1}{2}}^{\mathrm{p}}|| > \text{tolerance then} \\ & \mathbf{F}_{i+\frac{1}{2}}^{\mathrm{p}} \leftarrow \mathbf{F}_{i+\frac{1}{2}}^{\mathrm{c}} \\ & \text{go to Step 2} \\ & \text{end if} \\ & \mathbf{F}_{i+\frac{1}{2}} \leftarrow \mathbf{F}_{i+\frac{1}{2}}^{\mathrm{c}} \\ & \text{Step 5: Fock Build, } \mathbf{F}_{i+1} \leftarrow \mathcal{F}\left(\mathbf{P}_{i+1}\right) \\ & \text{end for} \\ \end{split}$$



1.2 Energy Conservation in RT-TDDFT Simulations

Figure S2: Energy propagation errors (in a.u.) from RT-TDDFT calculations on the stacked-long Ag₄–N₂ complex. The errors are computed with reference to the energy at t = 0. Results with a time step of 0.05 and 0.5 a.u. are shown in panels *a* and *b*, respectively. PBE0 functional and 6-31G(d) basis set were used.

2 Fluctuation of Energy Components Along RT-TDDFT Trajectories

The fluctuations in different energy components along RT-TDDFT trajectories are shown below for three Ag_4-N_2 complexes. PBE0 functional, LFLP-PC propagator, and a 0.5 a.u. time step were used in these simulations. Stuttgart effective core potential and basis set were employed for silver atoms, and 6-31G(d) basis functions were used on nitrogen atoms.



Figure S3: Fluctuation in different energy components along the RT-TDDFT trajectory for the **stacked long** complex.



Figure S4: Fluctuation in different energy components along the RT-TDDFT trajectory for the **stacked short** complex.



Figure S5: Fluctuation in different energy components along the RT-TDDFT trajectory for the **T-shaped** complex.

3 Initial Superposition

Table S1: Key excited states for the **stacked-long** complex with their excitation energies $\omega^{(m)}$, oscillation periods T, transition dipole moments $\mu_x^{(0,m)}$. Also shown are their contributions to the initial orbital rotation (t = 0), in terms of the expansion coefficients, $\tilde{a}_m(0)$ (computed using Eq. A15), $\tilde{b}_m(0)$ (computed using a density matrix equivalent of Eq. A16), and relative weight $p_m(0)$ (defined in Eq. A19), and the ratio of $a_m(0)$ values computed using Eqs. A15 and A12. Only states with a relative weight, $p_m > 0.01$, are shown. The total weight $\sum_m p_m$ is 0.87 for the first 200 excited states.

State	$\omega^{(m)}(au)$	$T(\mathrm{fs})$	$\mu_x^{(0,m)}$ (Debye)	$\tilde{a}_m(0)$	$\tilde{b}_m(0)$	$p_m(0)$	$\tilde{a}_m(0)/a_m(0)$
5	0.1263	1.2032	-0.8268	-0.0134	-0.0121	0.1926	1.0243
10	0.1570	0.9678	-0.3005	-0.0040	-0.0036	0.0168	1.0435
15	0.1646	0.9232	-1.1224	-0.0135	-0.0121	0.1947	0.9909
20	0.1726	0.8808	0.4158	0.0048	0.0042	0.0242	0.9964
34	0.1999	0.7601	1.6921	0.0169	0.0139	0.2778	0.9984
46	0.2099	0.7242	-0.9663	-0.0092	-0.0075	0.0824	0.9988
93	0.2573	0.5907	-0.4590	-0.0036	-0.0024	0.0101	0.9990
95	0.2579	0.5893	0.5411	0.0042	0.0028	0.0141	1.0011

Table S2: Key excited states for the **stacked-short** complex with their excitation energies $\omega^{(m)}$, oscillation periods T, transition dipole moments $\mu_x^{(0,m)}$. Also shown are their contributions to the initial orbital rotation (t = 0), in terms of the expansion coefficients, $\tilde{a}_m(0)$ (computed using Eq. A15), $\tilde{b}_m(0)$ (computed using a density matrix equivalent of Eq. A16), and relative weight $p_m(0)$ (defined in Eq. A19), and the ratio of $a_m(0)$ values computed using Eqs. A15 and A12. Only states with a relative weight, $p_m > 0.01$, are shown. The total weight $\sum_m p_m$ is 0.86 for the first 200 excited states.

State	$\omega^{(m)}(au)$	$T(\mathrm{fs})$	$\mu_x^{(0,m)}$ (Debye)	$\tilde{a}_m(0)$	$\tilde{b}_m(0)$	$p_m(0)$	$\tilde{a}_m(0)/a_m(0)$
12	0.1602	0.9487	1.3821	0.0173	0.0155	0.3477	1.0001
19	0.1724	0.8816	-0.3483	-0.0040	-0.0036	0.0188	1.0019
34	0.1993	0.7627	1.7065	0.0171	0.0142	0.3145	0.9985
46	0.2097	0.7247	-0.9239	-0.0088	-0.0073	0.0831	0.9988
90	0.2551	0.5957	0.6494	0.0051	0.0034	0.0222	1.0009
135	0.2739	0.5548	0.5838	0.0043	0.0032	0.0179	0.9999
178	0.2949	0.5153	0.6250	0.0043	0.0031	0.0172	1.0031

Table S3: Key excited states for the **T-shaped** complex with their excitation energies $\omega^{(m)}$, oscillation periods T, transition dipole moments $\mu_x^{(0,m)}$. Also shown are their contributions to the initial orbital rotation (t = 0), in terms of the expansion coefficients, $\tilde{a}_m(0)$ (computed using Eq. A15), $\tilde{b}_m(0)$ (computed using a density matrix equivalent of Eq. A16), and relative weight $p_m(0)$ (defined in Eq. A19), and the ratio of $a_m(0)$ values computed using Eqs. A15 and A12. Only states with a relative weight, $p_m > 0.01$, are shown. The total weight $\sum_m p_m$ is 0.85 for the first 200 excited states.

State	$\omega^{(m)}(au)$	$T(\mathrm{fs})$	$\mu_x^{(0,m)}$ (Debye)	$\tilde{a}_m(0)$	$\tilde{b}_m(0)$	$p_m(0)$	$\tilde{a}_m(0)/a_m(0)$
6	0.1261	1.2049	-0.7612	-0.0124	-0.0113	0.1597	1.0288
10	0.1559	0.9747	0.2850	0.0038	0.0034	0.0148	1.0457
13	0.1626	0.9346	1.2075	0.0147	0.0132	0.2214	0.9926
20	0.1721	0.8832	-0.3785	-0.0044	-0.0039	0.0193	0.9987
34	0.1995	0.7618	-1.7067	-0.0171	-0.0141	0.2740	0.9983
46	0.2095	0.7255	0.9502	0.0091	0.0075	0.0768	0.9987
94	0.2577	0.5897	0.6447	0.0050	0.0035	0.0196	1.0003

4 Comparison of Two Schemes for Partitioning Nuclear Attraction Energy

Below, Figs. S6, S7, and S8 show energy transfer between Ag_4 and N_2 along RT-TDDFT trajectories. Two schemes were used to partition the nuclear attraction energy. In panels (a), Eq. 26 (equal contribution from grid-based and nucleus partitioning) was used. In panels (b), Eq. 24 (grid-based partitioning) was used, and led to a fragment energy fluctuation that is 25–50 times larger.



Figure S6: Time evolution of the fragment energy of N_2 molecule in the "stacked-long" configuration of the Ag_4-N_2 complex. Obtained from RT-TDDFT simulation using the PBE0 functional. In panel (a), the fragment energy attraction was obtained using the hybrid scheme in Eq. 26. In panel (b), the fragment nuclear attraction energy was computed using the grid-decomposition in Eq. 24.



Figure S7: Time evolution of the fragment energy of N_2 molecule in the "stacked-short" configuration of the Ag_4-N_2 complex. Obtained from RT-TDDFT simulation using the PBE0 functional. In panel (a), the fragment energy attraction was obtained using the hybrid scheme in Eq. 26. In panel (b), the fragment nuclear attraction energy was computed using the grid-decomposition in Eq. 24.



Figure S8: Time evolution of the fragment energy of N_2 molecule in the "T-shape" configuration of the Ag_4-N_2 complex. Obtained from RT-TDDFT simulation using the PBE0 functional. In panel (a), the fragment energy attraction was obtained using the hybrid scheme in Eq. 26. In panel (b), the fragment nuclear attraction energy was computed using the grid-decomposition in Eq. 24.

5 Geometries

5.1 Stacked-long

Energy values (in Hartree) and nuclear coordinates (in Å) of silver-nitrogen configurations using the PBE0/6-31G(d) level of theory,

6						
the	total	energy	is	-697.274292	au	
Ag		-0.00000		-1.31103		0.00000
Ag		-0.00000		0.00000		2.40747
Ag		0.00000		-0.00000		-2.40747
Ag		0.00000		1.31103		-0.00000
Ν		3.90000		0.00000		0.55978
Ν		3.90000		0.00000		-0.55978

5.2 Stacked-short

Energy values (in Hartree) and nuclear coordinates (in Å) of silver-nitrogen configurations using the PBE0/6-31G(d) level of theory,

6

the	total	energy	is -697.27453	3
Ag		-0.00000	-1.31103	0.00000
Ag		-0.00000	0.00000	2.40747
Ag		0.00000	-0.00000	-2.40747
Ag		0.00000	1.31103	-0.00000
Ν		3.90000	0.55978	0.00000
Ν		3.90000	-0.55978	0.00000

5.3 T-shape

Energy values (in Hartree) and nuclear coordinates (in Å) of silver-nitrogen configurations using the PBE0/6-31G(d) level of theory,

6

$_{\mathrm{the}}$	total	energy	is -697.273318	
Ag		-0.00000	-1.31103	0.00000
Ag		-0.00000	0.00000	2.40747
Ag		0.00000	-0.00000	-2.40747
Ag		0.00000	1.31103	-0.00000
Ν		4.75978	0.00000	0.00000
Ν		3.64022	0.00000	0.00000