Quantum dynamics method with the use of a projected-space group diabatic Fock matrix for exploring excited electron migration in molecular aggregates in photochemistry

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Abstract

Recently, the authors proposed a practical quantum dynamics method for investigating the migration of an excited electron in a molecular aggregate system in a light field starting from any type of initial local excitation by using a group diabatic Fock matrix [ T. Yonehara and T. Nakajima, J. Chem. Phys. 147, 074110 (2017) ]. The aim of this method is to explore the quantum dynamics of excited electrons in light-induced energy transfer systems. As a branch of this theoretical method, we propose a concise scheme for extracting an essential Hilbert space in the form of the projected orbitals relevant to excited electron dynamics in this article. To study the performance of the present scheme, we used the frozen Fock approximation in that the Fock operator is not updated during electron dynamics. Within this approximation, the size of the active space involving the electron wave packet dynamics is examined by using a typical donor–acceptor pair as well as aggregate systems, namely, a naphthalene–tetracyanoethylene, a circularly orientated 20-mer ethylene aggregate, and a fullerene–five-unit-polythiophene dimer. We treat cases involving light fields and initial local excitations. The compact description scheme developed here makes it easy to investigate excited electron dynamics as a response in molecular aggregates to an internal local excitation as well as an external light field.
I. INTRODUCTION

Recently, the authors proposed a concise method for describing the quantum dynamics of excited electrons traveling over constituent molecules in a molecular aggregate system by utilizing a group diabatic Fock (GDF) matrix\(^1\) which was originally introduced by Thoss \textit{et al.}\(^2\) This block diabatic scheme for the electron dynamics provides an intuitive understanding of charge and exciton migration as the quantum mechanical transport of electronic energies in a molecular assembly subject to the inherent electronic propensities of the site molecules, starting from any prepared type of initial local excitations considering the light-electron couplings.

In the present article, on the basis of the characteristics of a nearly block structured diabatic representation in the GDF method, we introduce a compact representation within an extracted Hilbert subspace. The aim of this paper is three-fold: (1) to introduce a scheme for reducing the computational cost in keeping with an accurate description of the dynamics, (2) to investigate how many active orbitals are required for an accurate description with respect to different initial local excitations and external light fields under the frozen Fock matrix approximation without including dynamical effect of electron density, and (3) to demonstrate the usability of our scheme for analyzing the characteristics of quantum mechanical transport in molecular aggregates in cases using a hypothetical mathematical model Hamiltonian with the approximation mentioned above.

This article improves upon our previous work by providing and assessing a procedure for reducing the computational cost of electron dynamics calculation using the GDF method. Instead of real-time time-dependent density functional theory (RT-TDDFT), we use a frozen Fock approximation during electron dynamics calculations. This is done to focus on the formal scheme for extracting the essential parts of the Hilbert space within an employed approximate model.

The point is that electron migration of chemical interest over a molecular aggregate under moderate light conditions occurs in a manifold associated with a low number of excited states described by molecular orbitals within a relevant but not very large energy range around the Fermi energies of a system. It is also expected that higher energetic orbitals are needed for a description as the electronic coupling becomes stronger.

It is instructive to compare other studies with our present method. There are many studies intensively investigating molecular interactions and their effects on excited energy transfer proceeding in excited molecular aggregates\(^3\)\textsuperscript{–15} For example, Futera \textit{et al.}\(^16\) successfully
utilized and assessed the GDF method originally names a projection operator diabatization scheme to evaluate electronic coupling matrix elements with high level ab initio calculations in the electron-transfer process of a molecular-metal/semiconductor interface. However, a study on a systematic variable description of the excited electron dynamics in a bottom-up approach is rare. Compared to previous studies on excited electron transfer in molecular aggregates, the scheme introduced in the present article has the advantages of a compact description of excited electron migration with ab initio electronic structure calculations. In addition, our new scheme allows a systematic improvement of the results by enlarging the projection space. The most prominent feature is that our scheme is intended for a real-time dynamics of excited electrons in molecular aggregates in an external field starting from any pattern of initial local excitations prepared as a perturbation for the electronic state. The protocol introduced here allows for an intuitive understanding of the complex electron migration involving the excited states of molecular aggregates in photochemistry, which supports research on efficient excited energy transfer.

In the present article, we present the details of the procedures for constructing the projected active orbital space within the group diabatic (GD) representation, and numerical applications are described. We examine the size of the active space in a systematic way with an increasing energy range for projecting a diabatic local orbital space. As example systems, we use a typical donor–acceptor pair as well as aggregate systems, namely, naphthalene(NPTL)—tetracyanoethylene(TCNE), a circularly orientated 20-mer ethylene aggregate, and C$_{60}$-5uPT. We consider general applications to molecular aggregates involving an energetic degeneracy. To ensure the energy balance between local projection orbitals, we employ an energy width parameter for extracting a relevant subspace with the mean value of the highest occupied molecular orbital (HOMO) and lowest occupied molecular orbital (LUMO) energies in the whole system as a reference energy, and we do not use a scheme which requires direct orbital selection.

We treat cases including light fields and initial local excitations. It is shown that the case of initial excitations consisting of local HOMO-LUMO transition can be described well by using a rather small number of projected active orbitals. We also see that a rather large size of the active space is required for a correct result in cases with light-electron couplings with a moderate strength.

In Sect. II, we explain the theoretical method for describing the electron dynamics based on the GDF representation within projected local diabatic orbitals. In the following section,
numerical examples are presented for excited electron migration induced by an external light field as well as an initially prepared local excitation. We show there are cases where more than the HOMO and LUMO are needed for a description of excited electron dynamics. In the final section, we give the concluding remarks.

II. THEORETICAL METHOD

In this section, after a brief summary of the electron dynamics method\textsuperscript{1} using a GD representation\textsuperscript{1,3,6,10} we introduce a scheme for constructing a concise matrix form with use of projected diabatic local orbitals having a dominant contribution to the underlying dynamics. The determination of diabatic local projection orbitals playing a main role in the present work requires only the parameters of energy ranges for monomers covering the important orbitals around HOMO and LUMO playing in an excited electron dynamics.

A. Overview of the projected-space group diabatic representation

The transformation from an atomic orbital (AO) representation of physical operators to a GD form consists of the following two transformations being constructed sequentially:

(i) a transformation to a representation using the Löwdin orthogonalized atomic basis functions and

(ii) a unitary transformation made from the local orbital sets obtained by the diagonalizations of block sub-matrices corresponding to the predetermined monomer groups in the Fock matrix prepared in step (i).

The overview of the process of extracting the diabatic local projection orbitals as the primary topic of the present article is as follows:

(a) calculate the mean of the HOMO and LUMO orbital energies of the whole system;

(b) set an energy range covering the local orbitals for each monomer in which the value obtained in (a) is placed at the middle;

(c) obtain the diabatic local projection orbitals of the monomers in the energy range prepared in (b).
We refer to the matrix representation within these projection orbitals as the projected-space group diabatic Fock (P-GDF) representation, of which the details are explained in later subsections.

The multiplications of matrices associated with the electronic properties and the analyses of the time-dependent electron density using the newly introduced P-GDF representation are carried out within the projected orbital space. The information related to the size of the orbital space required for a description of the dynamics without loss of accuracy provides us with insight into the sub-Hilbert space relevant to it.

In the following subsection, for a self-contained form of the present article, we first summarize the electron dynamics scheme using a GD representation and then proceed to describe how to obtain the diabatic local projection orbitals and how to construct compact matrix representations by using them as a subset of the basis functions.

B. Group diabatic representation

1. Fock matrix in the Löwdin representation

The first step is to prepare a Fock matrix represented by the Löwdin orthogonalized atomic basis function

$$\tilde{F}_{mn} \equiv \langle \tilde{\chi}_m | \hat{F} | \tilde{\chi}_n \rangle,$$

(1)

where the orthogonalized Löwdin atomic orbitals (AOs) are expressed by

$$| \tilde{\chi}_n \rangle = \sum_j^{\text{AO}} | \chi_j \rangle (S^{-1/2})_{jn}$$

(2)

with $S_{jn} = \langle \chi_j | \chi_n \rangle$ being the AO overlap matrix element. Here $\{ \chi_n \}$ is the original basis set consisting of AOs.

2. Localized orbitals of a subgroup

After the classification of $\{ \tilde{\chi}_n \}$ into subgroups, e.g., monomers, the block structure of the Fock matrix within the Löwdin basis set is determined with its diagonal blocks $\{ \tilde{F}_{G_i,G_i} \}$ and off-diagonal ones $\{ \tilde{F}_{G_i,G_j} \}_{i \neq j}$ with i and j ranging from 1 to $N_g$. $G_i$ denotes the i-th subgroup. $N_g$ is the number of subgroups in the system. Note that we can employ arbitrary divisions of the component atoms in the whole system.
The diagonalization of diagonal blocks corresponding to subgroup $G$, 

$$
\widetilde{F}_{GG} = D_G \widetilde{F}_{GG} D_G^\dagger,
$$

(3)
gives rise to the unitary transformation matrix $D_G$, whose column vectors are the linear coefficient vectors of the localized eigenstates expanded in terms of the Löwdin orthogonalized atomic basis functions for the group $G$. The dagger symbol attached to a matrix indicates its adjoint form. $\widetilde{F}_{GG}$ is the diagonal matrix having the eigen energies $\{\epsilon_{j,G}\}_{j=1}^{M_G}$ of the corresponding subgroup $G$ as its elements, and $M_G$ is the number of local basis functions spanned at group $G$. Here, $G \in \{G_1, ..., G_{N_g}\}$.

The elements in off-diagonal blocks of the Fock matrix represented by these localized orbitals, associated with different groups, can take non-zero values, which provide a diabatic character in the representation with the use of the collection of these orbital sets. These group localized orbital sets provide a transformation matrix from a Löwdin representation to the GD one to be explained later.

3. Group diabatic Fock matrix

The GD representation of the Fock operator $\widetilde{F}$, as one of the main ingredients in the GDF electron dynamics scheme is constructed via the transformation of the Löwdin representation matrix of the Fock operator $\widetilde{F}$. By using the already obtained unitary matrices with the dimensions of the local basis functions associated with groups, $\{D_{G_i}\}_{i=1}^{N_g}$, this transformation is expressed by\textsuperscript{1,3–5}

$$
\begin{align*}
\widetilde{F}_{G_i,G_j} & = D_{G_i}^\dagger \widetilde{F}_{G_i,G_j} D_{G_j}, \\
& \quad \text{where } i \text{ and } j \text{ range from 1 to the number of groups } N_g.
\end{align*}
$$

(4)

where $i$ and $j$ range from 1 to the number of groups $N_g$. The assembly of these submatrices $\{\widetilde{F}_{G_i,G_j}\}_{i,j=1}^{N_g}$ constructs the GD representation which is called GDF matrix and expressed by $\widetilde{F}^{\text{GD}}$. The physical meaning of the components in this final form is as follows. This submatrices $\{\widetilde{F}_{G_i,G_i}\}_{i=1}^{N_g}$ in the diagonal blocks correspond to the local group eigenenergies, while $\{\widetilde{F}_{i,j,G_i}\}_{i \neq j}$, placed at the off-diagonal blocks, describes the interactions between different groups. Note that, in this transformation, the information included in the AO, Löwdin, and GDF representations are the same and no approximation is applied.
4. **Transformation from the AO representation to the GD representation**

A matrix representation of any observable operator $\hat{O}$ in terms of the constructed GD basis set, $O^{GD}$, is related to that of the original AO basis set, $O^{AO}$, as

$$O^{GD} = U^\dagger O^{AO} U,$$  \hspace{1cm} (5)

where $U \equiv S^{-1/2} W$. Here, the diagonal block in the subtransformation matrix $W$ is given by $W_{G_i G_i} \equiv D_{G_i}$ for $i$, while the off-diagonal one is defined as $W_{G_i G_j} \equiv 0$. The Fock matrix obeys the same transformation rule and is obtained by setting $\hat{O} = \hat{F}$ in the above equations, where we know that $F^{AO} = F$ and $F^{GD} = F$.

On the other hand, the transformation of the density matrix from the original AO basis set to the GD one is written as

$$\rho^{GD} = U \rho^{AO} U^\dagger.$$  \hspace{1cm} (6)

Note that the unitarity of $W$ assures total electron conservation with respect to this transformation,

$$\text{Tr} \left[ \rho^{AO} S \right] = \text{Tr} \left[ \rho^{GD} \right].$$  \hspace{1cm} (7)

5. **State coupling**

We can obtain the essential elements needed for the construction of light–electron coupling by setting $\hat{O} = \hat{r}$, $\partial_r$ in the previous subsection. Here, boldface denotes a vector in a three-dimensional Cartesian space, and $\mathbf{r}$ denotes a composite variable of the electron position in three-dimensional space. The first and second operators are responsible for the light–electron coupling in length and velocity forms.\textsuperscript{18,19} Here, we neglect the nonadiabatic coupling and molecular motion to allow us to focus on an examination of the electron dynamics scheme using projected local diabatic group orbitals. The effects of molecular motion and other types of electronic coupling will be reported in our next article.

6. **Time propagation of the density matrix in a GD representation**

In this study, the calculation of the time propagation of an electronic state is performed in terms of the Liouville–von Neumann equation associated with one particle density matrix.
as follows:

$$\frac{\partial}{\partial t} \rho^{GD} = -\frac{i}{\hbar} [\mathcal{F}^{GD}, \rho^{GD}], \quad (8)$$

where

$$\mathcal{F}^{GD} \equiv F^{GD} + L^{GD}. \quad (9)$$

$L^{GD}$ is a light–electron coupling matrix. For the length gauge, their corresponding matrix elements have forms of $L^{GD} = +e \rho^{GD} \textbf{E}$.\textsuperscript{18,19} Here, $\textbf{E}$ is the three-dimensional electric field vector, which generally depend on a point in a three-dimensional space.

We used the dipole approximation, namely, long wavelength approximation,\textsuperscript{18,19} since the wavelength of light treated here is sufficiently large compared to the size of the molecular system treated. We followed the dynamics for 15 femtosecond with the time step of 4 attosecond using a fourth-order Runge–Kutta time integrator. Hereinafter we abbreviate femtosecond to fs and attosecond to as.

The Fock, dipole, and electron velocity moment matrices within the AO representation required for the dynamics calculation were evaluated by using the electronic structure package NTChem2013.\textsuperscript{20}

7. Initial density matrix: local excitation and electron filling

According to this idea, the initial density matrices in the GDF representation are prepared so that the diagonal elements in each diagonal block of the corresponding monomer should be occupied up to the number of electrons assigned to this monomer. A simple example can be found in our previous article.\textsuperscript{1} Though an off-diagonal filling responsible for the initial coherence is also possible, for simplicity, we consider only the diagonal part in the preparation of the initial state of the density matrix. This issue will be reported in our future article. In the article, we treat the case of the spin-restricted model within the GDF representation as explained below. This is not rigorously the same as that within the canonical (KS or HF) orbital representation. In a restricted case with the same spatial orbitals for different alpha and beta spins in this model, the occupancy of the GDF local orbitals of each monomer is up to half of the number of electrons assigned to this group from the lowest energy orbital. Therefore, in a strict sense, the initial density matrix mentioned above differs from that of the true ground state of the whole system. In fact, this does not cause any problem for
examining the migration dynamics of charge and electronic excitations over the constituent monomers in an assembly.\textsuperscript{1}

Generally, we can make any type of excitation configuration starting from the reference occupations of the GD orbitals. If we want an initial density associated with an excess or a deficiency of electrons in each monomer for treating the case accompanied with a charge moiety, we merely need to set the occupations to the corresponding number of electrons in each monomer.\textsuperscript{1} Throughout this article, we treat cases with an overall singlet spin state in a spin-restricted manner.

C. Projected space made from subsets of local site orbitals

This subsection is an essential part of the present article proposing the P-GDF scheme. Here, we provide the concrete procedures used in it and the corresponding mathematical expressions.

Let us consider the diagonal block of the Fock matrix within the GD representation, $\{\tilde{F}_{G,G_i}\}$ and the associated local orbital energies $\{\epsilon_{j,G_i}\}_{j=1 \sim N_{G_i}}$ corresponding to the $i$–th group site. In a situation where the interactions between group monomers are weak compared to those among the atoms in each monomer, we can safely employ the referential local ground state, where all of the electrons assigned to a local site are filled in ascending order from the lowest-energy local orbital.

The excited electron dynamics in a molecular aggregate system under moderate sunlight conditions is expected to proceed in low-excited-state manifolds constructed from the local molecular orbitals in a relevant but not very large energy range around the Fermi energy of the system. In a situation involving rather strong light field or molecular interaction, the Hilbert subspace required for a description of the dynamics will become large. It is worthwhile to examine the size of the subspace relevant to the excited electron dynamics by varying the type of molecular interactions such as light-matter coupling and initial local excitations.

Thus, in order to examine the size of the orbital space needed for a description of the electron dynamics at a sufficient accuracy, we establish a procedure for projecting a Hilbert subspace around the Fermi energy of the whole molecular aggregate by using a width parameter for the energy range as follows:

(i) Set an energy width $\Delta \epsilon_i$ covering the local active orbitals for the $i$-th monomer, $G_i$. 

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Here $i$ ranges from 1 to $N_g$.

(ii) Calculate the mean $\eta$ of the HOMO and LUMO energies of the whole system.

(iii) Extract a subset of group diabatic local orbitals in the energy range $[\eta - \Delta \epsilon_i/2, \eta + \Delta \epsilon_i/2]$ from the whole orbital space. We refer to this as a projection of the active diabatic local orbitals.

(iv) Construct minor matrices as representations of the electronic operators within the projected orbital basis set obtained in (iii).

(v) Follow the same procedure as that in the GDF electron dynamics scheme other than the projection introduced here. This means that time propagation and property analysis are carried out using the obtained small size matrices.

The mathematical form of P-GDF procedure is compactly given in Appendix A.

The orbital projection scheme using an energy width allows for the natural treatment for general situations involving the unknown energy orders and spatial localities of the GD orbitals in molecular aggregates. For instance, in an application to a molecular aggregate having a quasidegeneracy in the orbital energies, this projection scheme ensures an energy balance of the local projection orbitals among monomers, which is essential for a correct description of electron migration.

In the following numerical demonstrations, for focusing on this essential point in the proposed scheme, we employ a parameter for the energy range independent of the monomers, namely, $\Delta \epsilon_i = \Delta \epsilon$, which is expressed by $E_{BW}$ in the figures. The resultant total number of projection orbitals of the monomers is denoted by $N_b$ throughout the present article.

D. On the limitation of approximation of the frozen Fock approximation

The main aim in this work is to investigate the formal usability of the scheme for extracting the projected space needed for the minimum description of electron dynamics using the frozen Fock approximation which allows a reduction of calculation cost. In the present
approximation, the Fock matrix is not updated during the electron dynamics,

$$\frac{\partial}{\partial t} \rho_{GD}^{GD}(t) = -\frac{i}{\hbar} \left[ \mathcal{F}^{GD}\{\rho_{GD}^{GD}(t), t\}, \rho_{GD}^{GD}(t) \right]$$

\(\Downarrow\) frozen Fock approximation

$$\frac{\partial}{\partial t} \rho_{GD}^{GD}(t) = -\frac{i}{\hbar} \left[ \mathcal{F}^{GD}\{\rho_{GD}^{GD}(t = 0), t\}, \rho_{GD}^{GD}(t) \right]$$  \hspace{1cm} (10)

The present approximation provides an unphysical description for a realistic electron dynamics in a stringent sense, namely, the present scheme with the frozen Fock matrix does not have the ability to predict correct time scales of charge migration and change of electronic characters along dynamics.

Intuitively, the frozen Fock approximation provides a faster time scale of dynamics due to an accompanied confined Hilbert space compared to those computed using the time-dependent Fock matrix which is affected by dynamical electron density in a more realistic description. The related discussion associated with numerical calculations will be given in section III C. The consideration of density relaxation in the Fock matrix and the associated efficiency of the projection scheme will be considered in our future work.

III. NUMERICAL DEMONSTRATION

For examining the size effect of the projected space on the calculation results, we mainly focus on the time-dependent behaviors of the Mulliken charge of electron donor molecules and the unpaired electrons of monomers since they characterize the excited electron dynamics in aggregate systems well.

Detailed information related to molecular configurations as well as transition dipole length matrices of monomers in group diabatic representation employed in this section are summarized in the supplementary material. With respect to the NPTL–TCNE dimer and circular 20-mer ethylene systems, readers can find further information in our previous article.\(^{1}\) In addition to these two systems, we examine one larger donor–acceptor systems that includes a fullerene molecule, namely, \(C_{60}\)-5uPT. The schematics of the molecular configurations used in this article as shown in Fig. 1.

We also provide information related to the dependence of the computational cost of the dynamics calculations on the size of the projection space in the supplemental materials, where readers can find the details on the reduction in the computational cost using our scheme.
A. NPTL–TCNE dimer

As a first test system, we treat a dimer system consisting of NPTL and TCNE. NPTL serves as an electron donor molecule, while TCNE has the properties of an electron acceptor. The molecular geometries and relative orientations of the monomers used here are the same as those in Panel (l) in Fig. 3 in our previous article on the original GDF electron dynamics scheme where readers can find further information including ab initio data as well as the literature of experimental data.

The geometry of each monomer was optimized at the DFT/6-31G(d) level with the use of the CAM-B3LYP exchange correlation functional. This functional was chosen to describe charge transfer moderately at the present computational level. Although the diffuse basis functions are required for an accurate description of the charge transfer throughout this article we did not include the diffuse functions in the calculations since the assignment of Löwdin orthogonalized AOs to monomers becomes ambiguous in the present localization scheme due to the delocalization of diffuse functions covering different atoms than the ones they are centered on.

The Fock matrix for optimized KS orbitals, which is needed for the construction of the GDF matrix, was also calculated at the same CAM-B3LYP/6-31G(d) level. Both molecules have planar geometries in the optimized geometry in their ground electronic states. Here, as shown in Fig. 1 the principal axis of NPTL was set to be parallel to the X axis, while we set TCNE to be parallel to the Y axis. The molecular planes of these flat molecules are parallel to the X–Y plane. They were placed in a parallel orientation with a slide of 1.24 Å along the Y axis. The distance between molecular planes was fixed at 4 Å. Although a dimer is treated here, we considered the crystal data reported in the literature with respect to the relative orientation. This selection of molecular configuration yields a non-vanishing overlap between the frontier orbitals, i.e., the HOMO of NPTL and the LUMO of TCNE. See the supplemental material for information related to geometrical coordinates of this system.

Fig. 2 provides the results of the excited electron dynamics involving initial local excitations and external light fields. The time dependent behaviors of the Mulliken charge of the donor molecule, NPTL, are displayed with the variation in the energy range covering the projection orbital space $\Delta \epsilon$. In the panels of the figure, $\Delta \epsilon$ is expressed as $E_{BW}$. The exact results obtained by using the full orbitals are shown as reference data. For clarifying the performance of the P-GDF electron dynamics method, we also present the results obtained by using only the set of the group local HOMO and LUMO of the monomers. To present the
convergence of time dependent charge of donor molecule in Fig. 2 with respect to the increase of number of projected orbitals, we summarized the max deviations of the approximation results measured from the reference data obtained by full orbitals in Tab. I

The first two panels (a) and (b) show the results of the dynamics starting from the initial local excitations of a single side of NPTL and TCNE, respectively. In these two cases no external field was applied. More specifically, in the case in (a) only the NPTL molecule as an electron donor is initially excited, and TCNE as an electron acceptor starts from the local ground state. In the case in (b), the initial excitation pattern is inverted among these two monomers. Here, a local excitation means a local HOMO–LUMO single excitation from the local ground state configuration within the GDF representation.

Throughout the present paper, we use this notation when referring to the term “initial local excitation”.

As clearly seen in panels (a) and (b), the dynamics calculation using \( \Delta \epsilon = 0.5 \) a.u. with the corresponding number of resultant projected orbitals \( N_b = 16 \) qualitatively reproduces the exact result obtained by using all 296 orbitals. Quantitative convergences were obtained by using \( \Delta \epsilon = 3 \) a.u. associated with \( N_b = 162 \) active orbitals, as seen in Tab. I with their corresponding max deviations from the exact results being 0.00332 and 0.00219 respectively for the case (a) and (b).

Another important finding is that we cannot reproduce the correct result for the dynamics by using the smallest projected space consisting of sets of the group local HOMO and LUMO of the monomers in this case. This failure in the description of the correct result is caused by the lack of the local orbital contributing to the population dynamics of diabatic orbitals. Through the analysis of population of the diabatic orbitals, we found that in the case of (a) the pair of LUMO of NPTL and LUMO+1 of TCNE transfer their population from the former to the latter. In fact, the coupling element in the P-GDF matrix between LUMO of NPTL and LUMO+1 of TCNE has non-zero value while that between LUMO of NPTL and LUMO of TCNE has zero value as shown in Sect. II in the supplemental material. This is the reason why the smallest projected space is insufficient for the description. In the same way, for the case of (b), the dominant population transfer among two monomers occur between HOMO of TCNE and HOMO−4 of NPTL, which cannot be covered by the smallest projected space. Again, these transition propensities are well reflected in the emergence of non-vanishing coupling element of P-GDF matrix as shown in Sect. II in supplementary material where the population dynamics for key orbitals are also presented.

Furthermore, we validate this assertion on the correlating local orbitals by examining
the oscillation period of the donor charge as well as orbital population. In the case of (a), the energy difference of the LUMO of NPTL and LUMO+1 of TCNE, as found in the supplemental material, is $\Delta \varepsilon_{(a)} = 0.001 - (-0.003) = 0.004$ a.u. and its corresponding time period of oscillation is $T_{(a)} = 2\pi/\Delta \varepsilon_{(a)} = 1570$ a.u., which is about 38.0 fs. In turn, from the simulation, in the panel (a) we can estimate the time period of charge oscillation being twice of 14 fs, namely, 28 fs, which is moderately close to 38 fs. This time scale, 28 fs, is the same as the population dynamics of these key local orbitals as seen in Sect.II in the supplemental material. For the case of (b), we also examine the time period of charge and population oscillation. The energy difference of the GH of TCNE and GH−4 of NPTL, is $\Delta \varepsilon_{(b)} = -0.3815 - (-0.3991) = 0.0176$ a.u. The corresponding time period of oscillation is $T_{(b)} = 2\pi/\Delta \varepsilon_{(b)} = 356.8$ a.u., which is about 8.6 fs. This is a very close value to the time period read from the panel (b) and the corresponding population dynamics given in Sect.II in the supplemental material. The more precise estimation of the time period of (b) compared to (a) is attributed to the larger energy differences between correlating GDF orbitals. Note that a small energy difference of GDF orbitals between different groups is sensitive to generally weak interactions between groups while the large one is robust to them. Thus, we found that these key orbitals examined above play dominant role in the charge transfer dynamics in the case of (a) and (b).

By comparing the peak values of the positive charge on the donor side between the cases in (a) and (b), 0.5 and 0.075, respectively, we know that the initial excitation on the donor NPTL side has the driving force larger than that on the acceptor side with respect to the charge migration among the present donor–acceptor system. This is consistent with the fact that the local LUMO energy of NPTL, 0.0316 a.u., is significantly higher than that of TCNE, −0.003 a.u., as found in Tab. III which summarizes the energies of parts of the diabatic local orbitals of the monomers as well as the canonical orbitals of the whole aggregate systems treated in this article. The tendency in the superiority of the initial excitation at the donor site is in contrast to the dimer systems including a fullerene molecule as an acceptor, where the initial excitation of the acceptor site provides the charge migration greater than that of the donor site, which will be discussed in a later subsection.

We proceed to the cases including external light fields, of which the results are given in (c) and (d). In these cases, no initial local excitation is carried out for the two monomers. In other words, both molecules are initially prepared in their local ground states within the GDF representation. Most of the parameters of the continuum light field are the same as
those employed in Panel (l) in Fig. 3 in the our original article on electron dynamics with
the GDF scheme; namely, the wave length and unit vector of polarization are 700 nm and
\((\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}})\) in the XYZ Cartesian coordinate, respectively. The wavelength of 700 nm
corresponds to 0.065 a.u. as one photon energy. The calculation conditions for the two cases
are different with respect to the field strength. For panel (c), the strength of the light field
is 0.015 a.u., while a larger strength of 0.02 is applied for (d).

In both cases, the energy range of the orbital projection space, \(\Delta \epsilon = 0.75\) a.u., is sufficient
to reproduce quantitatively the exact results in panels (c) and (d). We can also see the
gradual recovery from the incorrect result when using \(\Delta \epsilon = 0.5\) a.u. to the best one with
\(\Delta \epsilon = 0.75\) a.u. via \(\Delta \epsilon = 0.65\) a.u. The other important observations are the correct behavior
up to 5 fs and its following growth in the variance from the exact result after this time as
seen in the cases with \(\Delta \epsilon = 0.5\) a.u. and 0.65 a.u. This means that the orbital subspace
needed for the correct description of the excited electron dynamics generally becomes large
as electronic diffusion proceeds in the electronic Hilbert space. Here, we need the space
larger than the smallest projected space consisting of sets of the group local HOMO and
LUMO of the monomers in order to obtain the correct result for the dynamics, despite the
moderate reproduction in the initial 4 fs.

As the final part for this subsection, we provide an explanation why many more states
are needed to obtain the convergence in case of interaction with light starting from GDF
ground states (as seen in the panels (c) and (d), 44 orbitals) compared to the case without
light where the initial state is prepared as a local LUMO excitation of one side (as seen in
the panels (a) and (b) 16 orbitals).

The view of state population dynamics provides the explanation. The reason of this
characteristic difference is summarized as follows; (1) The case of (c) and (d) include the
continuum light non-resonant to optical transition from local occupied orbitals to higher
ones as well as the transitions between different sites, which causes a resultant population
distribution over a large number of orbitals. (2) On the contrary, in the case of (a) and (b) the
population dynamics in orbital space occurs near the initially local excitation states through
the diabatic coupling between two monomers, which leads to the rather small number of
orbitals essentially contributing to the electron dynamics under consideration.
FIG. 1. Schematics of the geometries of the molecular aggregates treated in this article: (a) NPTL–TCNE dimer, (b) circular 20-mer ethylene, and (c) C₆₀-5uPT. The centroids of aggregates were set to origin for all the systems. See the supplemental material for detailed information of their Cartesian coordinates.
FIG. 2. Convergence of the results for the charge separation dynamics in an NPTL–TCNE dimer with an increase in the energy range determining the active orbital space. The energy width used for orbital projection is expressed by $E_{BW} = \Delta \epsilon$ in Hartree, with the number of corresponding projected orbitals $N_b$. The exact results obtained by using the full orbitals are indicated by circles, while those for the primitive one using only the set of the group HOMO and LUMO of the monomers are indicated by the cross points labeled with $gHLset$. The Mulliken charge of NPTL as an electron donor system was plotted for each case corresponding to the vertical axis. The horizontal axis denotes the time in femtoseconds. Panels (a) and (b) show the results starting from the initial local excitation in the donor NPTL and acceptor TCNE, respectively, while the other moieties are initially in the ground states within the GDF representation. In these two panels, no light field irradiates the system. In panels (c) and (d), a continuum light field is applied, and its field parameters as a wave length and unit vector of polarization are 700 nm and $\left(\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}\right)$ in the XYZ Cartesian coordinate, respectively. The field strength in (c) is 0.015 a.u., while a larger strength of 0.02 is applied in the case in panel (d).
| $\Delta \epsilon$ | (a)  | (b)   |
|--------------|------|-------|
| 0.5          | 0.03514 | 0.01819 |
| 0.75         | 0.03683 | 0.01633 |
| 1.5          | 0.02074 | 0.00943 |
| 3.0          | 0.00332 | 0.00219 |

| $\Delta \epsilon$ | (c)  | (d)   |
|--------------|------|-------|
| 0.5          | 0.15370 | 0.80155 |
| 0.6          | 0.06617 | 0.23744 |
| 0.75         | 0.01358 | 0.01515 |

**TABLE I.** Max deviations of the time dependent charge of donor molecules obtained using the P-GDF scheme with the various $\Delta \epsilon = E_{BW}$ measured from the exact results using full orbitals for the NPTL–TCNE cases. This table corresponds to Fig. 2. Unit is a.u.
B. Circular 20-mer ethylene

Next, by using a circular 20-mer ethylene molecule having moderate interactions among the monomers, we demonstrate that the present P-GDF scheme enables a significant simplification of the description of the exciton dynamics without a loss of accuracy.

The radius of the circle on which centers of masses of the monomers are placed is 12 Å and the distance between the centers of the masses of nearest neighbor monomers is roughly 3.77 Å. The molecular configuration is the same as that used in our previous article. All information related to the molecular configuration is included in the supplementary material.

From Tab. III which includes the energies of the orbitals around the frontier ones, the group HOMO and LUMO energies moderately differ from the HOMO and LUMO energies of the whole system, where we find the existence of moderate interactions among monomers. Note that this is in contrasts to the other systems treated in this article.

Fig. 3 shows the time-dependent behaviors of the number of effectively unpaired electrons (EUPEs) at local site $i$ in panels (a)–(c) and the Mulliken charge in panels (d)–(f) for specific sites, namely, the 1st, 5th, and 10th ethylene monomer sites. The EUPEs of each atom were evaluated by applying a Mulliken population analysis to the filtered density operator with the use of natural orbitals at every time, $\hat{\rho}^{\text{EUPE}} = \sum_i |\phi_i^{\text{NO}}\rangle n_i (2 - n_i) \langle \phi_i^{\text{NO}}|$, with $\hat{\rho} |\phi_i^{\text{NO}}\rangle = n_i |\phi_i^{\text{NO}}\rangle$. Here, $\phi_i^{\text{NO}}$ and $n_i$ denote the $i$-th natural orbital and its corresponding natural population, respectively. $\hat{\rho}$ is a one-electron density operator for the whole system. Its usability for obtaining information concerning proton-electron coupled wave packet coherent transfer and the polyradical features of a complex system is well examined.

Here we use a two site excitation as an initial electronic state. This initial modeling was partly applied in our previous article in order to assess the GDF electron dynamics method in a wide class of dynamics involving complicated quantum interference. There a light field was also applied to control the exciton flow. In this subsection we use the same parameters shown later. While we consider that this initial modeling combined with light field help us to enlarge the possibility for extracting inherent dynamics trend in the molecular aggregates, here we just focus on the performance of the present P-GDF scheme with respect to the reduction of computational cost.

At the initial simulation time, only the 1st and 11th monomers are singly excited from the local HOMO to LUMO, and the other moieties are in their local ground states within the GDF representation. The 10th monomer is placed at the counter position against the 1st one on the circle. During the dynamics, a continuum light field irradiates the system.
The field strength, wavelength and unit vector of polarization of the applied light field are respectively 0.02 a.u., 700 nm, and \( \left( \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}} \right) \) in XYZ Cartesian coordinates.

We can clearly see that all of the properties for the case of \( E_{BW} = 0.5 \) a.u. with the resultant \( N_b = 40 \) active orbitals converge to those using the full GD orbitals. Since the number of monomers is 20, this means that only the local HOMO and LUMO are sufficient to reproduce the results of the exciton dynamics using full orbitals. This success indicates the usability of the present projection method within the GD representation for the construction of a compact molecular Hamiltonian in a bottom-up approach based on an ab initio calculation.

We comment on the observed interesting feature between a charge and an exciton. In this case, the two Frenkel excitons initially prepared at opposite positions on the circle split and proceed accompanied with weak delocalization. By comparing the (a)–(c) with (d)–(f) respectively, we find that the transient quantum state of a site with a moderately localized unpaired electron causes an electron flow to the neighboring sites. The electron instability at the sites is correlated with the local existence of an exciton characterized by an EUPE\(^{1,24}\) as predominantly singly occupied component in a density matrix within a natural orbital representation. This is clearly illustrated by the behaviors of the properties in the first 2 fs in (a) and (d), 6-8 fs in (b) and (e), and 4-6 fs in (c) and (f). We also find that the growth of the positive charge follows the emergence of the maximum peak in the number of EUPEs in each group, which is more clearly illustrated in panels of (g)–(i) by using trajectories in a two-dimensional space consisting of EUPEs and charge. The details of time-dependent behaviors of the properties for all monomers were presented in our previous article.\(^{1,24}\)
FIG. 3. Convergence of the results of charge transfer exciton migration in a 20-mer ethylene circle with respect to the width of the energy range covering the projection diabatic local orbital space. The meanings of $E_{BW}$ and $N_b$ are the same as those in Fig. 2. The calculation conditions with respect to the molecular geometries, relative orientation, and light field are the same as those employed in panel (h) in Fig. 5 in our previous article. In this case, the light field irradiates the system. Only the 1st and 11th ethylene monomers are initially singly excited from the local HOMO to the LUMO. See the text for the details of the calculation conditions. For the brevity, we show the time-dependent number of EUPEs in the 1st, 5th, and 10th ethylene monomers in panels (a), (b), and (c), respectively, while panels (d), (e), and (f) show the group Mulliken charges in the same order. Panels (g), (h), and (i) show the correlations between the number of EUPEs and charge of groups as trajectories for the calculation using all orbitals. In the bottom three panels, the blue circles denote the initial point of the dynamics.
C. C₆₀-5uPT dimer

Here, we treat a C₆₀–polythiophene dimer system. It is worthwhile to apply our scheme to this system because it is one of the minimum acceptor–donor model systems having charge migration properties, and microscopic information is highly demanded for the understanding of its mechanism in the research field of efficient solar energy conversion using organic molecular materials with a low cost. The essential difference in the electronic structure of this system from the NPTL–TCNE system treated in a previous subsection is the strong electron-accepting ability of the acceptor molecule, here, C₆₀, due to its high aromaticity and the existence of dense states around the HOMO and LUMO, as indicated in Tab. III. As a polythiophene, we employed a five-unit linearly linked polythiophene denoted by 5uPT. Ab initio calculations were carried out at the CAM-B3LYP/6-31G level. We employed this functional in order to describe the moderate charge transfer as accurately as possible within this hypothetical electronic Hamiltonian for the same reason explained in the subsection of NPTL-TCNE. Both monomers were separately geometrically optimized. As shown in Fig. the centers of the masses of the two monomers were placed on the Z axis. The tangent plane of C₆₀ was set parallel to the molecular plane of 5uPT. The distance between the centers of the mass of the two moieties was fixed at 6.5 Å. Complete information related to the geometry of this molecular aggregate can be found in the supplementary material in Cartesian coordinates. The transition dipole length matrices of monomers within group diabatic representation are also shown in the same material.

Fig. 4 shows the results of the excited electron dynamics with initial local excitations and an external light field for the C₆₀-5uPT system. The time-dependent behaviors of the Mulliken charge of the donor molecule, 5uPT, are displayed with the variation in the width of the energy range for the orbital space projection, ∆ε, in the same manner as Fig. 2 for the NPTL–TCNE system. We also presented the max deviations from the reference data obtained by full orbitals in Tab. III in order to check the convergence of time dependent charge of 5uPT in Fig. 4 with respect to the increase of number of projected orbitals.

1. Cases of initial local excitations

The dynamics corresponding to panels (a) and (b) start from the initial local excitations of a single side of C₆₀ and 5uPT, respectively. In the case in (a) only, the C₆₀ molecule as an electron acceptor is initially HOMO–LUMO excited, and 5uPT as an electron donor is
in the local ground state. On the other hand, in the case in (b), the pattern of the initial excitation is inverted among these two monomers. No external light field is applied in these two cases.

In both cases, $E_{BW} = 0.25$ a.u. with $N_b = 14$ qualitatively reproduces the exact result obtained by using all 809 GDF orbitals, despite a slight difference. Moderately quantitative reproductions are attained by using $E_{BW} = 0.5$ a.u. with $N_b = 60$ projected orbitals as seen in Tab.II with their max deviation from the reference data being 0.05611 and 0.06407 for the cases of (a) and (b), respectively. We obtained perfect convergence to the exact result by using $E_{BW} = 3$ a.u. with $N_b = 644$. We can see that the amount of temporal charge transfer by the initial local excitation on the acceptor C$_{60}$ side is larger than that on the 5uPT side as a donor molecule. This indicates that modification of the C$_{60}$ side is important if we modulate the strength of charge migration. This superiority of the initial excitation of the acceptor side is in contrast to the results associated with the comparisons between the cases in (a) and (b) in Fig. 2. This tendency is consistent with the fact that the HOMO energy of C$_{60}$, $-0.2668$ a.u., is moderately lower than that of 5uPT, $-0.2316$ a.u., and their difference, 0.0352 a.u., is moderately small compared to that of an NPTL–TCNE pair, 0.1094, a.u. as read from Tab. III. In the present case with a high density of states around the local HOMO and LUMO of C$_{60}$, we can safely state that any qualitative description of the electron dynamics is never possible within the smallest projected space consisting of sets of the group local HOMO and LUMO of the monomers. Therefore, the orbital projection scheme using the energy threshold is natural for treating a system having a high density of states around the frontier orbital regions.

Let us go back to the discussion of the size effect of the active orbital space. Considering that the total number of orbitals is 809, a successful compact description using merely 60 projected orbitals strongly suggests the usefulness of the present scheme for modeling excited electron migration in the case of naive exciton dynamics without a light field.

It is worthwhile to examine the dependence of the charge migration dynamics on the choice of the basis set and functional ( though the main issue in the article is the projection scheme using rather than the hypothetical model ). We also examined the difference when using a basis set, 6-31G(d), which includes polarization functions as well as other long-range corrected hybrid functionals, $\omega$B97X, LC$\omega$PBE, and a conventional non-corrected hybrid functional, B3LYP. The corresponding results and discussions are given in sections V and VI of the supplemental materials.
2. Cases including continuum light fields

In turn, let us return to panels (c) and (d), which display the results in the cases involving external light fields. In these cases, both molecules are initially in their local ground states within the GDF representation. The wavelength and unit vector of polarization of the applied continuum light fields are respectively 700 nm and \( \left( \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}} \right) \) in the XYZ Cartesian coordinates. The strength of the light field is 0.015 a.u for (c), while a larger field of 0.02 is used for (d).

From (c) and (d), the convergence of the results with respect to \( \Delta \epsilon \) is significantly different from that observed in panels (a) and (b). In fact, a qualitative reproduction of the exact result is reached by using the active energy range \( E_{BW} = 1.5 \) a.u. with \( N_b = 339 \) in both cases. Perfect reproductions of the exact results are attained using \( E_{BW} = 3 \) a.u. with \( N_b = 644 \). In the same way as panels (a) and (b), we also see the failures in the description by merely using the smallest projected space consisting of sets of the group local HOMO and LUMO of the monomers. In this sense, we again find that the orbital projection scheme using the energy threshold is natural for treating a system having a high density of states around the frontier orbital regions.

The cases with a light field require a larger Hilbert space for a description, even if the field strength is small, as seen in panel (c). Despite the necessity for a larger number of projected orbitals compared to the cases with no light field and initial local excitations, the total number of orbitals can be reduced by approximately half in the calculations while retaining qualitative accuracy in the description of the dynamics in this difficult situation with strong electronic coupling.

3. Cases including short light pulses

So far we used the 700nm continuum light wave associated with the main component of the solar light, which is non-resonant to the electric transition of the systems. An initial preparation of non-equilibrium excited state in molecular aggregate by using a near resonant short pulse field is useful to examine a quantum transport propensity in the system from a time-dependent aspect both in experimental as well as theoretical studies. Furthermore, considering the recent and future advancement of ultrafast measurement of chemical dynamics associated with electron migration, it is worthwhile to examine a performance of the present P-GDF scheme in the case of resonant transitions by using ultrafast laser pulse
In the panels of (e) and (f), we displayed the results in the cases involving light pulse fields with a central wave length of 250nm. Both monomers start from their local ground states in the dynamics. The wave length of 250nm with its corresponding photon energy being 4.95 eV (0.182 a.u.) is almost resonant to the local HOMO–LUMO transitions for both moieties. As found in Tab. III the local HOMO–LUMO energy differences are 5.03 eV (0.185 a.u.) and 5.05 eV (0.1857 a.u.) correspondingly for C_{60} and 5uPT.

With relation to the discussion in the subsection II D, we discuss the difficulty of obtaining a realistic description of this system using the frozen Fock approximation. The energy gap for C_{60}, 5.03 eV (0.185 a.u.) is larger than the lowest absorption peak corresponding to the excitation from the ground state to the first excited state in a spin singlet manifold observed in the experimental electronic spectrum, 2.00 eV.33 With respect to the functional dependency of the excitation energies, we also found that the calculations performed with the LCωPBE and ωB97X functionals result in the higher values, 6.42 and 6.62 eV, than with CAM-B3LYP/6-31G at the same geometry. In the CAM-B3LYP/6-31G(d) level calculation with the geometry optimized with CAM-B3LYP/6-31G(d), the corresponding values were 6.35 and 6.49 eV for LCωPBE and ωB97X, respectively, and the degree of overestimation is the same as that obtained using the basis set without the polarization functions. Thus, the HOMO-LUMO gap does not match with the realistic transition energy of absorption within the present hypothetical calculation model. Therefore, the simple use of the frozen Fock approximation results in a higher excitation peak in the absorption spectrum. If we take into account the dynamical density effect on the Fock operator in the electron dynamics calculation, the theory is equivalent to RT-TDDFT, though here we do not employ this as mentioned in the subsection II D. By construction, the linear response time dependent density functional theory (LR-TDDFT) provides an electronic spectrum for lower excitations consistent with that of RT-TDDFT.37–39 Therefore, we can examine the more reliable excitation energy by using LR-TDDFT without an electron dynamics calculation. The excitation energy from the ground to the first excited state within the spin singlet manifold obtained by LR-TDDFT for C_{60} was 2.76 eV with the 6-31G basis set and CAM-B3LYP functional. This value does not change significantly using the basis set 6-31G(d) including polarization functions, which gives rise to an excitation energy of 2.56 eV. It is the same for the 5uPT system with respect to the relaxation effects of electron. The excitation energy between ground and first excited states which is the optically allowed first excitation was 3.02 eV in
LR-TDDFT calculation within the CAM-B3LYP/6-31G level while the HOMO-LUMO gap is 5.05 eV (0.1857 au). As further and more important information about the dimer system, the lowest excitation energy of optically allowed excitation obtained by LR-TDDFT was 2.66 eV for the C\textsubscript{60}-5nPT dimer at the employed geometry with the same basis set, 6-31G and functional, CAM-B3LYP while it was 2.56 eV in the CAM-B3LYP/6-31G(d) level. These observations mean that the frozen Fock approximation is insufficient for the correct description of excitation energies and a feedback into the Fock matrix from a dynamics of electron density is necessary for this purpose.

We now return to the explanation of the parameters of light pulses. Here a characteristic pulse width, \( t_w \), and field peak time, \( t_c \), were set to be 1.93 and 4.84 fs, respectively. The polarization vectors are the same as those used in (c) and (d). The peak strength of pulse field is 0.015 for (e) while that used in (f) is 0.02 a.u. The information on the function form of the vector potential of the laser field is given in the supplemental material where we provided the discussion on the difference in the population dynamics for group diabatic local orbitals around local Fermi levels between the cases involving these concerned non-resonant and resonant field and demonstrate the usability of the GDF representation in an analysis of electron dynamics in molecular aggregate system.

The convergence behavior with respect to \( \Delta \epsilon \) seen in (e) and (f) is more clear than the previous cases of (c) and (d). A qualitative reproduction of the exact result is attained slightly faster than the non-resonant field cases and the energy range of projection space \( E_{BW} = 1 \) a.u. associated with \( N_b = 215 \) is sufficient in both cases of (e) and (f). The perfect reproductions of the exact results are attained using \( E_{BW} = 3 \) a.u. with \( N_b = 644 \). Here also we find the failures in the description within the smallest orbital subspace consisting of sets of group local HOMO and LUMO of monomers as well as quasidegenerate local HOMOs and LUMOs. The charge migrations observed in these resonant pulse cases are larger than (c) and (d) about by two times, which indicates the superiority of the use of near resonant pulse field for investigating the charge migration propensity experimentally.

Here also about the half size of total orbital space was needed to reproduce the exact results which tells us the information of the volume of Hilbert space relevant to the cases involving complicated electronic transitions.
4. *Reasoning for number of required states*

At the last part of this subsection, we provide an explanation for the many more states required for the convergence in case of interaction with light starting from GDF ground states (as found (c), (d), (e), and (f) about 215 orbitals) than those in the case without light starting from the local HOMO-LUMO excitation of one side (as seen in the panels of (a) and (b), 14 orbitals). In the same manner of the last part of the subsection for NPTL-TNCE dimer, the view of population dynamics is useful for this explanation. The characteristic difference is essentially attributed to the non-resonant and moderately strong light-electron coupling leading to a large population distribution for (c-f) and rather weak diabatic coupling associated with resultant population dynamics for (a,b).
FIG. 4. Convergence of the behaviors of the charge migration dynamics in the C₆₀-5uPT dimer system with the increase in the energy width for orbital projection. The meanings of $E_{BW}$ and $N_b$ are the same those in Fig. 2. The exact results given by the full orbitals are indicated by circles while, the primitive data obtained by using only the set of the group HOMO and LUMO orbitals of the monomers is indicated by the cross points, which are labeled with gHLset. Triangle points labeled with QDgHLset correspond to the result by using fivefold HOMOs and threefold LUMOs with quasi-degeneracy in C₆₀ and HOMO and LUMO of 5uPT. See also the caption of Tab. III. In the panel (a), no light field is applied and only the fullerene as an acceptor part is initially excited from the HOMO to LUMO, while the other part is at the local ground state. On the contrary, in the panel (b) without a light field, only the 5uPT moiety as a donor part is initially excited from the HOMO to LUMO in the same way. In panels (c) and (d), both monomers start from their local ground states corresponding to the cases with a continuum light field having a wavelength of 700 nm and a polarization vector of \((\frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}}, \frac{1}{\sqrt{3}})\) in Cartesian XYZ coordinates. The employed field strengths are 0.015 and 0.02 a.u. for (c) and (d), respectively. Panel (e) and (f), where both monomers are their local ground states at the initial time, present the results in the cases using light pulse fields having the central wave length of 250nm. See the main text for details of the calculation conditions.
| $\Delta \epsilon$ | (a)  | (b)  | (c)  | (d)  | (e)  | (f)  |
|------------|------|------|------|------|------|------|
| 0.25       | 0.10767 | 0.06400 | 0.10437 | 0.27025 | 0.20759 | 0.40803 |
| 0.5        | 0.05611 | 0.06407 | 0.11608 | 0.13299 | 0.14030 | 0.23719 |
| 1.0        | 0.06697 | 0.07417 | 0.12462 | 0.14119 | 0.07461 | 0.07462 |
| 1.5        | 0.05195 | 0.05106 | 0.04514 | 0.10427 | 0.05089 | 0.05089 |
| 3.0        | 0.01086 | 0.01145 | 0.00443 | 0.00942 | 0.00910 | 0.00711 |

TABLE II. Max deviations of the time dependent charge of donor molecules of P-GDF calculations with the various $\Delta \epsilon = E_{BW}$ measured from the exact results using full orbitals for the $C_{60}-5uPT$ cases, corresponding to Fig. 4. Unit is a.u.
IV. CONCLUDING REMARKS

In this article, we proposed a novel electron dynamics method called the P-GDF method as a combination of the local orbital projection and GDF electron dynamics schemes. As a first step of the assessment of the P-GDF method introduced here, we employed a frozen approximation without updating the Fock matrix during electron dynamics. With the use of this hypothetical model, we found that the present method allows us to investigate the essential sizes of the Hilbert space associated with the complicated excited electron dynamics of molecular aggregates.

The findings from the present study with the hypothetical approximation are summarized as follows:

(1) The dynamics for various patterns of initial local excitations without an external light field can be described by small numbers of local orbitals covering the HOMO and LUMO of the whole system. On the contrary, in the cases involving light field more orbitals are required for correct descriptions.

(2) Among the cases investigated here, this feature is remarkable in cases with initial local HOMO–LUMO excitations without an external light field. In the demonstration using the circular ethylene 20-mer aggregate having moderate interactions among monomers, we found a perfect description of the excited dynamics using only the subspace consisting of a set of the local HOMO and LUMO.

(3) In the other cases including rather dense levels, although the number of needed orbitals became large, the whole Hilbert space can be reduced safely to a relevant one; in fact, the number of projected orbitals needed for a qualitative reproduction of the exact result are $\sim 10$ times smaller than the total number of bases in these systems without a light field. On the contrary, in cases including a light field, owing to the complicated electronic transitions, more active orbitals were needed for a correct description.

(4) Additionally, chemically interesting features were observed through the numerical examinations. We found a charge density flow induced by the exciton-charge correlation in the ethylene aggregates.

(5) The compact description scheme introduced here allows a useful check of the excited electron dynamics as a response in molecular aggregates to an internal local excitation
as well as an external light field, which provides fundamental information related to the quantum mechanical transfer of excited electrons in molecular aggregates in a photochemical process.

(6) Though based on the frozen Fock approximation, the many successful reproductions of the results with a small number of projected orbitals indicate that the present method may support a development of a robust bottom-up scheme for constructing a practically useful realistic model Hamiltonian based on ab initio calculations intended for an exploration of the electron dynamics in molecular aggregates involving complicated interactions.

For a more realistic description of the charge migration dynamics, the examination of the effect of feedback of electron dynamics into the Fock operator within the P-GDF scheme remains as a subject of future study.
TABLE III. (Upper table) Energies of the group diabatic orbitals of monomers in aggregates. The local HOMO−1, HOMO, LUMO, and LUMO+1, which correspond to GH−1, GH, GL, and GL+1, respectively. Note that the monomer interactions are included in the evaluations of the local orbital energies of monomers. As additional information, we comment that HOMO and LUMO states of C₆₀ are correspondingly fivefold and threefold quasi-degenerate with respect to orbital energy. For this moiety, the orbital energies of GH−4, GH−3 and GH−2 are −0.2688, −0.2687, and −0.2682, respectively, while that of GL+2 is −0.081. (Lower table) HOMO and LUMO energies of the whole systems, labeled with WH and WL, respectively. In both tables, the unit is atomic unit.

V. SUPPLEMENTARY MATERIAL

See supplementary material for the issues of (I) computational cost of the electron dynamics, (II) analysis of key orbitals associated with Fig.2 (a) and (b) for NPTL–TCNE dimer using population dynamics and diabatic coupling elements between different groups, (III) function form of laser pulse field, (IV) non-resonant and resonant field response of C₆₀-5uPT dimer, (V) Basis set dependency of charge migration dynamics for C₆₀-5uPT dimer (VI) Functional dependency of charge migration dynamics for C₆₀-5uPT dimer (VII) transition dipole length matrices within group diabatic representation for C₆₀-5uPT dimer, and
(VIII) geometry data of molecular aggregates of a NPTL-TCNE dimer, 20-mer-ethylene, and a $C_{60}$-5uPT dimer.

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Appendix A: Mathematical form of P-GDF procedure

Here we provide the formal mathematical expression of P-GDF scheme. At first, one knows that within the GD representation the identity operator is written as

$$\hat{1} \simeq \sum_{i=1}^{N_g} \sum_{j=1}^{N_{G_i}} |\phi_j^{G_i}\rangle \langle \phi_j^{G_i}|,$$

where $\{ |\phi_j^{G_i}\rangle \equiv |\tilde{\chi}_{i,G_i}\rangle D_{i,G_i}\}$ with $|\tilde{\chi}_{i,G_i}\rangle$ being the i-th Löwdin orthogonalized atomic orbital basis function spanned in the $G_i$-th group is the set of GD localized orbitals for the group labeled by $G_i$ and $j$ ranges from 1 to $N_{G_i}$, which denotes the number of basis functions spanned at the site, $G_i$. $i$ ranges from 1 to $N_g$, i.e., the number of monomer group sites. We used the symbol for approximation in the equation because of the practical use of a finite basis set during computation. Note that the GDF orbitals created from Löwdin orthonormal basis remain to be orthogonal under unitary transformations even if the transformations are carried out in each group. In turn, with respect to the structure of matrix representation of the Fock operator, only the GDF orbital pairs between different monomers are Fock non-orthogonal while the pairs within the same group are Fock orthogonal.

Next, we introduce projection operators in order to realize steps (i)–(v) in Subsect. in as follows:

$$\hat{P} \equiv \sum_{i=1}^{N_g} \sum_{j \in \Omega_i} |\phi_j^{G_i}\rangle \langle \phi_j^{G_i}|$$

33
where

\[ \Omega_i \equiv \{ j; |\epsilon_{j,Gi} - \bar{\epsilon}| \leq \Delta \epsilon_i/2 \} \quad \text{and} \quad \bar{\epsilon} \equiv (\epsilon_H + \epsilon_L)/2. \]  

(A3)

Here, \( \epsilon_{j,Gi} \) is the local orbital energy associated with the GD orbital \( \phi_{j}^{Gi} \), while \( \epsilon_H \) and \( \epsilon_L \) are the HOMO and LUMO energies of the whole system.

By using these mathematical tools within P-GDF formulation, we approximate a one electron operator \( \hat{O} \) as follows:

\[ \hat{O} \approx \hat{O}_P \equiv \hat{P}\hat{O}\hat{P}. \]  

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Supplementary material for “Quantum dynamics method with the use of a projected-space group diabatic Fock matrix for exploring excited electron migration in molecular aggregates in photochemistry”

Appendix I: Computational cost of the electron dynamics

Here, we provide information about the computational cost of electron dynamics calculation including the time-dependent property analysis and initial ab initio electronic structure calculation, which are separately summarized in Tab.SII and Tab.SIII respectively. The aim here is to show examples of the performance in the case with moderate computer facilities corresponding to the calculations carried out in our article. The specifications of the computer used in this article are as follows: Intel(R) Xeon(R) CPU E5-2680 0 @ 2.70GHz, a cache size of 20480 kB, and a total 32 GB of memory. The Intel FORTRAN compiler (Version 14.0.3.174) was used for source code using the option of level three optimization.

In order to focus on the dynamics calculation, we summarize in Tab.SI the CPU time accumulated over all CPU cores measured by the cputime command in FORTRAN and the wall-clock time for the electron dynamics calculations including the time-dependent analysis for the systems of NPTL–TCNE, circular 20-mer ethylene, and C_{60}-5uPT. The CPU time and wall clock time are shown with the variation in the energy width for the orbital projection, Δε, associated with its corresponding number of projected orbitals, N_b. In the electron dynamics calculations, we employed openMP with 16 CPU cores mainly for matrix–matrix products, where our own codes were utilized but not BLAS program suites. Note that the times include the cost of the analysis calculation for the electronic properties at each time step. We omitted the computational time in the ab initio calculation, which was performed only once for the construction of the approximated Fock matrix in the present demonstrations. Data correspond to a total 3750 time steps using a 4th order Runge–Kutta propagator in the Liouville–von Neuman equation of motion for the density matrix. For details, see the main text.

Tab.SII presents the real computational times but not the CPU times for the ab initio calculations with a 16–CPU–core MPI calculation using NTChem.
| (a) | \( \Delta \epsilon \) | \( N_b \) | CPU time | Wall time |
|-----|----------------|-------|----------|-----------|
| 0.5 | 16             | 329   | 22(1565%)|
| 1.5 | 81             | 859   | 62(1567%)|
| 3.0 | 162            | 3495  | 224(1578%)|
| FULL| 296            | 16327 | 1032(1587%)|

| (b) | \( \Delta \epsilon \) | \( N_b \) | CPU time | Wall time |
|-----|----------------|-------|----------|-----------|
| 0.5 | 40             | 8083  | 632(1511%)|
| 0.75| 140            | 11791 | 864(1523%)|
| 1.5 | 260            | 24174 | 1641(1547%)|
| 3.0 | 480            | 63147 | 5783(1170%)|
| FULL| 760            | 86000 | 17790(541%)|

| (c) | \( \Delta \epsilon \) | \( N_b \) | CPU time | Wall time |
|-----|----------------|-------|----------|-----------|
| 0.25| 14             | 9660  | 538(1561%)|
| 1.5 | 399            | 44539 | 2768(1554%)|
| 3.0 | 644            | 110404| 12651(1053%)|
| FULL| 809            | 98743 | 19832(697%)|

**TABLE S I.** Computational time for the dynamics calculations plus the time-dependent analysis for (a) NPTL–TCNE (b) circular 20-mer ethylene and (c) C\textsubscript{60}\textsuperscript{-5uPT}. The unit of time is second. See the text for the calculation conditions, \( \Delta \epsilon \), and \( N_b \). The wall time means the wall clock time, and the values in parentheses denote the CPU efficiency in percent associated openMP.

(a) (b) (c) 252 906 4854

**TABLE S II.** Computational time for the ab initio electronic structure calculations for (a) NPTL–TCNE, (b) circular 20-mer ethylene and (c) C\textsubscript{60}\textsuperscript{-5uPT}. The unit is seconds. See the text for the details of the calculation conditions.
Appendix II: Dominant orbitals contributing to population dynamics in NPTL-TCNE case without light field

In this section, we offer the information about the GD orbitals having dominant contributions to the charge migration dynamics in the panels (a) and (b) of Fig.2 in the main text. We can find such orbitals by analyzing the population dynamics of GD orbitals and couplings of diabatic orbitals between different monomers represented as off-diagonal elements in GDF matrix.

Fig. S1 shows the population dynamics for diabatic local orbitals for the two cases starting from initial local excitations of NPTL and TCNE, which are respectively included in the panel (a) and (b). Full orbitals are used in the calculations. As seen in the panel (a) where we highlighted the local LUMO and LUMO+1 for two monomers, we found clear population transfer between the local LUMO of NPTL and the local LUMO+1 of TCNE. In turn, from the panel of (b) we can read the dominant population transfer between the local HOMO of TCNE and the local HOMO−4 of NPTL.

We can explain these propensities of population transfer using the information of the diabatic couplings of local orbitals between different monomers. Tab. SIII presents coupling elements of group diabatic(GD) orbitals in different monomers as projected-space group diabatic Fock(P-GDF) matrix elements with $\Delta \epsilon = 0.5$ accompanied with the resultant 16 projected orbitals of which details are shown in the caption. The GD orbital energies are also shown in this table.

For the case of (a), the transition propensity is characterized by the following three points: (a:i) The local LUMOs of NPTL and TCNE have no diabatic coupling. This is also the case for the local HOMOs of two monomers. (a:ii) The local LUMO of NPTL and the local LUMO+1 of TCNE have non-zero coupling element. In the same way, the transition propensities in (b) is attributed to the following facts, namely, (b:i) The coupling elements between the local HOMO of TCNE and the local HOMO−$k$ of NPTL with $k$ running from 0 to 3 are zero or negligibly small. (b:ii) The coupling between the local HOMO of TCNE and the local HOMO−4 of NPTL has the value with a moderate magnitude compared to other local occupied orbitals. We also note that both in the cases of (a) and (b) the time periods observed in the charge migration and population dynamics are consistent with the energy difference of correlating local orbitals in different monomers mentioned above, of which explanation with a numerical analysis is given in the main text.

Thus, we could clarify the key orbitals in the electron transfer dynamics in this case.
through the analysis of the population dynamics and diabatic coupling elements for local orbitals between different monomers.

FIG. S1. Population dynamics for key diabatic local orbitals with dominant contribution in the case of NPTL-TCNE dimer without light field. GH−k, GH, GL and GL+k denote group diabatic local HOMO−k, HOMO, LUMO, and LUMO+k, respectively. (a) and (b) correspond to the panels (a) and (b) of Fig. 2 in the main text. In the panel of (a) with the initial excitation of NPTL side, we can see a clear correlation between GL of NPTL and GL+2 of TCNE, which is well reflected in the population flow from the former to the latter. In this case, the population transfer mainly occurred in the locally unoccupied space higher than local HOMO. On the contrary, the case of (b), GL of TCNE and local occupied space of NPTL exchange the orbital populations. “(from GH−k to GH)” in NPTL side denotes the summation of the population from GH-k to GH. The reduction and addition to this value, for example, −8 and +1, are intended for the presentation so that the initial value match with the initial population of GL of TCNE.
|       | A(1)  | A(2)H | A(3)L | A(4)  | A(5)  | A(6)  | A(7)  |
|-------|-------|-------|-------|-------|-------|-------|-------|
| D(1) | -0.4378 | 0.0000 | 0.0004 | 0.0000 | 0.0002 | 0.0000 | 0.0001 | 0.0001 |
| D(2) | -0.4056 | 0.0001 | 0.0000 | -0.0001 | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| D(3) | -0.3991 | 0.0000 | 0.0022 | 0.0000 | -0.0005 | 0.0000 | 0.0000 | -0.0020 |
| D(4) | -0.3977 | 0.0000 | -0.0002 | 0.0000 | 0.0000 | 0.0000 | -0.0001 | -0.0003 |
| D(5) | -0.3512 | 0.0002 | 0.0000 | -0.0039 | 0.0000 | 0.0012 | 0.0000 | 0.0000 |
| D(6) | -0.3012 | 0.0000 | -0.0006 | 0.0000 | 0.0001 | 0.0000 | 0.0005 | -0.0055 |
| D(7)H| -0.2721 | -0.0003 | 0.0000 | -0.0077 | -0.0000 | 0.0005 | 0.0000 | 0.0000 |
| D(8)L| 0.0010  | 0.0000 | 0.0027 | 0.0000 | 0.0019 | 0.0000 | -0.0002 | 0.0021 |
| D(9) | 0.0316  | 0.0002 | 0.0000 | 0.0006 | 0.0000 | 0.0004 | 0.0000 | 0.0000 |

TABLE S III. Diagonal elements in groups and off-diagonal block between different groups of Fock matrix within projected-GDF representation for NPTL-TCNE dimer in the case of $\Delta \epsilon = 0.5$ associated with 16 projected GD orbitals. D and A correspond to NPTL and TCNE, respectively. Here, 9 projected orbitals are used for D while 7 orbitals are assigned to A. k in D(k) and A(k) means the label of projected GD orbitals for each monomer. H and L attached with D(k) and A(k) denote the local HOMO and LUMO for groups, respectively. Diagonal elements for D, namely, the local orbital energies of D are shown just at the right of D(k). For A, they are presented just below A(k). The other values denote off-diagonal coupling matrix elements for D(k)-A(l), where k runs from 1 to 9 and l runs from 1 to 7. Unit of matrix elements is atomic unit.
Appendix III: Function form of Laser pulse field

The vector potential of light field as a function of time in the long wavelength approximation employed in the (e) and (f) in Fig.4 takes a form of

\[ A(t) = \sum_{j}^{N_p} A_j f(t; t_{c_j}, t_{w_j}) \cos(\omega_1(t - t_{c_j}) + \delta_j), \]  

(III1)

where bond font means the three dimensional vector in the Cartesian coordinate space. Here, the envelope function is defined by

\[ f(t; t_{c}, t_{w}) \equiv \exp\left(-\left(\frac{t - t_{c}}{t_{w}}\right)^2\right). \]

The physical meanings of parameters appeared above are as follows; \( t \) denotes time, \( t_c \) is a field peak time, \( t_w \) stands for a typical gaussian decay time, \( \omega \) means a central angular frequency of field, and \( \delta \) is a carrier envelope phase. \( N_p \) denotes a number of pulses. The electric field vector of external light corresponding to \( A(t) \) is given by \( E(t) = -\frac{1}{c} \frac{\partial A(t)}{\partial t} \). In the present article, we employed \( N_p = 1 \) and \( \delta = 0 \).

Appendix IV: Non-resonant and resonant field response of \( C_{60}-5uPT \) dimer

We show the population dynamics for group diabatic orbitals corresponding to the panels of (c)–(f) in Fig.4 in the main part of the present paper. Fig. S2 and S3 correspond to the panels (c/d) with non-resonant continuum field and (e/f) with resonant short pulse field in Fig.4 in the main part of the article, respectively. All the orbitals were employed in the calculations. See the main text for the details on the calculation conditions and light field parameters.

The non-resonant and resonant features are found in their time dependent behaviors, such as, fluctuated and stable population transfer, respectively. As seen in Fig.S2 of the non-resonant case, the increase of field strength enhances the excitation in the 5uPT side. On the contrary, in Fig.S3 of the resonant case, we find that the excitation in the \( C_{60} \) side rather than 5uPT is enhanced by the increase of field strength at the final simulation times. Both in the cases of weaker field strength in Fig.S2 and S3 the excitation of 5uPT is superior to that of \( C_{60} \).

With aid of the group diabatic representation, we can reveal propensities of optically induced electron migration for monomers in molecular assembly.
FIG.S 2. Population dynamics for key diabatic local orbitals in the non-resonant field case for C\textsubscript{60}-5uPT dimer. Notations of GH\textsuperscript{−2}, GH\textsuperscript{−1}, GH, GL and GL+1 are group diabatic local HOMO\textsuperscript{−2}, HOMO\textsuperscript{−1}, HOMO, LUMO, and LUMO+1, respectively. Only the α spin component is shown because of the spin restricted calculation. (a/b) and (c/d) correspond to the key orbital populations of C\textsubscript{60} and 5uPT. The field strength in the cases of (a/c) and (b/d) are respectively, 0.015 and 0.02 a.u. The calculation conditions in (a/c) and (b/d) of this figure are the same as (c) and (d) of Fig. 4 in the main part of the article.
FIG.S 3. Population dynamics for key diabatic local orbitals in the resonant field case for C$_{60}$-5uPT dimer. Notations of GH$^{-2}$, GH$^{-1}$, GH, GL and GL+1 are group diabatic local HOMO$^{-2}$, HOMO$^{-1}$, HOMO, LUMO, and LUMO+1, respectively. Only the $\alpha$ spin component is shown because of the spin restricted calculation. (a/b) and (c/d) correspond to the key orbital populations of C$_{60}$ and 5uPT. The field strength in the cases of (a/c) and (b/d) are respectively, 0.015 and 0.02 a.u. The calculation conditions in (a/c) and (b/d) of this figure are the same as (e) and (f) of Fig. 4 in the main part of the article.
Appendix V: Basis set dependency of charge migration dynamics: C$_{60}$-5uPT

Fig. S4 presents a comparison of the charge migration dynamics between the basis set, 6-31G and 6-31G(d), for the case of C$_{60}$-5uPT using the functional CAM-B3LYP. This figure corresponds to panels (a) and (b) of Fig. 4 in the main text without a light field.

In this comparison, we did not include the diffuse functions since the assignment of Löwdin orthogonalized AOs to monomers becomes ambiguous in the present localization scheme due to the delocalization of diffuse function covering different atoms than the ones they are centered on.

The details of the calculation conditions for the panels are given in the figure caption. In these four cases, the geometries of moieties are optimized using the corresponding ab initio levels employed in the calculations of electron dynamics.

The common features found in these results obtained using different basis set with and without the polarization functions are;

1. The peak values of charge transfer in the cases starting from initial excitation of the C$_{60}$ side, 0.9 and 0.6 respectively in panels (A) and (C), are larger than those of the 5uPT side, 0.2 and 0.3 in panels (B) and (D).

2. The moderate convergence of the time dependent behaviors with $E_{BW}=0.5$ and the use of about 60 active orbitals.

On the other hand, we find mainly two points of difference between the obtained with these basis sets.

1. The global shapes of the time dependent curves are qualitatively different in the cases starting from the initial excitations of 5uPT. In fact, the use of 6-31G(d) results in complicated oscillation patterns, which is attributed to the complexity of the structure of the associated electronic Hilbert space.

2. We find a reduction in the difference of the peak values of temporal charge transfer between the different local excitations. The difference in peak values between (A) and (B) is about 0.9-0.2=0.7 while that between (C) and (D) is about 0.6-0.3=0.3.
FIG. S 4. Comparison of the charge migration dynamics between the basis functions of 6-31G and 6-31G(d) for the case of C_{60}-5uPT using the functional CAM-B3LYP. Panels of (A) and (B) present the time dependent Mulliken charge of donor molecule, 5uPT, for the case of the initial local excitations of C_{60} and 5uPT, respectively, using 6-31G while panels (C) and (D) are the counterparts of (A) and (B) using 6-31G(d). See the main text in the article for the definitions of E_{BW} and N_{b}. 
Appendix VI: Functional dependency of charge migration dynamics: $C_{60}$-$5uPT$

Fig. S5 shows a comparison of the charge dynamics of 5uPT in $C_{60}$-5uPT system using the 6-31G basis set with respect to the choice of exchange-correlation functionals. Here also the presentations correspond to the panels of (a) and (b) Fig. 4 without a light field.

CAM-B3LYP, $\omega$B97X and B3LYP provide similar results while those obtained using LC$\omega$PBE are qualitatively different in charge oscillations and peak values. This is caused by the tuning of the last functional, LC$\omega$PBE, for long distance charge transfer. In fact, as seen in Fig. S5, only in panel (F) with LC$\omega$PBE starting from the initial excitation of 5uPT, is there a negative charge of donor molecule during dynamics. However, this necessarily represent a defect of this functional because the basis set employed in this calculation does not include the diffuse functions which are used for data set for the determination of the parameters of LC$\omega$PBE. Only in cases with moderate distance between donor and acceptor using 6-31G basis set, we found that CAM-B3LYP, $\omega$B97X and B3LYP are suitable for the description of dynamics.

We comment on the convergence with respect to an increase of number of projected active orbitals. As clearly seen in Fig. S5, independent of the choice of functional the use of an energy cut-off value of $E_{BW} = 0.5$ gives rise to moderate convergence of the results with their associated projected active orbitals of which number is about 40 - 100.

Fig. S6 shows the results using the basis set 6-31G(d) instead of the 6-31G basis set employed in Fig. S5. Though the values are different between the basis sets, the results using the same functional show the same trend in the dynamics including the observation that CAM-B3LYP, $\omega$B97X and B3LYP provides a reasonable result in that the initial excitation correspond to the electron transfer from 5uPT to $C_{60}$. 
FIG. 5. Comparison of the charge migration dynamics with respect to the exchange-correlation functionals for the cases of C$_{60}$-5uPT using the 6-31G basis set. Geometries of monomers used in this figure are optimized using CAM-B3LYP/6-31G. The employed functionals in the panels are as follows; (A/B) CAM-B3LYP, (C/D) ωB97X, (E/F) LCωPBE and (G/H) B3LYP. The upper and lower panels in each column correspond to the cases starting from the initial local excitations of C$_{60}$ and 5uPT, respectively.
FIG.S 6. Comparison of the charge migration dynamics with respect to the choice of exchange-correlation functional for the case of C$_{60}$-5uPT using the 6-31G(d) basis set. Geometries of monomers used in this figure are optimized using CAM-B3LYP/6-31G(d). The functionals used in these panels are the same as in Fig. S5.
Appendix VII: Transition dipole length matrices within group diabatic representation for C\textsubscript{60}-5uPT dimer

Here we display the transition dipole length matrices for moieties in C\textsubscript{60}-5uPT dimer in the GD representation associated with Fig. 2, 3, and 4 of the main text.

The data of NPTL and TCNE are separately displayed in Tab.SIV and V, respectively, while that of 1st ethylene monomer in 20-mer circular ethylene is displayed in Tab.SVI. In the same way, Tab.SVII and VIII correspond to C\textsubscript{60} and 5uPT, respectively.

Note that the centroid of each aggregate is equal to origin in the Cartesian coordinates and any center of mass of monomer is not placed at the origin.
|   | GH−2  | GH−1  | GH    | GL    | GL+1  | GL+2  |
|---|-------|-------|-------|-------|-------|-------|
| GH−2 | −1.0435 | −0.0000 | +2.5248 | +0.0000 | +0.0418 | −0.0000 |
| GH−1 | −0.0000 | −1.2461 | +0.0000 | −2.1075 | −0.0000 | −0.0478 |
| GH   | +2.5248 | +0.0000 | −1.2746 | −0.0000 | +2.0856 | +0.0000 |
| GL   | +0.0000 | −2.1075 | −0.0000 | −1.0585 | +0.0000 | −2.5170 |
| GL+1 | +0.0418 | −0.0000 | +2.0856 | +0.0000 | −1.1197 | −0.0000 |
| GL+2 | −0.0000 | −0.0478 | +0.0000 | −2.5170 | −0.0000 | −1.3105 |

|   | GH−2  | GH−1  | GH    | GL    | GL+1  | GL+2  |
|---|-------|-------|-------|-------|-------|-------|
| GH−2 | −0.0000 | −0.0040 | −0.0000 | +0.0736 | +0.0000 | −1.3900 |
| GH−1 | −0.0040 | +0.0000 | −0.0328 | −0.0000 | +1.4397 | +0.0000 |
| GH   | −0.0000 | −0.0328 | −0.0000 | +1.4510 | +0.0000 | +0.0735 |
| GL   | +0.0736 | −0.0000 | +1.4510 | +0.0000 | −0.0231 | +0.0000 |
| GL+1 | +0.0000 | +1.4397 | +0.0000 | −0.0231 | −0.0000 | +0.0346 |
| GL+2 | −1.3900 | +0.0000 | +0.0735 | +0.0000 | +0.0346 | −0.0000 |

|   | GH−2  | GH−1  | GH    | GL    | GL+1  | GL+2  |
|---|-------|-------|-------|-------|-------|-------|
| GH−2 | −3.7814 | +0.0000 | −0.0004 | −0.0000 | +0.0010 | −0.0000 |
| GH−1 | +0.0000 | −3.7795 | −0.0000 | +0.0002 | +0.0000 | −0.0006 |
| GH   | −0.0004 | −0.0000 | −3.7801 | −0.0000 | −0.0011 | −0.0000 |
| GL   | −0.0000 | +0.0002 | −0.0000 | −3.7773 | −0.0000 | −0.0036 |
| GL+1 | +0.0010 | +0.0000 | −0.0011 | −0.0000 | −3.7803 | +0.0000 |
| GL+2 | −0.0000 | −0.0006 | −0.0000 | −0.0036 | +0.0000 | −3.7759 |

TABLE S IV. Transition dipole matrices within local diabatic orbitals for NPTL in NPTL-TCNE dimer in the cases of Fig. 2. Only the elements associated with GH−2, GH−1, GH, LH, LH+1, and LH+2 are shown.
|   | GH−2   | GH−1   | GH     | GL     | GL+1   | GL+2   |
|---|--------|--------|--------|--------|--------|--------|
| X | +1.0762| +0.0263| −0.0000| +1.6083| −0.0000| −0.0036|
| GH−2 |          |        |        |        |        |        |
| GH−1 | +0.0263| +1.0362| +0.0000| −0.0052| −0.0000| −1.3513|
| GH   | −0.0000| +0.0000| +1.1384| +0.0000| −0.0025| +0.0000|
| GL   | +1.6083| −0.0052| +0.0000| +1.1767| +0.0000| +0.0035|
| GL+1 | −0.0000| −0.0000| −0.0025| +0.0000| +1.2254| −0.0000|
| GL+2 | −0.0036| −1.3513| +0.0000| +0.0035| −0.0000| +1.1979|
| Y   |        |        |        |        |        |        |
| GH−2 | +0.0000| +0.0000| +0.0546| +0.0000| −0.0033| +0.0000|
| GH−1 | +0.0000| +0.0000| −0.0048| −0.0000| +0.0107| +0.0000|
| GH   | +0.0546| −0.0048| −0.0000| −2.1112| −0.0000| −0.0039|
| GL   | +0.0000| −0.0000| −2.1112| +0.0000| −0.0104| −0.0000|
| GL+1 | −0.0033| +0.0107| −0.0000| −0.0104| +0.0000| +2.7252|
| GL+2 | +0.0000| +0.0000| −0.0039| −0.0000| +2.7252| −0.0000|
| Z   |        |        |        |        |        |        |
| GH−2 | +3.7800| −0.0504| +0.0000| +0.0004| −0.0000| −0.0006|
| GH−1 | −0.0504| +3.7813| −0.0000| +0.0005| −0.0000| +0.0000|
| GH   | +0.0000| −0.0000| +3.7827| +0.0000| −0.1305| −0.0000|
| GL   | +0.0004| +0.0005| +0.0000| +3.7868| +0.0000| −0.0451|
| GL+1 | −0.0000| −0.0000| −0.1305| +0.0000| +3.7833| +0.0000|
| GL+2 | −0.0006| +0.0000| −0.0000| −0.0451| +0.0000| +3.7815|

TABLE S V. Transition dipole matrices within local diabatic orbitals for TCNE in NPTL-TCNE dimer in the cases of Fig. 2. Only the elements associated with GH−2, GH−1, GH, LH, LH+1, and LH+2 are shown.
| X   | GH−2  | GH−1  | GH   | GL   | GL+1 | GL+2 |
|-----|-------|-------|------|------|------|------|
| GH−2| 22.6769 +0.0000 −0.0000 −0.0000 −0.0211 −0.8328 |
| GH−1| +0.0000 22.6762 +0.0000 +0.0000 −0.0000 +0.0000 |
| GH  | −0.0000 +0.0000 22.6798 −0.0000 +0.0000 −0.0000 |
| GL  | −0.0000 +0.0000 −0.0000 22.6812 +0.0000 +0.0000 |
| GL+1| −0.0211 −0.0000 +0.0000 +0.0000 22.7776 +1.8637 |
| GL+2| −0.8328 +0.0000 −0.0000 +0.0000 +1.8637 22.5812 |

| Y   | GH−2  | GH−1  | GH   | GL   | GL+1 | GL+2 |
|-----|-------|-------|------|------|------|------|
| GH−2| +0.0000 −0.0000 +0.0430 −0.0000 −0.0000 +0.0000 |
| GH−1| −0.0000 −0.0000 +0.0000 −0.0031 −0.0000 +0.0000 |
| GH  | +0.0430 +0.0000 −0.0000 −0.0000 +0.0895 −0.0058 |
| GL  | −0.0000 −0.0031 −0.0000 +0.0000 −0.0000 +0.0000 |
| GL+1| −0.0000 −0.0000 +0.0895 −0.0000 +0.0000 −0.0000 |
| GL+2| 0.0000 +0.0000 −0.0058 +0.0000 −0.0000 −0.0000 |

| Z   | GH−2  | GH−1  | GH   | GL   | GL+1 | GL+2 |
|-----|-------|-------|------|------|------|------|
| GH−2| −0.0000 −0.0003 −0.0000 +0.0000 −0.0000 +0.0000 |
| GH−1| −0.0003 +0.0000 −0.0000 −0.0000 −0.0254 −1.0482 |
| GH  | −0.0000 −0.0000 +0.0000 −1.3581 +0.0000 +0.0000 |
| GL  | +0.0000 −0.0000 −1.3581 −0.0000 −0.0000 +0.0000 |
| GL+1| −0.0000 −0.0254 +0.0000 −0.0000 +0.0000 −0.0000 |
| GL+2| +0.0000 −1.0482 +0.0000 +0.0000 −0.0000 −0.0000 |

TABLE S VI. Transition dipole matrices within local diabatic orbitals for 1st ethylene monomer in circular 20-mer ethylene in the cases of Fig. 3. Only the elements associated with GH−2, GH−1, GH, LH, LH+1, and LH+2 are shown.
TABLE S VII. Transition dipole matrices within local diabatic orbitals for C$_{60}$ in C$_{60}$-5uPT dimer in the cases of Fig. 4. Only the elements associated with GH−4, GH−3, GH−2, GH−1, GH, LH, LH+1, and LH+2 are shown.

| X   | GH−4 | GH−3 | GH−2 | GH−1 | GH  | GL  | GL+1 | GL+2 |
|-----|------|------|------|------|-----|-----|------|------|
| GH−4| +0.0139 | −0.0080 | −0.0064 | −0.0096 | +0.0024 | +0.0008 | −0.0044 | +0.0066 |
| GH−3| −0.0080 | −0.0087 | +0.0488 | −0.0162 | −0.0039 | −0.0057 | −0.0124 | −0.0291 |
| GH−2| −0.0064 | +0.0488 | +0.0025 | −0.0796 | −0.0188 | −0.0092 | −0.0135 | +0.0017 |
| GH−1| −0.0096 | −0.0162 | −0.0796 | +0.0084 | −0.0394 | +0.0156 | −0.0001 | +0.0035 |
| GH  | +0.0024 | −0.0039 | −0.0188 | −0.0394 | +0.0340 | +0.0086 | +0.0153 | −0.0121 |
| GL  | +0.0008 | −0.0057 | −0.0092 | +0.0156 | +0.0086 | +0.0262 | +0.0725 | +0.0118 |
| GL+1| −0.0044 | −0.0124 | −0.0135 | −0.0001 | +0.0153 | +0.0725 | −0.0351 | −0.0525 |
| GL+2| +0.0066 | −0.0291 | +0.0017 | +0.0035 | −0.0121 | +0.0118 | −0.0525 | −0.0108 |

| Y   | GH−4 | GH−3 | GH−2 | GH−1 | GH  | GL  | GL+1 | GL+2 |
|-----|------|------|------|------|-----|-----|------|------|
| GH−4| −0.0204 | +0.0162 | +0.0016 | +0.0115 | +0.0099 | +0.0049 | +0.0186 | +0.0012 |
| GH−3| +0.0162 | +0.0254 | +0.0070 | +0.0345 | +0.0121 | −0.0011 | +0.0192 | −0.0112 |
| GH−2| +0.0016 | +0.0070 | −0.0143 | −0.0184 | −0.0324 | +0.0129 | −0.0063 | +0.0007 |
| GH−1| +0.0115 | +0.0345 | −0.0184 | +0.0247 | +0.0041 | +0.0088 | −0.0011 | +0.0030 |
| GH  | +0.0099 | +0.0121 | −0.0324 | +0.0041 | −0.0927 | +0.0013 | +0.0124 | +0.0139 |
| GL  | +0.0049 | −0.0011 | +0.0129 | +0.0088 | +0.0013 | −0.0212 | +0.0172 | −0.0753 |
| GL+1| +0.0186 | +0.0192 | −0.0063 | −0.0011 | +0.0124 | +0.0172 | −0.0165 | +0.0013 |
| GL+2| +0.0012 | −0.0112 | +0.0007 | +0.0030 | +0.0139 | −0.0753 | +0.0013 | +0.0632 |

| Z   | GH−4 | GH−3 | GH−2 | GH−1 | GH  | GL  | GL+1 | GL+2 |
|-----|------|------|------|------|-----|-----|------|------|
| GH−4| +4.4698 | +0.0008 | −0.0035 | +0.0032 | +0.0000 | +0.0018 | +0.0135 | −0.0000 |
| GH−3| +0.0008 | +4.4359 | +0.0003 | +0.0201 | +0.0051 | +0.0002 | +0.0155 | −0.0006 |
| GH−2| −0.0035 | +0.0003 | +4.3444 | −0.0032 | +0.0156 | −0.0062 | −0.0006 | −0.0119 |
| GH−1| +0.0032 | +0.0201 | −0.0032 | +4.2859 | +0.0235 | +0.0016 | +0.0078 | +0.0019 |
| GH  | +0.0000 | +0.0051 | +0.0156 | +0.0235 | +4.1025 | −0.0104 | +0.0023 | −0.0136 |
| GL  | +0.0018 | +0.0002 | −0.0062 | +0.0016 | −0.0104 | +4.4956 | +0.0244 | +0.0384 |
| GL+1| +0.0135 | +0.0155 | −0.0006 | +0.0078 | +0.0023 | +0.0244 | +4.6539 | −0.0016 |
| GL+2| −0.0000 | −0.0006 | −0.0119 | +0.0019 | −0.0136 | +0.0384 | −0.0016 | +4.6851 |
| X  | GH−4 | GH−3 | GH−2 | GH−1 | GH  | GL  | GL+1 | GL+2 |
|----|------|------|------|------|-----|-----|------|------|
| GH−4 | 0.2543 | −8.8687 | −0.0672 | −0.8405 | −0.0149 | −0.1504 | +0.0028 | −0.2527 |
| GH−3 | −8.8687 | −0.2053 | −0.2661 | +0.0797 | +0.9666 | −0.0092 | −0.1885 | −0.0186 |
| GH−2 | −0.0672 | −0.2661 | +0.1448 | −8.3209 | −0.0306 | −0.1679 | −0.0085 | +0.8967 |
| GH−1 | −0.8405 | +0.0797 | −8.3209 | −0.1088 | +8.0624 | −0.0009 | +1.8583 | +0.0054 |
| GL  | −0.0149 | +0.9666 | −0.0306 | +8.0624 | +0.0451 | +3.7812 | −0.0056 | −0.2279 |
| GL+1 | +0.0028 | −0.1885 | −0.0085 | +1.8583 | −0.0056 | +7.8174 | −0.0596 | −8.1294 |
| GL+2 | −0.2527 | −0.0186 | +0.8967 | +0.0054 | −0.2279 | −0.0271 | −8.1294 | +0.0142 |

| Y  | GH−4 | GH−3 | GH−2 | GH−1 | GH  | GL  | GL+1 | GL+2 |
|----|------|------|------|------|-----|-----|------|------|
| GH−4 | −0.1363 | +0.0037 | −0.4108 | +0.0019 | +0.2067 | −0.0009 | +0.4063 | −0.0052 |
| GH−3 | +0.0037 | −0.1455 | −0.0188 | −0.0394 | −0.0003 | −0.2581 | +0.0090 | +0.0804 |
| GH−2 | −0.4108 | −0.0188 | +0.8620 | +0.0037 | −0.0338 | −0.0080 | −0.3790 | −0.0080 |
| GH−1 | +0.0019 | −0.0394 | +0.0037 | +0.0289 | +0.0036 | +0.1127 | −0.0048 | −0.5884 |
| GH  | +0.2067 | −0.0003 | −0.0338 | +0.0036 | +0.0063 | −0.0048 | +0.1129 | −0.0056 |
| GL  | −0.0009 | −0.2581 | −0.0080 | +0.1127 | −0.0048 | +0.0114 | +0.0029 | −0.1580 |
| GL+1 | +0.4063 | +0.0090 | −0.3790 | −0.0048 | +0.1129 | +0.0029 | +0.1421 | +0.0013 |
| GL+2 | −0.0052 | +0.0804 | −0.0080 | −0.5884 | −0.0056 | −0.1580 | +0.0013 | −0.2255 |

| Z  | GH−4 | GH−3 | GH−2 | GH−1 | GH  | GL  | GL+1 | GL+2 |
|----|------|------|------|------|-----|-----|------|------|
| GH−4 | −7.8118 | +0.0004 | −0.0010 | −0.0002 | −0.0012 | +0.0005 | +0.0011 | −0.0001 |
| GH−3 | +0.0004 | −7.8369 | −0.0022 | +0.0053 | −0.0026 | −0.0056 | +0.0022 | −0.0041 |
| GH−2 | −0.0010 | −0.0022 | −7.8223 | −0.0013 | −0.0119 | +0.0030 | +0.0038 | +0.0027 |
| GH−1 | −0.0002 | +0.0053 | −0.0013 | −7.8165 | −0.0007 | +0.0064 | −0.0007 | +0.0041 |
| GH  | −0.0012 | −0.0026 | −0.0119 | −0.0007 | −7.8244 | +0.0020 | +0.0058 | +0.0018 |
| GL  | +0.0005 | −0.0056 | +0.0030 | +0.0064 | +0.0020 | −7.8245 | +0.0005 | −0.0114 |
| GL+1 | +0.0011 | +0.0022 | +0.0038 | −0.0007 | +0.0058 | +0.0005 | −7.8156 | +0.0004 |
| GL+2 | −0.0001 | −0.0041 | +0.0027 | +0.0041 | +0.0018 | −0.0114 | +0.0004 | −7.8217 |

TABLE S VIII. Transition dipole matrices within local diabatic orbitals for 5uPT in C_{60}-5uPT dimer in the cases of Fig. 4. Only the elements associated with GH−4, GH−3, GH−2, GH−1, GH, LH, LH+1, and LH+2 are shown.
Appendix VIII: Geometry data of molecular aggregates

We summarize the data of Cartesian coordinates in Angstrom for the molecular systems used in the present article. The information of atoms are also included below.

1. **NPTL-TCNE**

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | 1.803832  | 0.707130  | -1.999379 |
| C    | 1.803832  | -0.707130 | -1.999379 |
| C    | 0.621502  | -1.396550 | -1.999379 |
| C    | -0.619808 | -0.710930 | -1.999379 |
| C    | -0.619808 | 0.710930  | -1.999379 |
| C    | 0.621502  | 1.396550  | -1.999379 |
| C    | -1.861118 | 1.396550  | -1.999379 |
| C    | -3.043448 | 0.707130  | -1.999379 |
| C    | -3.043448 | -0.707130 | -1.999379 |
| C    | -1.861118 | -1.396550 | -1.999379 |
| H    | 2.747752  | 1.243330  | -1.999379 |
| H    | 2.747752  | -1.243330 | -1.999379 |
| H    | 0.616962  | -2.483200 | -1.999379 |
| H    | 0.616962  | 2.483200  | -1.999379 |
| H    | -1.856578 | 2.483200  | -1.999379 |
| H    | -3.987368 | 1.243330  | -1.999379 |
| H    | -3.987368 | -1.243330 | -1.999379 |
| H    | -1.856578 | -2.483200 | -1.999379 |
| N    | 2.819942  | 2.039850  | 2.000621  |
| N    | -1.579558 | 2.039850  | 2.000621  |
| C    | 1.841302  | 1.425290  | 2.000621  |
| C    | -0.600918 | 1.425290  | 2.000621  |
| C    | 0.620192  | 0.678870  | 2.000621  |
| C    | 0.620192  | -0.678870 | 2.000621  |
| C    | 1.841302  | -1.425290 | 2.000621  |
| C    | -0.600918 | -1.425290 | 2.000621  |
| N    | 2.819942  | -2.039850 | 2.000621  |
N -1.579558 -2.039850 2.000621

2. 20-mer-ethylene

H 11.076884 0.000000 1.235520
H 12.923116 0.000000 1.235520
C 12.000000 0.000000 0.662819
C 12.000000 0.000000 -0.662819
H 11.076884 0.000000 -1.235520
H 12.923116 0.000000 -1.235520
H 10.534743 3.422945 1.235520
H 12.290614 3.993462 1.235520
C 11.412678 3.708204 0.662819
C 11.412678 3.708204 -0.662819
H 10.534743 3.422945 -1.235520
H 12.290614 3.993462 -1.235520
H 8.961387 6.510829 1.235520
H 10.455020 7.596017 1.235520
C 9.708204 7.053423 0.662819
C 9.708204 7.053423 -0.662819
H 8.961387 6.510829 -1.235520
H 10.455020 7.596017 -1.235520
H 6.510829 8.961387 1.235520
H 7.596017 10.455020 1.235520
C 7.053423 9.708204 0.662819
C 7.053423 9.708204 -0.662819
H 6.510829 8.961387 -1.235520
H 7.596017 10.455020 -1.235520
H 3.422945 10.534743 1.235520
H 3.993462 12.290614 1.235520
C 3.708204 11.412678 0.662819
C 3.708204 11.412678 -0.662819
H 3.422945 10.534743 -1.235520
H  3.993462  12.290614  -1.235520
H  0.000000  11.076884   1.235520
H  0.000000  12.923116   1.235520
C  0.000000  12.000000   0.662819
C  0.000000  12.000000  -0.662819
H  0.000000  11.076884  -1.235520
H  0.000000  12.923116  -1.235520
H -3.422945  10.534743   1.235520
H -3.993462  12.290614   1.235520
C -3.708204  11.412678   0.662819
C -3.708204  11.412678  -0.662819
H -3.422945  10.534743  -1.235520
H -3.993462  12.290614  -1.235520
H -6.510829   8.961387   1.235520
H -7.596017  10.455020   1.235520
C -7.053423   9.708204   0.662819
C -7.053423   9.708204  -0.662819
H -6.510829   8.961387  -1.235520
H -7.596017  10.455020  -1.235520
H -8.961387   6.510829   1.235520
H -10.455020   7.596017   1.235520
C -9.708204   7.053423   0.662819
C -9.708204   7.053423  -0.662819
H -8.961387   6.510829  -1.235520
H -10.455020   7.596017  -1.235520
H -10.534743   3.422945   1.235520
H -12.290614   3.993462   1.235520
C -11.412678   3.708204   0.662819
C -11.412678   3.708204  -0.662819
H -10.534743   3.422945  -1.235520
H -12.290614   3.993462  -1.235520
H -11.076884    0.000000   1.235520
H -12.923116    0.000000   1.235520
C  -12.000000  0.000000  0.662819
C  -12.000000  0.000000 -0.662819
H  -11.076884  0.000000 -1.235520
H  -12.923116  0.000000 -1.235520
H  -10.534743 -3.422945  1.235520
H  -12.290614 -3.993462  1.235520
C  -11.412678 -3.708204  0.662819
C  -11.412678 -3.708204 -0.662819
H  -10.534743 -3.422945 -1.235520
H  -12.290614 -3.993462 -1.235520
H  -8.961387  -6.510829  1.235520
H  -10.455020 -7.596017  1.235520
C  -9.708204  -7.053423  0.662819
C  -9.708204  -7.053423 -0.662819
H  -8.961387  -6.510829 -1.235520
H  -10.455020 -7.596017 -1.235520
H  -6.510829  -8.961387  1.235520
H  -7.596017 -10.455020  1.235520
C  -7.053423 -9.708204  0.662819
C  -7.053423 -9.708204 -0.662819
H  -6.510829 -8.961387 -1.235520
H  -7.596017 -10.455020 -1.235520
H  -3.422945 -10.534743  1.235520
H  -3.993462 -12.290614  1.235520
C  -3.708204 -11.412678  0.662819
C  -3.708204 -11.412678 -0.662819
H  -3.422945 -10.534743 -1.235520
H  -3.993462 -12.290614 -1.235520
H  -0.000000 -11.076884  1.235520
H  -0.000000 -12.923116  1.235520
C  -0.000000 -12.000000  0.662819
C  -0.000000 -12.000000 -0.662819
H  -0.000000 -11.076884 -1.235520
H  -0.000000  -12.923116  -1.235520
H   3.422945  -10.534743   1.235520
H   3.993462  -12.290614   1.235520
C    3.708204  -11.412678   0.662819
C    3.708204  -11.412678  -0.662819
H    3.422945  -10.534743  -1.235520
H    3.993462  -12.290614  -1.235520
H    6.510829  -8.961387   1.235520
H    7.596017  -10.455020   1.235520
C    7.053423   -9.708204   0.662819
C    7.053423   -9.708204  -0.662819
H    6.510829  -8.961387  -1.235520
H    7.596017  -10.455020  -1.235520
H    8.961387  -6.510829   1.235520
H    10.455020  -7.596017   1.235520
C    9.708204   -7.053423   0.662819
C    9.708204   -7.053423  -0.662819
H    8.961387  -6.510829  -1.235520
H    10.455020  -7.596017  -1.235520
H    10.534743  -3.422945   1.235520
H   12.290614  -3.993462   1.235520
C   11.412678  -3.708204   0.662819
C   11.412678  -3.708204  -0.662819
H    10.534743  -3.422945  -1.235520
H   12.290614  -3.993462  -1.235520

3.  C_{60}^{5uPT}

C    2.228436   0.589392   5.060505
C    3.137451   0.155274   4.010482
C    1.345424  -0.315937   5.630972
C    3.121169  -1.163732   3.580494
C    3.220826  -1.467522   2.160861

60
| C  | 3.254262 | 1.235005 | 3.042077 |
| C  | 3.348998 | 0.945389 | 1.688460 |
| C  | 3.332030 | -0.437839 | 1.237455 |
| C  | -0.449969 | 1.367701 | 5.606559 |
| C  | 0.475967 | 2.317194 | 5.007618 |
| C  | -0.025585 | 0.082405 | 5.911080 |
| C  | 1.783849 | 1.937628 | 4.741584 |
| C  | 2.417690 | 2.336621 | 3.493677 |
| C  | -0.261328 | 3.114498 | 4.039464 |
| C  | 0.343026 | 3.495709 | 2.850150 |
| C  | 1.714342 | 3.097197 | 2.570614 |
| C  | -2.138918 | -0.853087 | 5.062158 |
| C  | -2.583898 | 0.494862 | 4.742621 |
| C  | -0.890189 | -1.054279 | 5.632272 |
| C  | -1.759532 | 1.578587 | 5.008259 |
| C  | -1.642730 | 2.658017 | 4.039876 |
| C  | -3.332044 | 0.437855 | 3.495922 |
| C  | -3.220889 | 1.467524 | 2.572480 |
| C  | -2.356175 | 2.604086 | 2.851253 |
| C  | -0.503969 | -3.004472 | 4.180561 |
| C  | -1.813671 | -2.793422 | 3.582629 |
| C  | -0.053103 | -2.155426 | 5.181041 |
| C  | -2.611653 | -1.743185 | 4.012970 |
| C  | -3.349016 | -0.945293 | 3.044882 |
| C  | -1.714287 | -3.097024 | 2.162811 |
| C  | -2.417653 | -2.336651 | 1.239625 |
| C  | -3.254356 | -1.235058 | 1.691281 |
| C  | 2.195367 | -2.113091 | 4.178955 |
| C  | 1.722365 | -3.003255 | 3.129610 |
| C  | 1.328510 | -1.699305 | 5.180240 |
| C  | 0.405018 | -3.438387 | 3.130230 |
| C  | -0.343046 | -3.495526 | 1.883228 |
| C  | 2.356124 | -2.604031 | 1.882123 |
C  1.642798 -2.658068  0.693425
C  0.261348 -3.114586  0.693853
C -2.228406 -0.589361 -0.327042
C -1.783848 -1.937626 -0.008236
C -0.475977 -2.317346 -0.274268
C -1.345414  0.315901 -0.897621
C -2.195309  2.113123  0.554484
C -3.121118  1.163720  1.152918
C -3.137481 -0.155301  0.722989
C -1.328537  1.699308 -0.446858
C  0.503961  3.004275  0.552963
C -0.405010  3.438387  1.603177
C -1.722393  3.003311  1.603815
C  0.053041  2.155520 -0.447721
C  2.138932  0.853039 -0.328795
C  2.611688  1.743210  0.720362
C  1.813690  2.793351  1.150917
C  0.890206  1.054339 -0.898867
C  0.449905 -1.367707 -0.873054
C  1.759518 -1.578605 -0.274849
C  2.583928 -0.494901 -0.009203
C  0.025633 -0.082407 -1.177585
C -8.611577  1.404946 -4.133302
C -9.153196  0.160691 -4.133302
S -7.897085 -1.109143 -4.133302
C -6.615302  0.165069 -4.133302
C -7.180059  1.409406 -4.133302
H -9.206854  2.308008 -4.133302
H -10.191391 -0.127848 -4.133302
H -6.591720  2.317732 -4.133302
C -4.656857 -1.449752 -4.133302
C -5.224448 -0.206632 -4.133302
S -3.946528  1.069994 -4.133302
| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| C       | -2.666645 | -0.204885 | -4.133302 |
| C       | -3.233005  | -1.449264  | -4.133302 |
| H       | -5.244945  | -2.358098  | -4.133302 |
| H       | -2.644401  | -2.357360  | -4.133302 |
| C       | -0.711624  | 1.411406   | -4.133302 |
| C       | -1.278944  | 0.167132   | -4.133302 |
| S       | -0.000001  | -1.108734  | -4.133302 |
| C       | 1.278944   | 0.167128   | -4.133302 |
| C       | 0.711627   | 1.411404   | -4.133302 |
| H       | -1.300131  | 2.319540   | -4.133302 |
| H       | 1.300137   | 2.319536   | -4.133302 |
| C       | 3.233007   | -1.449267  | -4.133302 |
| C       | 2.666645   | -0.204889  | -4.133302 |
| S       | 3.946526   | 1.069993   | -4.133302 |
| C       | 5.224448   | -0.206630  | -4.133302 |
| C       | 4.656859   | -1.449751  | -4.133302 |
| H       | 2.644406   | -2.357365  | -4.133302 |
| H       | 5.244950   | -2.358096  | -4.133302 |
| C       | 7.180060   | 1.409408   | -4.133302 |
| C       | 6.615302   | 0.165072   | -4.133302 |
| S       | 7.897083   | -1.109142  | -4.133302 |
| C       | 9.153196   | 0.160690   | -4.133302 |
| C       | 8.611578   | 1.404945   | -4.133302 |
| H       | 6.591722   | 2.317735   | -4.133302 |
| H       | 10.191392  | -0.127849  | -4.133302 |
| H       | 9.206857   | 2.308006   | -4.133302 |