Photo-induced reactions from efficient molecular dynamics with electronic transitions using the FIREBALL local-orbital density functional theory formalism

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Abstract
The computational simulation of photo-induced processes in large molecular systems is a very challenging problem. Firstly, to properly simulate photo-induced reactions the potential energy surfaces corresponding to excited states must be appropriately accessed; secondly, understanding the mechanisms of these processes requires the exploration of complex configurational spaces and the localization of conical intersections; finally, photo-induced reactions are probability events, that require the simulation of hundreds of trajectories to obtain the statistical information for the analysis of the reaction profiles. Here, we present a detailed description of our implementation of a molecular dynamics with electronic transitions algorithm within the local-orbital density functional theory code FIREBALL, suitable for the computational study of these problems. As an example of the application of this approach, we also report results on the [2 + 2] cycloaddition of ethylene with maleic anhydride and on the [2 + 2] photo-induced polymerization reaction of two C60 molecules. We identify different deactivation channels of the initial electron excitation, depending on the time of the electronic transition from LUMO to HOMO, and the character of the HOMO after the transition.

Keywords: density functional theory, non-adiabatic molecular dynamics, local-orbital basis set, photo-induced cycloaddition

(Some figures may appear in colour only in the online journal)

1. Introduction
One of the greatest challenges in simulation methodology is to accurately and efficiently interpret photo-induced reaction mechanisms which are critically important in many chemical processes, such as vision, photodamage, UV absorption, photosynthesis, photography, etc. In Born–Oppenheimer (or adiabatic) molecular dynamics—the nuclei follow classical
trajectories defined on a single potential energy surface (PES); this PES corresponds to the ground state electronic energy of the system, for frozen atomic configurations. To accurately simulate photo-induced reactions, the excited potential energy surface must be appropriately accessed beyond the Born–Oppenheimer approximation. Additionally, the ability of the electron to transition between the ground PES and the excited PES in the region close to the conical intersection between the two PESs is very important in accurately portraying the transition that will occur in photo-induced reactions.

Photo-induced processes in large molecular systems are computationally intensive to simulate due to the complexities in modelling the vast search space associated with photo-activated reaction mechanisms. Also, the search for conical intersections is quite more complex than geometry optimization [1–4]. Photo-induced polymerization reactions, such as the photo-induced [2 + 2] cycloaddition reactions of two C_{60} molecules, would easily require geometry optimization [1–4]. Photo-induced polymerization with photo-activated reaction mechanisms. Also, the complexities in modelling the vast search space associated are computationally intensive to simulate due to the adiabatic electronic states are determined using the probabilistic approach; in particular, the transitions between different PES are determined through a transition that will occur in photo-induced reactions.

PES in the region close to the conical intersection between electron to transition between the ground PES and the excited PES. Oppenheimer approximation. Additionally, the ability of the surface must be appropriately accessed beyond the Born–Oppenheimer approximation. To accurately simulate reaction mechanisms, hundreds, if not thousands, of trajectories are required to obtain the proper statistical information. Thus, efficient algorithms are needed, at least, at an exploratory level. There is a definitive need for simulation tools that can, at minimum, obtain sufficiently accurate results that will efficiently yield significant insight in photo-induced reaction mechanisms without overburdening computational resources.

Broadly speaking, two types of non-adiabatic methods dominate the literature: Ehrenfest Dynamics (ED) methods and surface hopping (SH) methods [6–8]. In the ED approach, the nuclei move classically on a single effective PES obtained by averaging over all the adiabatic states involved; however, in SH methods the classical degrees of freedom (nuclei coordinates) evolve on single adiabatic surfaces [6], and make probabilistic hops from one PES to another. Surface-Hopping methods present key advantages over ED methods, because the system is always on a certain pure adiabatic state, not in an average non-physical state. Moreover, ED calculations sometimes lead to non-physical features, such as energetically inaccessible levels populated or violation of microscopic reversibility [9]. Tully’s molecular dynamics with electronic transitions (MDET) algorithm [10] employs a surface hopping strategy [11] to switch between different adiabatic states. In Tully’s MDET approach, the system evolves on one of the PES corresponding to a particular adiabatic state of the system. Using the idea of ensemble of trajectories, the transitions between different PES are determined through a probabilistic approach; in particular, the transitions between adiabatic electronic states are determined using the fewest-switches algorithm that considers the minimum number of non-adiabatic transitions that are compatible with the correct statistical distribution of state populations at all times. The MDET method is probably the most used and successful method to deal with problems in which coupling between electrons and ions is required.

The most efficient first-principles molecular dynamics (MD) approaches are based on density functional theory (DFT). In recent years the MDET approach has been implemented using DFT and applied to several problems [9, 12–24]. Our goal is to target large-scale photo-polymerization trajectory ensembles that include several hundreds of atoms and explore several hundreds of trajectories. As such, we have focused primarily on implementing a MDET algorithm within FIREBALL, an efficient local-orbital DFT MD technique [25]. We have previously demonstrated a successful application of the FIREBALL DFT–MDET in the photo-isomerization processes of stilbene and azobenzene [19].

The remainder of this paper is organized as follows. In section 2, we present a detailed description of our implementation of DFT–MDET within the FIREBALL code. In section 3, we present results for two different photo-induced cycloaddition reactions: the [2 + 2] cycloaddition of ethylene with maleic anhydride to form cyclobutane-1,2-dicarboxilic anhydride and the [2 + 2] photo-induced polymerization reaction of two C_{60} molecules. Finally, in section 4, we summarize the main conclusions.

2. Description of the method

2.1. Local-orbital DFT: FIREBALL

FIREBALL [25–29] is an efficient simulation DFT package that is specifically designed for the study of complex systems using MD simulations. The main characteristics of FIREBALL are: (i) basis sets of short-range numerical atomic-like orbitals [26, 30]; (ii) the technique is completely formulated in real-space (no need for supercells) and does not require the use of grids for the charge density and potential calculations; (iii) self-consistency is achieved using the orbital occupation numbers [27]; (iv) a practical tabulation-interpolation scheme is used so that all the interactions/integrals required during the MD simulation can be calculated beforehand and stored in data-tables [26], speeding up the calculations.

In this approach, the energy functional is written as:

\[ E_{\text{tot}}[\rho(r)] = E_{\text{BS}} - E_{\text{ee}}[\rho(r)] + E_{\text{xc}}[\rho(r)] \]

\[ = \int \rho(r) V_{\text{ion}}[\rho(r)] d^3r + E_{\text{ion}} - \text{occ.} \]  

where \( \rho(r) \) is the input electron density [31,32], which is determined in a selfconsistent way in terms of the orbital occupation numbers [27, 33, 34], see below. \( E_{\text{BS}} \) is a sum over occupied eigenvalues, \( E_{\text{BS}} = \sum_{i<\text{occ}} \epsilon_i \), of the self-consistent (SCF) solution of the Kohn–Sham (KS) Schrödinger equation:

\[ \hat{H}_{\text{KS}} \psi_i(r) = \left( -\frac{\hbar^2}{2m_e} \nabla^2 + V_{\text{ion}}(r) + V_{\text{xc}}[\rho(r)] \right) \psi_i(r) + e^2 \int \frac{\rho(r')}{|r-r'|} d^3r' \psi_i(r) = \epsilon_i \psi_i(r), \]  

where \( V_{\text{ion}} \) is the ion potential and \( V_{\text{xc}} \) the exchange-correlation potential.

The second term \( E_{\text{ee}} \) in equation (1) represents an average electron–electron energy:

\[ E_{\text{ee}}[\rho(r)] = \frac{e^2}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} d^3r d^3r', \]  

where \( E_{\text{ee}} \) is the electron–electron energy:

\[ E_{\text{ee}}[\rho(r)] = \frac{e^2}{2} \int \frac{\rho(r)\rho(r')}{|r-r'|} d^3r d^3r'. \]
$E_{\text{ion-ion}}$ is the ion–ion interaction energy:

$$
E_{\text{ion-ion}} = e^2 \sum_{j} \frac{Z_{\alpha} Z_{\beta}}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|}.
$$

($Z_{\alpha}$ is the nuclear or pseudopotential charge on atom $\alpha$ at position $\mathbf{R}_{\alpha}$, and $E_{xc}$ is the exchange-correlation energy.

In the FIREBALL method, a basis set of optimized atomic-like orbitals, $\phi_{\mu}(\mathbf{r})$, is used to solve equation (2) and to determine the density $\rho(\mathbf{r})$ ($\mu \equiv (\alpha, l, m)$, $\alpha$ is the atomic site, $l$ represents the atomic subshell—e.g., 3s, 4s, 3p, 3d, etc, and $m$ is the magnetic quantum number); these orbitals are strictly localized in real-space [26, 30]. The computational efficiency of FIREBALL is associated with the possibility to choose $\rho(\mathbf{r})$ in the above equations as a sum of atomic-like densities, $\rho_{\alpha}(\mathbf{r})$ [27]. In particular, in the FIREBALL approach the electron density $\rho(\mathbf{r})$ is written in terms of the atomic-like orbitals, $\phi_{\mu}(\mathbf{r})$ as

$$
\rho(\mathbf{r}) = \sum_{\alpha} \rho_{\alpha}(\mathbf{r}) = \sum_{\mu} n_{\mu} |\phi_{\mu}(\mathbf{r})|^2,
$$

where $n_{\mu}$ represents the charge on the orbital $\phi_{\mu}$. In this way four-center integrals are not required for the calculation of $E_{\text{tot}}$ or the forces $\mathbf{F}_{\alpha}$, and all the two- and three-center interactions are tabulated beforehand and placed in interpolation data-tables which are no larger than 2D [25, 26]. In particular, for the calculation of the exchange-correlation matrix elements different approaches may be used, see [28, 29, 35]; in the calculations presented in section 3 we have used the multicenter weighted exchange-correlation density approximation (McWEDA) [28]. All the matrix elements required during the MD simulation are evaluated by looking up the necessary information from the data-tables (which are read at the beginning of the calculation and stored in memory throughout the MD simulation).

In practice, the atomic densities $\rho_{\alpha}$ are approximated to be spherically symmetric around each atomic site $\alpha$ (i.e. $n_{\alpha lm} = n_{\alpha lm'}$). Self-consistency is achieved defining output orbital charges $n_{\mu}^{\text{out}}$ from the occupied eigenvectors $\psi_{i}$ of equation (2); and imposing that in the self-consistent solution $n_{\mu}^{\text{out}}$ and the input orbital charges $n_{\mu}^{\text{in}}$ coincide [27]. Different methods can be used to project the output electron density from equation (2) into the form given by equation (5) using for example Löwdin Orbitals [27, 36, 37] or Natural Atomic Orbitals [38].

DFT MD simulations can be performed once the forces

$$
\mathbf{F}_{\alpha} = -\frac{\partial E_{\text{tot}}}{\partial \mathbf{R}_{\alpha}}.
$$

on each atom $\alpha$ are evaluated [26].

2.2. DFT-MDET

In DFT-MDET simulations the atoms follow classical trajectories $\{\mathbf{R}_{\alpha}(t)\}$ on one of the PESs corresponding to a particular adiabatic state $E_{\alpha}$. The coupling between the nuclear motion and the electronic quantum state is taken into account by means of probabilistic hops between different adiabatic PESs ($E_{\alpha} \rightarrow E_{\beta}$). The probability for these hops is determined from the time evolution of the electronic states and their non-adiabatic coupling vectors (see below).

In the following discussion, we present details about our implementation of the MDET algorithm within the FIREBALL local-orbital DFT code.

The MDET simulation consists of two nested time loops corresponding to the time evolution of the atomic positions and electronic states; the outer time loop corresponds to the atomic motion and the inner time loop to the propagation of the electronic states. The computational procedure consists of 5 algorithm steps (after an initialization step) as shown schematically in figure 1.

Step 1: Solution of the stationary Kohn–Sham Hamiltonian. In this first step we obtain the SCF solution of the stationary KS Hamiltonian for the current atomic configuration and adiabatic state:

$$
\hat{H}_{\text{KS}}[\mathbf{R}]\psi_{\mu}(\mathbf{r}; \mathbf{R}) = \epsilon_{\mu}(\mathbf{R})\psi_{\mu}(\mathbf{r}; \mathbf{R}),
$$

where $\mathbf{R}$ represents the atomic positions $\{\mathbf{R}_{\alpha}(t)\}$ at time $t$ and $\psi_{\mu}(\mathbf{r}; \mathbf{R})$ are the single-particle adiabatic KS orbitals (at time $t$). The different adiabatic states, $E_{\alpha}$, are defined by means of the corresponding set of occupied KS adiabatic orbitals or, in other words, by the occupancies $f_{\mu}$ of the $\psi_{\mu}$ orbitals, with $f_{\mu} = 1$ (occupied) or 0 (empty). For example, the ground state PES is related to the Slater determinant formed by the set of lowest energy occupied adiabatic KS orbitals $\psi_{\mu}$; for the excited states, we assume in the following that the PES are related to singly excited Slater determinants. Thus, the KS Hamiltonian in equation (7) is defined in a selfconsistent way using the occupancies $\{f_{\mu}\}$ for the current PES. For this purpose, we perform a constrained DFT calculation in which the level occupancy is imposed for a particular PES to maintain the electronic configuration during the SCF cycle. In order to keep track of the identity of the adiabatic KS states at different time steps we calculate the overlaps $\langle \psi_{\mu}(t - \Delta t)|\psi_{\mu}(t) \rangle$.

Step 2: Calculation of the non-adiabatic couplings. The time evolution of the electronic state is calculated using time-dependent KS theory [39–41]. For this purpose, we expand the time-dependent KS orbitals, $\psi_{i}$, in terms of the adiabatic KS states

$$
\psi_{\mu}(\mathbf{r}, t) = \sum_{k} c_{ik}(t) \psi_{k}(\mathbf{r}; \mathbf{R}),
$$

and evolve them using the time-dependent, Schrödinger-like, KS equations:

$$
\hat{H}_{\text{KS}}[\mathbf{R}]\psi_{\mu}(\mathbf{r}, t) = i\hbar \frac{\partial \psi_{\mu}(\mathbf{r}, t)}{\partial t}.
$$

This yields the equations of motion for the coefficients $c_{ik}(t)$ in equation (8):

$$
i\hbar \frac{\partial c_{ik}(t)}{\partial t} = c_{ik}(t)\epsilon_{k}(\mathbf{R}) - i\hbar \sum_{m} c_{im}(t)\mathbf{d}_{km} \cdot \mathbf{V}.
$$

In this equation the coupling between the classical motion of the atoms and the time evolution of the electronic quantum state is reflected in the non-adiabatic coupling (NAC) term:

$$
\mathbf{d}_{km} \cdot \mathbf{V} \equiv \sum_{\alpha} \mathbf{d}_{km}^{\alpha} \mathbf{V}_{\alpha},
$$
where \( V_\alpha = \frac{\partial R_\alpha}{\partial t} \) is the atomic velocity of atom \( \alpha \) and \( \mathbf{d}_{km}^\alpha \) are the non-adiabatic coupling vectors (NACV) between adiabatic KS states \( k \) and \( m \):

\[
\mathbf{d}_{km}^\alpha = \langle \psi_k \frac{\partial \psi_m}{\partial R_\alpha} \rangle. \tag{12}
\]

The NACVs \( \mathbf{d}_{km}^\alpha \) are the central quantity for non-adiabatic molecular dynamics. The atomic motion induces changes in the adiabatic states populations \( |c_{jk}(t)|^2 \) through the coupling of the atomic velocities and the NACVs, see equation (10). Recently, we have derived an expression to calculate the NACVs \( \mathbf{d}_{km}^\alpha \) in a basis set of local-orbitals on the fly along the MD simulation in a practical and computationally efficient way [42]. Alternatively, the NAC for the time evolution (equation (10)) of the coefficients \( c_{jk}(t) \) can be directly calculated using the following numerical derivative [43]:

\[
\mathbf{d}_{km} \cdot \mathbf{V} = \langle \psi_k \frac{\partial \psi_m}{\partial t} \rangle = \frac{1}{2\Delta t} \left[ \langle \psi_k (t - \Delta t) \rangle - \langle \psi_k (t) \rangle \langle \psi_m (t - \Delta t) \rangle \right], \tag{13}
\]

which gives the value of the NAC at time \((t - \Delta t/2)\).

Step 3: Time evolution of the electronic states. Once the NACs have been calculated, we propagate the coefficients \( c_{ik} \) from time \((t - \Delta t)\) to time \(t\) using a small time step \(\Delta t_{el}\) and a 4-th order Runge–Kutta numerical scheme to integrate equation (10). In this numerical solution the quantities used in different electronic time steps \(\Delta t_{el}\) are linearly interpolated from the corresponding values for the ionic steps. Typically \(\Delta t_{el} \sim \Delta t/500\). This is the inner loop for the propagation of the electronic states for each step, \(\Delta t\), in the atomic motion.

Step 4: Surface hopping. At each time step \(\Delta t\), a transition between adiabatic PESs \( E_A \rightarrow E_B \) may occur through a probabilistic ‘hop’ using the fewest switches algorithm [10]. The MDET algorithm incorporates the following switching probability \( g_{jk}(t) \) to define the transition between electronic states \( \psi_j \rightarrow \psi_k \) in the time interval \([t - \Delta t, t]\):

\[
g_{jk}(t) = \frac{b_{kj}(t)\Delta t}{|c_{kj}(t)|^2}, \tag{14}
\]

where the coefficient \( b_{kj} \) is defined as:

\[
b_{kj}(t) = -2Re[c_{jk}(t)c_{kj}(t)d_{kj} \cdot \mathbf{V}]. \tag{15}
\]

The transitions are determined using a Monte-Carlo approach following the probabilities \( g_{jk}(t) \). When a transition takes place, the occupancies of the adiabatic KS orbitals \( \psi_j \) and \( \psi_k \) are modified: \( f_j : 1 \rightarrow 0; f_k : 0 \rightarrow 1 \), and the stationary KS Hamiltonian, equation (7), is re-calculated for the new electronic configuration (see Step 1). In this case, energy conservation is imposed by re-scaling velocities along the direction of the NACV, equation (12) [44, 45]. Hops to higher energy PESs are rejected if insufficient kinetic energy is present. Velocity rescaling and hop rejection ensures detailed balance between transitions up and down in energy. If the switch does not occur, the simulation continues on the current PES.

Step 5: Motion of the atoms. Finally, the atomic positions are updated \( t \rightarrow t + \Delta t \) using the forces corresponding to the current PES, \( E_A \):

\[
\mathbf{F}_\alpha = -\frac{\partial E_A}{\partial R_\alpha}. \tag{16}
\]

where \( \mathbf{F}_\alpha \) is the force acting on atom \( \alpha \). The calculation goes back to step 1 using the new atomic positions. This scheme is repeated until the simulation is finished.

We now describe the parameters used during simulations of photo-cycloaddition (PCA) reactions discussed in the next section. The optimized atomic structure in the ground state is used as the initial molecular configuration for the reactant.
3. Results: cycloaddition

3.1. Cycloaddition reaction of two small organic molecules: reaction of maleic anhydride with ethylene

To demonstrate the efficiency of our method, we first report DFT–MDET simulations of the photo-cycloaddition (PCA) reaction of maleic anhydride (C$_2$O$_3$H$_2$) with ethylene (C$_2$H$_4$), forming cyclobutane-1,2-dicarboxilic anhydride (C$_4$O$_3$H$_6$), as seen in Figure 2(a). This PCA reaction is a prototypical reaction frequently encountered in organic chemistry. The reaction is generated by a single electron excitation induced by the interaction with light. During the PCA reaction the two π bonds perish and two σ bonds arise, thus 4 bonding electrons are involved in the reaction process. The frontier molecular orbital description of PCA is schematically presented in Figure 2(a), where the $p_c$ character of the frontier orbitals, the HOMO and LUMO of the isolated reactants, are displayed on the right and left sides of the figure. The formation of a molecular complex by the two reactants leads to four linear combinations of the frontiers orbitals (shown in center of Figure 2(a)). Kohn–Sham HOMO and LUMO orbitals in real space for the molecular complex are shown in the bottom of Figure 2(b). The HOMO orbital is formed by the overlap of π bonds of opposing signs, which gives rise to the intermolecular anti-bonding character of the HOMO orbital, see Figure 2(a). Consequently, the intermolecular anti-bonding character of the HOMO orbital inhibits a thermally activated reaction. In contrast, the LUMO orbital shows intermolecular bonding characteristics. Thus, a photo-induced electron excitation from the HOMO to the LUMO induces an additional attractive force which facilitates the PCA reaction, as discussed below.

To gain more insight into the reaction mechanisms, we performed, in total, 50 independent DFT–MDET simulations, each with total time of 2 ps; in each simulation, a single electron was initially promoted from the HOMO to the LUMO state of the molecular complex (C$_2$H$_4$ + C$_2$O$_3$H$_2$). Each simulation took approximately 16 h on single CPU Intel Xeon E5420 @ 2.50 GHz which demonstrates the computational efficiency of our FIREBALL-MDET code. All simulations were initiated from an identical configuration—both planar molecules were oriented parallel and the carbon–carbon double bond (C$_1$=C$_4$) of ethylene was positioned above the carbon–carbon double bond (C$_1$=C$_2$) of maleic anhydride (see Figure 2(b) top). The initial distance between the molecular planes of the anhydride and ethylene was 3 Å. The velocities were initialized with a normal distribution corresponding to an initial temperature of 500 K. In order to show clearly the stochastic nature of the MDET algorithm, the same initial positions and velocities were applied for each trajectory. Four frontier orbitals (HOMO-1, LUMO-1, HOMO, LUMO) were considered for the 2D-PCA reaction.
traced a time evolution of a characteristic distance $d_{\text{REAC}}$ measured from the center of ethylene carbon–carbon bond ($C_1$–$C_2$) to the center of anhydride carbon–carbon bond ($C_3$–$C_4$). This distance $d_{\text{REAC}}$ measures the distance from the center of ethylene carbon–carbon bond to the center of anhydride carbon–carbon bond. We also evaluated the forces acting between the two molecules as $f_{\text{REAC}} = \sum F_{\text{ethylene}} - \sum F_{\text{anhydride}}$ projected along the vector from the center of ethylene carbon–carbon bond to the center of anhydride carbon–carbon bond ($d_{\text{REAC}}$). The time evolution of the energy $E_{\text{REAC}}$ and force $f_{\text{REAC}}$ between reactants are plotted in figure 3(d) by the red and blue curves, respectively.

Initially, the HOMO and LUMO have intermolecular antibonding and bonding characters, respectively. The partial occupancy of the bonding state (LUMO) induces an attractive force acting between reactants. Consequently their distance $d_{\text{REAC}}$ reduces significantly from 3.0 Å to 2 Å. Within $\approx 60$ fs the system approaches towards the region of the conical intersection and the HOMO and LUMO exchange their characters—the HOMO is now a bonding orbital and vice versa. In this particular case, after the ‘crossing’ of the HOMO and LUMO, a de-excitation of the electron from LUMO (antibonding) to HOMO (bonding) happens at approximately 86 fs, which stabilizes the final molecular complex and produces the addition reaction. The force $f_{\text{REAC}}$ becomes strongly attractive, driving the system to the final bound state with the distance $d_{\text{REAC}}$ oscillating around 1.6 Å.

We should note that, in this particular case, the switching mechanism does not occur at the distance with the NACV maximum, but later due to the stochastic nature of the fewest switches MDET procedure. In other trajectories we observe a LUMO to HOMO electron transition near the crossing region. In these cases the electronic transition from LUMO to HOMO happens at approximately 61 fs, very near to the conical intersection, with the HOMO exhibiting an intermolecular bonding character. After this transition, the PCA reaction is completed.

The second deactivation channel consists of the direct nonreactive de-excitation. In our simulations, we have detected 13 cases (out of 50) of the direct dissociation. In these cases...
cases, the system evolves initially along the same trajectory as in the previous cases. The electron hopping occurs between the LUMO and the HOMO at 104 fs, where HOMO and LUMO have anti-bonding and bonding characteristics, respectively, similar to the initial configuration, which leads to a double occupancy of the intermolecular anti-bonding HOMO state; this induces an important change in the force between both molecules, that after the transition presents a large repulsive value (2 eV Å$^{-1}$), driving the molecules far from each other. Thus, the addition reaction is not produced.

The third deactivation channel is related with the formation of an intermediate state which is characterized by the formation of just one carbon–carbon bond between maleic anhydride and ethylene. In this intermediate state the distance $d_{REAC}$ oscillates around 2.3 Å as shown on figure 4. In this case the system typically finalizes (22 cases out of 50) in the decoupling of the molecular reactants but we detected 3 cases where the intermediate case produces the complete addition reaction (see figure 4).

### 3.2. Polymerization of two C$_{60}$ molecules via cycloaddition

Here, as a second example of the application of our FIREBALL-MDET code, we present simulations of the polymerization process of two free-standing C$_{60}$ molecules via a 2 + 2 PCA reaction. This reaction was first reported by Rao et al in 1993 [47]. The basic principles for this case are similar to our discussion in the previous section, see figure 2. Accordingly, the HOMO of the molecular complex C$_{60}$–C$_{60}$ has an intermolecular anti-bonding character while the bonding character is mainly associated to the LUMO + 1 orbital (see figure 5(c)). We should note that the LUMO and LUMO + 1 orbitals are nearly degenerate with an energy difference of 0.08 eV in the initial configuration. Nevertheless the LUMO+1 shows a strong bonding character with pronounced electron densities localized between the frontiers atoms of the two C$_{60}$ molecules.

Here we consider the case where two C$_{60}$ molecules are oriented by 56/65 edges (see figure 5(b)) against each other [48]. In the first step, we examine the PESs as a function of distance between the two C$_{60}$ molecules in the ground S$_0$, first excited S$_1$, and second excited S$_2$ states for distances in the range from 1.3 to 3.0 Å, with incremental changes in the distance of 0.05 Å. In this calculations we fixed x and y coordinates of the four interacting carbon atoms forming the 56/65 edge see figure 5(b), i.e. those involved in the cycloaddition chemical bond, and the rest of the atomic positions were allowed to relax. The calculated PES S$_0$, S$_1$, and S$_2$ are plotted in figure 5(a). We can identify two minima on the S$_0$ PES: (i) a global one located at the distance of $\approx$2.69 Å, which corresponds to two weakly interacting C$_{60}$ molecules; (ii) and the second, a local minimum found at the distance of $\approx$1.56 Å. This second minimum corresponds to two chemically bonded C$_{60}$ molecules. In between these two energy minima, there is an energy barrier of $\approx$0.6 eV located at a distance of 1.75 Å, which avoids a spontaneous transition from the energetically higher chemically bound state to the weakly bound state. At this distance there is a conical intersection between S$_0$ and S$_1$.

Figure 5(a) also shows the ground state PES as calculated with the AIMS code [49] (which employs high-accuracy numerical orbitals and thus allows better sampling of the Hilbert space). This PES is quite similar to our result; in particular, the conical intersection is found at the same distance, 1.75 Å.

In our DFT-MDET simulations, we initially placed two C$_{60}$ molecules at a distance of 2.0 Å (vertical line in figure 5(a)) i.e. 0.25 Å away from the conical intersection, and one electron was promoted from the HOMO to the LUMO+1 state. During the simulation, we let the system evolve in time for 0.5 ps at a constant temperature of 100 K, with initial velocities chosen as discussed in the previous section. Electron transitions are allowed between three orbitals—HOMO, LUMO and LUMO + 1. Our simulations identify two scenarios: (i) a PCA reaction forming a C$_{60}$ bonded dimer; or (ii) a complete decoupling of the two C$_{60}$ molecules towards the weakly bound minimum. In total, we carried 20 trajectories and 3 of the simulations yielded the polymerization process; 17 simulations lead to the separation of the C$_{60}$ molecules.

Figure 6 shows the time evolution for a case where electron de-excitation happens via the 2 + 2 cycloaddition reaction. Figure 6(a) represents the HOMO, LUMO and LUMO + 1 KS orbitals at three different snapshots corresponding to the vertical black lines in figure 6(b). Figure 6(b) shows the time evolution of the HOMO, LUMO and LUMO + 1 KS eigenvalues. Figure 6(c) shows the PESs corresponding to the ground S$_0$, first S$_1$ and second S$_2$ excited states throughout the simulation. The cyan circles identify on which PES the system is located at a given time during the simulation. The solid/dashed grey line represents the evolution of the NACVs between the LUMO and HOMO and between the LUMO + 1 and LUMO, respectively. Finally, figure 6(d) displays the evolution of the force $F_{REAC}$ acting between the two molecules and their distance $d_{REAC}$, which is defined as an average distance between the frontiers atoms on the 56/65 edges of each.
molecule. Similarly, the force $F_{\text{REAC}}$ is the difference between the sum of forces acting on each C$_{60}$ molecule projected along the vector $d_{\text{REAC}}$.

Initially, the S$_1$ and S$_2$ states are almost degenerate, see figure 6(c). Very rapidly in the simulation, the LUMO and LUMO + 1 energy states show a strong mixing and a large NACV, and an electronic hopping between LUMO + 1 and LUMO occurs (at $t = 4.75$ fs). The system evolves now in the S$_1$ excited state and the LUMO and LUMO + 1 energy levels move away from each other. The LUMO orbital (occupied by one electron) has now the stronger intermolecular bonding character, see figure 6(a) ($t = 23$ fs). As shown in figure 6(d), in this part of the trajectory there is a repulsive force $F_{\text{REAC}}$ between the two C$_{60}$ molecules but the distance $d_{\text{REAC}}$ decreases. A detailed analysis of the motion of the system shows that while most of the carbon atoms in each molecule move away from the other molecule, the two frontiers atoms on each molecule actually approach closer towards the two frontier atoms on the other molecule due to the excited electron in the bonding LUMO orbital. Consequently, both C$_{60}$ molecules tend to elongate. The repulsive force $F_{\text{REAC}}$ and the distance $d_{\text{REAC}}$ diminish in time and the system evolves towards a conical intersection between S$_0$ and S$_1$, which increases the NACV between the HOMO and LUMO. The proximity of the conical intersection induces an electron switching between the LUMO and HOMO. After this transition the HOMO and LUMO exchange their bonding and anti-bonding characters. Now, the bonding HOMO has two electrons and the antibonding LUMO is empty. Consequently, strong chemical bonds are established between the frontier carbon atoms and the PCA reaction is completed. In the remaining simulation time the distance $d_{\text{REAC}}$ oscillates around its equilibrium position while all the carbon atoms relax in a complex way to minimize the initial elongation.

An example of the non-reactive pathway is presented in figure 7. Initially, the system evolves very similarly to the previous case where the system approaches a conical intersection between S$_1$ and S$_2$; due to the probabilistic nature of the fewest switches method, the electronic transition from LUMO + 1 to LUMO takes place now a little later, at $t = 5.75$ fs, see figure 7(b). The system evolves then in the S$_1$ state, moving towards a S$_0$–S$_1$ conical intersection, but the electron hopping does not occur now. Thus, the systems stays in the S$_1$ PES, with a repulsive force $F_{\text{REAC}}$ acting between both molecules; the distance $d_{\text{REAC}}$ oscillates (figure 7(d)), due to the attraction associated with the bonding LUMO (occupied with one electron), see figure 7(a). During the second oscillation cycle, when $d_{\text{REAC}}$ decreases again the S$_1$ and S$_0$ PESS (and the LUMO and HOMO energy levels) approach each other again and the electron hop takes place now, at time $t = 100$ fs (figure 7(b) and (c)). The HOMO (occupied by two electrons) presents an intermolecular anti-bonding character now (see figure 7(a), $t = 110$ fs), enhancing the repulsive force $F_{\text{REAC}}$. Consequently the distance $d_{\text{REAC}}$ increases and the system goes to the weakly interacting ground state (figure 5) and the PCA reaction does not occur.

4. Conclusions

The computational simulation of photo-induced processes in large molecular systems is a very challenging problem. Here, we have presented a detailed description of our implementation of a DFT–MDET technique within our local-orbital code FIREBALL, suitable for the computational study of these problems. The MDET technique consists of two nested time loops: an outer loop for the motion the atoms and an inner loop for the propagation of the electronic states. The atoms move in adiabatic PESSs, that are calculated using constrained DFT calculations for the different electronic configurations. The time evolution of the electronic states is calculated using time-dependent KS theory. The coupling of the atomic motion and the time evolution of the electronic states is taken into account by means of probabilistic hops between different PESSs, using the fewest switches algorithm. When hops take place, energy conservation is imposed re-scaling the velocities along the direction of the non-adiabatic coupling vectors, that are calculated on the fly along the molecular dynamics simulation [42].

As an example of the application of this DFT–MDET approach, we have presented some simulations for two
different photo-induced cycloaddition reactions: the reaction of two small organic molecules (maleic anhydride and ethylene, forming cyclobutane-1,2-dicarboxilic anhydride) and the polymerization reaction of two C60 molecules. In the first case, an electron is initially promoted from the HOMO to the LUMO; the LUMO presents an intermolecular bonding character, inducing an attractive force between both molecules. At a time of \( \sim 60 \) fs, the system goes through a S1–S0 conical intersection, with a large value of the NACV between HOMO and LUMO. We identify three different deactivation channels of the initial electron excitation, depending on the time of the electronic transition from LUMO to HOMO, and the character of the HOMO after the transition. In particular, the cycloaddition reaction is established when the HOMO is an intermolecular bonding state after the transition. In the case of the larger C60 molecules, the S1 and S2 states are initially almost degenerate and we promote one electron from the HOMO to the LUMO + 1. Very rapidly in the simulations (%5 fs) the electron hops from the LUMO + 1 to the LUMO and the system evolves in the S1 state towards a S1–S0 conical intersection. In this part of the simulations there is an overall repulsive force between both molecules and an attractive force between the frontier atoms on each molecule due to the excited electron in the bonding LUMO state; thus, the molecules tend
to elongate. We identify two different scenarios, depending on the time of the electronic transition from LUMO to HOMO and the character of the HOMO state after the transition: (i) a PCA reaction forming a bonded C60 dimer; and (ii) the motion of the system towards the weakly coupled ground state.

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