Artifacts due to trivial unavoided crossings in the modeling of photoinduced energy transfer dynamics in extended conjugated molecules

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ABSTRACT

A previously developed algorithm to identify potential energy surface crossings involving interacting or noninteracting states during nonadiabatic excited-state molecular dynamics simulations, allows the diabatic pathway to be followed through the crossing region so that there is no experienced change in the states identity. In this Letter, we investigate the transition from interacting/delocalized states to noninteracting/localized states in oligomers of poly-phenylene vinylene separated by varying distances. We demonstrate that the appearance of trivial unavoided crossings during nonadiabatic dynamics leads to artifacts in the state population analysis. Consequently, changes in the localization of the electronic transition density must be followed instead.

1. Introduction

Excited state molecular dynamics of any polyatomic molecular system [1–3] is likely to experience multiple regions of potential energy surface (PES) crossings within its excited state lifetime [4]. Consequently, either weakly or strongly avoided crossings, as well as unavoided crossings are common events during radiation-less vibronic relaxation [5–10]. Conical intersections dominate nonadiabatic nuclear dynamics on very short (femtosecond) time-scales [4]. In extended polyatomic molecules, special cases of unavoided crossings can also take place between two noninteracting states occupying the same energy range while different moieties are spatially separated and their wavefunctions have vanishing interactions. In such cases, denoted as trivial unavoided crossings, the nonadiabatic couplings behave as sharp peaks strongly localized at the exact crossing points while vanishing elsewhere. Here the wavepacket trajectory must cross the conical intersection seam following the diabatic pathway of its parent wavefunction along the respective adiabatic PES. Failure to follow the correct pathway can lead to unphysical sudden changes in the spatial localization of the current state [11].

Within the domain of small and medium sized molecules, at least within some regions of phase space, intramolecular excited states that are close in energy will commonly interact with one another. As a consequence, these states mix and cross, their identities temporarily change, and electronic population is transferred between them. Because of that, the use of energy ordering to identify the states becomes useless and adiabatic state populations lose their relevance. Instead, changes in the electronic transition density must be followed. Similar behavior can be expected between electronic excited states belonging to similar molecules separated by short intermolecular distances. Nevertheless, while states on two different molecules or on two separate fragments within the same molecule may be interacting at short separation distances, they become noninteracting when the separation distance increases.

In this Letter, we analyze the transition from interacting to noninteracting states, which can lead to the appearance of trivial unavoided crossings during dynamics. As was recently demonstrated by our group, these crossings play a critical role in the dynamics of organic conjugated polymers. For example, during energy transfer dynamics in PPV oligomers, torsional fluctuations can cause excited state energy reordering [12]. Failure to detect such crossings can lead to unphysical population transfer between electronic states and an apparently high efficiency of energy transfer [11]. Here, we address artifacts observed when analyzing the populations of adiabatic electronic excited states. These artifacts are associated with the incidence of trivial unavoided crossings, and we discuss how they vanish when the number of trivial unavoided crossings during photoinduced dynamics decreases.

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2. Theoretical methodology

2.1. Nonadiabatic excited-state molecular dynamics

We have performed Nonadiabatic Excited-State Molecular Dynamics (NA-ESMD) simulations [13] of the photoexcited dynamics in the model system depicted in Figure 1A composed of 3-ring and 4-ring poly-phenylene vinylene (PPV) oligomers. The NA-ESMD formalism combines the fewest switches surface hopping (FSSH) approach [14,15] with "on the fly" analytical calculations of excited state energies [16,17], gradients [18], and nonadiabatic coupling terms (NACTs) [13,19,20] in order to simulate photoinduced dynamics in large conjugated organic molecules involving many coupled electronic excited states on time scales of tens of picoseconds [21,22,2,23]. Correlated excited states are described using the Collective Electronic Oscillator (CEO) method [24–26] applied at the Austin Model 1 (AM1) [27] level of theory in combination with a Configuration Interaction Singles (CIS) formalism. At any given time, the nuclei are evolved on a single adiabatic PES, and transitions between coupled electronic states are possible depending on the nonadiabatic coupling strength [28]. Although dielectric medium effects are not explicitly included in the excited state calculations underlying our MD simulations, a phenomenological description of solvent effects is included in the nuclear propagation through the use of constant-temperature Langevin dynamics algorithm [29] developed to be consistent with the velocity Verlet integration technique [30] incorporating frictional damping and a fluctuating force following the fluctuation–dissipation theorem [31]. Details of NA-ESMD implementation and limitations can be found in our previous work [13,32].

2.2. Min-Cost identification of unavoided crossings

We have recently developed a novel procedure to identify crossing events by tracking the identities of states over time. Using the so-called Min-Cost assignment algorithm, new states at the current time step i can be assigned in terms of old states at the preceding time step $(i - 1)$. The correspondence between states is found at each time step based on maximizing the trace of the square of the overlap matrix, $\mathbf{S}$, whose elements are defined as

$$s_{\alpha\beta}(t; t + \Delta t) \equiv \phi_\beta(\mathbf{r}; \mathbf{R}(t)) \cdot \phi_\alpha(\mathbf{r}; \mathbf{R}(t + \Delta t)) \tag{1}$$

where ϕ_α and ϕ_β are the adiabatic electronic state wavefunctions, $\mathbf{r}$ and $\mathbf{R}$ represent electronic and nuclear coordinates, respectively, and Δt is the classical time step used for NA-ESMD simulations. This is done by selecting one element from each row, each pertaining to a different column (or vice versa), from the matrix $\mathbf{S}(t; t + \Delta t)$ such that the sum of their squared values is maximized. If a maximum overlap greater than an arbitrary threshold, s_{lim}, is identified, then the states are reassigned by interchanging their populations and cancelling their couplings without evaluating the hopping probability. This removes the arbitrary effect of the nonadiabatic coupling strength depending on the proximity to the exact crossing point. Thus, unavoided crossings involving interacting states (simulated by quantum hops) can be differentiated from trivial unavoided crossings between noninteracting states (detected by tracking state identities). Further details of its implementation within the NA-ESMD [13] framework are provided elsewhere [11].

2.3. Simulation details

The separation distance, r_{CM}, is defined as the distance between the centers of mass of each oligomer and is varied according to Ta-
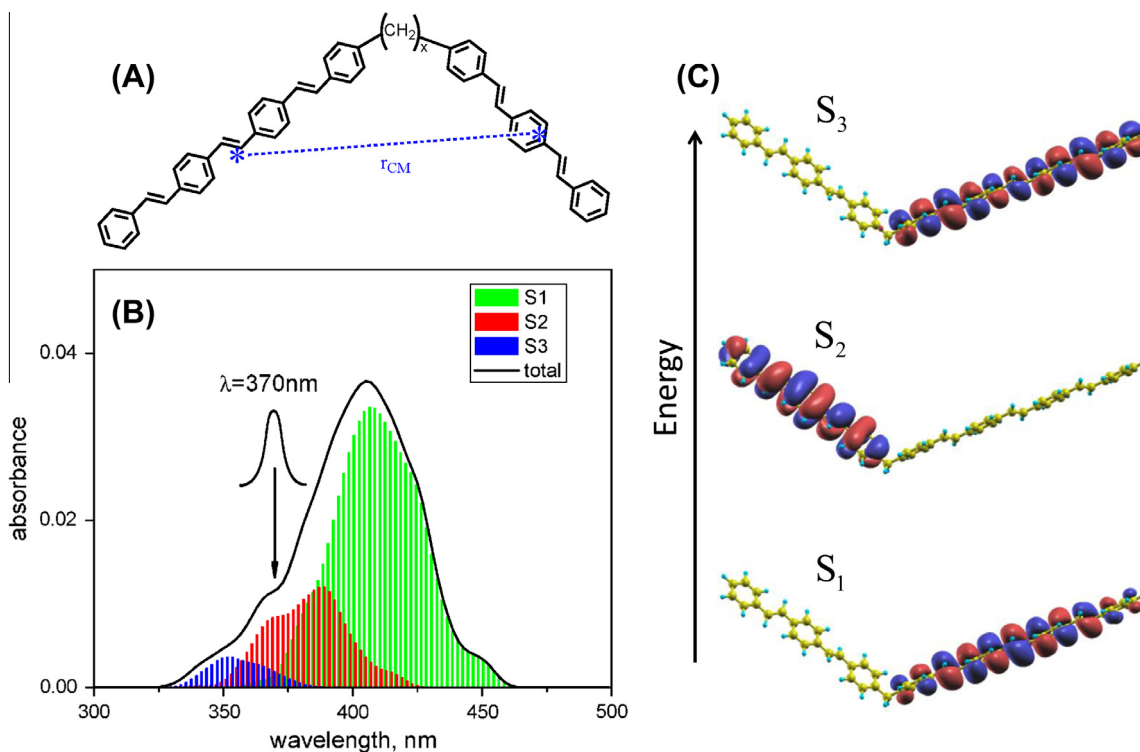

Figure 1. (A) Chemical structure of 3-ring and 4-ring PPV segments connected by an alkyl chain of length x (C_xH_{2x}). r_{CM} defines the separation distance between the centers of mass of the two segments. For larger separation distances, the alkyl chain is removed. (B) Simulated absorption spectrum for the x = 1 (19 Å) system (black line) and the density of excited states (sticks). The arrow indicates the maximum excitation wavelength used to populate the initial excited states. (C) Initial transition density localization for the three lowest energy excited electronic states.