Nonadiabatic electron wavepacket study on symmetry breaking dynamics of the low-lying excited states of cyclic-B₄

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ABSTRACT

Symmetry allowed conical intersection plays a central role in excited state symmetry-forbidden reactions. As an illustrative example as such, we track the dynamical sequence of spatial-symmetry breaking of B₄ cluster, which has a rich electronic structure in the low-lying excited states, to see how the relevant reaction proceeds. We use the semiclassical Ehrenfest method to detect the nonadiabatic electronic state mixing along the reactions. The essential feature of the nonadiabatic electron dynamics is clarified in terms of electron flux and unpaired-electron distribution induced by the nonadiabatic transitions. To facilitate understanding electron dynamics of symmetry breaking, we begin with symmetry consideration in terms of the Hückel orbitals, which are shown to be qualitatively useful enough to foresee the possible existence of symmetry allowed conical intersections.

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1. Introduction

Boron atoms form various non-classical bonds to avoid empty $2p$ orbital left [1–3], which is important for chemists to develop valence structures theory. The concept of "3c-2e bond" proposed by Lipscomb and co-workers in 1954 [4] is a landmark work. It is very interesting to study not only the ground sate but also excited states of "electron-deficient" molecule, which owns more valence orbitals than electrons. Those irregular bonds lead to anomalous structures in ground state. The Lipscomb theory has successfully explained almost all the sorts of strange topological models of boranes [5], with the most famous example being diborane for the bridge hydrogen bond. The deltahedra structure has now been thought as the key unit for boron chemistry [6]. Among them, rhomboidal B₄ framework, which was first noticed by Lipscomb in 1966 when he studied the fluxionality of boranes, is known as the so-called Diamond-Square-Diamond (*dsd*) rearrangement (Fig. 1) [7]. It occurs by pseudo-rotation or pseudo-reflection process according to the detailed symmetry of individual polyhedra. In this conjunction several selection rules such as geometry-allowed (-forbidden) and orbital symmetry-allowed (-forbidden) have been reported in the frame of three-center theory [8–13].

Pure boron cluster B₄ as well as its ions are also studied both theoretically and experimentally [14–21]. Now it is widely recognized that the global minimum of neutral B₄ is singlet D_{2h} but

not D_{4h} due to the pseudo-Jahn–Teller effect [14,22]. We here simply call them cyclic-B₄ regardless of the global minimum. Its bonding characters, such as σ–π double aromaticity and sp hybridization have been discussed by high level *ab initio* calculations [17–19]. On the other hand, Reddy et al. simulated the photodetachment process of B_4^{-1} with considering nonadiabatic coupling between the ground and excited states [23,24]. To the best of our knowledge, it is the only nonadiabatic electronic dynamics of B₄ reported so far. Besides, for their focus was vibrational coupling, nuclear dynamics was limited within small displacements along normal modes. Considering the high symmetry of B₄, a real-time nonadiabatic excited state dynamics is anticipated. Take *dsd* process for example, and we readily observe a crossing of degenerate orbitals forming conical intersections and/or avoided crossings on the potential energy surfaces (PES) [2]. We here dynamically track those series of symmetry breaking with the method of nonadiabatic electron wavepacket dynamics. These dynamical processes constitute a theoretical foundation for chemical reaction theory for the class of the so-called symmetry forbidden reactions (in the terminology of Woodward–Hoffmann rule of conservation of orbital symmetry), in which symmetry-allowed conical intersections are usually involved. Therefore the present work serves also as a basic dynamical process of symmetry breaking (or mixing of electronic states belonging to different irreducible representations) caused by nonadiabatic interactions.

Nonadiabatic electron wavepacket scheme is quite useful to track the electronic state dynamics [25]. In this theory, electron wavepackets are propagated and bifurcated along branching

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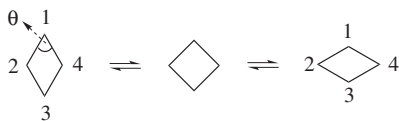
Fig. 1. Diamond-square-diamond process. The angle B2–B1–B4 (θ) defines a reaction coordinate retaining D_{2h}.

nuclear paths, which are in turn driven under the nonadiabatic couplings [26]. This general scheme is called the theory of path-branching representation [27]. With the help of sophisticated *ab initio* quantum chemistry, tracking nonadiabatic electronic dynamics has now become feasible. However, it is quite often sufficient to track the electronic state mixing only along representative nuclear paths that are an average of those possible branching paths. This is the so-called semiclassical Ehrenfest theory (SET), the theoretically correct form of which has been derived from the path-branching representation with correction terms that are missing from the intuitive way of derivation [26]. These progresses have been employed to study several systems, such as bonding process of diborane [28], proton–electron transfer of Phenol–$(NH_3)_3$ and so on [29,30]. (For more general scope and recent progress in the theory of nonadiabatic dynamics, see [27,31–34].)

We begin the present studies with clarifying and visualizing orbital symmetry by applying the Hückel theory. Although nothing quantitatively accurate can be expected in this theory, it is still quite often useful for qualitative understanding of chemistry. Not only to see molecular orbital bases belonging to each irreducible representation, but also to locate a position of possible conical intersections we will see that the Hückel theory is still useful and instructive.

The article consists as follows. Section 2 summarizes the outline of the theoretical method and quantities to be used for the analyses of the results, with which for our computation to rest on. Before the study of nonadiabatic electron dynamics with SET, we begin Section 3 with a symmetry consideration of the system in terms of the Hückel theory. This paper concludes with some remarks in Section 4.

2. Theoretical method

The theoretical frame we work with to propagate nonadiabatic electron dynamics is outlined first along with illustrative quantities to highlight the resultant dynamics. The mass-weighted coordinates are used throughout.

2.1. Nonadiabatic electronic dynamics

The electronic state is expressed by

$$\Psi(\mathbf{r}, t; \mathbf{R}(t)) = \sum_I^{CSF} C_I(t)\Phi_I(\mathbf{r}; \mathbf{R}(t)), \tag{1}$$

which means that the electronic wavepackets are propagated along a nuclear path $\mathbf{R}(t)$. Basis functions $\Phi_I(\mathbf{r}; \mathbf{R}(t))$ can be rather arbitrary but here we adopt configuration state functions (CSF), which are assumed to be orthonormal at each nuclear configuration. The time-dependent variational principle for the Schrödinger equation gives coupled equations of motion for the coefficients $\{C_I(t)\}$ are [26]

$$i\hbar\frac{\partial}{\partial t}C_I = \sum_J^{CSF}\left(H_{IJ}^{el} - i\hbar\sum_k^{nuc}\dot{R}_k X_{IJ}^k - \frac{\hbar^2}{2}\sum_k^{nuc}Y_{IJ}^k\right)C_J, \tag{2}$$

wherein

$$H_{IJ}^{(el)} = \left\langle\Phi_I\left|\widehat{H}^{(el)}\right|\Phi_J\right\rangle, \quad X_{IJ}^k = \left\langle\Phi_I\left|\frac{\partial}{\partial R_k}\right|\Phi_J\right\rangle \text{ and } Y_{IJ}^k = \left\langle\Phi_I\left|\frac{\partial^2}{\partial R_k^2}\right|\Phi_J\right\rangle. \tag{3}$$

Note that the second-order terms Y_{IJ}^k are missing in the conventional form of the SET. We here neglect these terms throughout this work anyway, which is justified by the presence of $\hbar^2$. In what follows, the expectation values represented in terms of the ket and bra vectors indicate integration over only the electronic coordinates.

Obviously, the first term in the right-hand side of Eq. (2) comes from interactions among electronic states, while the second and third terms represent the kinematic couplings with the motion of nuclei. Since CSFs form a quasi-diabatic basis set, most of nonadiabatic effects are actually contributed from the first term. In case where $\widehat{H}^{(el)}$ happens to have a symmetry at a given molecular geometry, the adiabatic electronic states (in the Born–Oppenheimer approximation) belonging to different irreducible representations are not mixed together by $H_{IJ}^{(el)}$, and spatial-symmetry breaking is realized only through X_{IJ}^k. Therefore nuclear motions as those in the vibrational modes can cause the electronic state mixing of different symmetries, and the initial electronic wavefunction of an irreducible representation can be contaminated by other electronic states of different irreducible representation, which we refer to as symmetry breaking. Thus the nuclear kinematic coupling terms are critically important in this work.

2.2. Nonadiabatic nuclear dynamics

The nuclear path solutions $\mathbf{R}(t)$ are obtained with the Euler–Lagrange variational principle, which brings about the force matrix $\mathbf{F}(\mathbf{R})$ [35], a matrix representation of the force operator $\hat{\mathcal{F}}^k$ to drive the nuclear motion in the kth direction, which is defined as

$$\mathbf{F}_{IJ}^k = \langle\Phi_I|\hat{\mathcal{F}}^k|\Phi_J\rangle = -\left[\frac{\partial H_{IJ}^{(el)}}{\partial R_k} + \sum_K\left(X_{IK}^k H_{KJ}^{(el)} - H_{IK}^{(el)}X_{KJ}^k\right)\right]$$
$$+ i\hbar\sum_l\dot{R}_l\left[\frac{\partial X_{IJ}^l}{\partial R_k} - \frac{\partial X_{IJ}^k}{\partial R_l}\right]. \tag{4}$$

If the basis functions were complete, this matrix element becomes dramatically simpler as

$$\mathbf{F}_{IJ}^k = \left\langle\Phi_I\left|\frac{\partial H^{(el)}}{\partial R_k}\right|\Phi_J\right\rangle. \tag{5}$$

Note that if the off-diagonal matrix elements X_{IJ}^k are negligibly small in the adiabatic representation, the force matrix has only the diagonal elements, which are equivalent to the ordinary forces given by the energy gradients of the individual potential energy surfaces (or the Hellmann–Feynman forces). If X_{IJ}^k is not small, on the other hand, the nuclear motion coupled with the dynamics of electronic-state mixing can branch into many pieces in a cascade manner, mimicking the nuclear wavepacket bifurcation and deformation. The paths thus branching eventually proceed to their individual adiabatic potential surfaces, which are usually specified in terms of the electronic state symmetry in spectroscopic notations. After all, the total wavefunction is represented by coherent superposition of those branching pieces of electronic and nuclear wavefunctions. (See the examples of full quantum electronic and nuclear quantum calculations of wavepacket bifurcation through avoided crossing in Refs. [36,37] and conical intersections in [38,39], and the relevant experimental observation in [40].) Such a wavepacket bifurcation can be well described in mixed quantum and classical representation, the algorithms of which are provided in Refs. [27,41–43].

The mean-field paths in the SET [44–49] appear to be as a special case of the present theory if we take a force average in the kth direction over the electron wavepacket such that