

論文の内容の要旨

論文題目 Theoretical Study on Spatial Symmetry Breaking
in Nonadiabatic Dynamics in Excited States
(空間対称性の破れを伴う励起状態非断熱動力
学の理論的研究)

氏名 李 中偉
Li Zhong-wei

Motivation and theoretical background

In chemical reactions, the conservation of orbital symmetry called Woodward-Hoffmann rule is an useful tool for chemists to predict whether a reaction occurs readily or hard. One of the requirements to use it is that a symmetry element must pass through the process of bond formation or broken. But in real conditions many reactants may loss their symmetries during the reaction, which is out of the scope of the rule. As an illustrative example as such, the present work tracks the dynamical sequence of spatial-symmetry breaking of cyclic-B₄ cluster to see how the relevant reaction proceeds.

The initial symmetry of this system is D_{2h} . Generally, if consider the non-relativistic Hamiltonian in the framework of Born-Oppenheimer approximation, any symmetric operation belonging to D_{2h} point group should not break the symmetry. Since all relevant symmetry operators commute with the symmetric Hamiltonian. Thus to seek the truth of symmetry-breaking in a practical and realistic way, a non-Born-Oppenheimer scheme is primarily needed.

We employ an *ab initio* nuclei-electrons coupled dynamics in which the electronic wavepackets are propagated along a nuclear path $\mathbf{R}(t)$

$$\Psi(\mathbf{r}, t; \mathbf{R}(t)) = \sum C_I(t) \Phi_I(\mathbf{r}; \mathbf{R}(t)) \quad (1)$$

Basis functions $\Phi_I(\mathbf{r}; \mathbf{R}(t))$ are assumed to be orthonormal at each nuclear configuration, and the equations of motion for the coefficients $\{C_I(t)\}$ are

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

wherein

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

In case where $\hat{H}^{(el)}$ happens to have a symmetry at a given molecular geometry, the adiabatic electronic states (in the BO 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 (the second-order terms Y_{IJ}^k are neglected throughout this work due to the presence of \hbar^2). 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.

On the other hand, the nuclear path solutions $\mathbf{R}(t)$ are obtained by

$$\ddot{\mathbf{R}}^k = - \sum_{I,J,K} C_I^* \left(X_{IK}^k H_{KJ}^{(el)} - H_{IK}^{(el)} X_{KJ}^k \right) C_J - \sum_{I,J} C_I^* \frac{\partial H_{IJ}^{(el)}}{\partial R_k} C_J, \quad (4)$$

which is equivalent to the Hellmann-Feynman force

$$\ddot{\mathbf{R}}^k = - \left\langle \Psi(\mathbf{R}(t)) \left| \frac{\partial H^{(el)}}{\partial R_k} \right| \Psi(\mathbf{R}(t)) \right\rangle, \quad (5)$$

only if the electronic basis set happens to be complete. Note that this is the mean-field path which we take a force average in the k th direction over the electron wavepacket, which is also called semiclassical Ehrenfest theory (SET). More faithful treatment of the force matrix can reproduce branching nuclear paths but not our focus here. B_4 has six vibrational normal modes and each relates to its own irreducible representation orbitals. Therefore the present work is devoted to observation of the way how these normal modes can be mixed up together as the total electron wavepackets develop through the nuclear kinematic couplings.

Results and conclusions

Symmetry consideration in the Hückel framework

Prior to the study on dynamics, Hückel theory is chosen to identify the irreducible representations of molecular symmetry and the spatial distribution of the bases of them. Although nothing quantitatively accurate can be expected in this theory, it is still quite often useful for qualitative understanding of chemistry. For cyclic- X_4 cluster (X denotes the second period element), if reorient the sixteen valence atomic orbitals into four sets, such as $2s$, radial (p_r), tangential (p_t) and perpendicular (p_π) (Fig. 1 (a)), only p_t gives three bonding orbitals while each of the rests has merely one bonding orbital to be available. Considering that there are twelve valence electrons involved in B_4 , sp hybridization is a key to make the bonds (Fig. 1 (b)). As a result, among six occupied orbitals, one σ and one π 4c-2e orbitals as well as four sp hybridization orbitals are prettily reproduced by the Hückel theory suggesting that such a way of bonding is of necessity to form electron-deficient bonds of cyclic- B_4 , which makes a stable four-member ring without relying on the traditional deltahedral structure of boron.

Not only to see molecular orbital bases belonging to each irreducible representation, but also Hückel theory be instructive to guess the positions of possible conical intersections. Take the weakest vibrational mode (denoted by $\omega_1(A_g)$) for example, if draw the potential curve of the relevant excited states along the reaction coordinate, many crossings can be observed (Fig. 2(a)). Comparing with *ab initio* calculations, except the crossing between the two B_{3g} states which should be avoided along this one-dimensional coordinate but exhibiting a direct crossing by Hückel theory due to the pseudo-diabatic wavefunctions, each of the rest crossings represents the symmetry-allowed conical intersection. They are referred to characterization of the nonadiabatic dynamics of symmetry-breaking discussion later.

Dynamics of symmetry-breaking

To show the general mechanism of symmetry-breaking, several excited state dynamics are studied and an illustrative example is briefly presented here. In Fig. 2(a) the B_{2u} state is optical y -allowed transition from the ground state and seven frontier orbitals ($1b_{1g}$, $1b_{1u}$, $2a_g$, $3a_g$, $2b_{2u}$, b_{3g} , $2b_{3u}$) are involved to construct dominant symmetric configurations. Due to two singly occupied orbitals $2a_g$ and $2b_{2u}$ (which are HOMO and LUMO+1, respectively), B_4 automatically vibrates along the $\omega_1(A_g)$ direction with no initial nuclear momentum. But the regular D_{2h} point group is just retained up to about 62 fs and then the z -symmetry is markedly broken, which is realized due to the nonadiabatic interaction. Such a symmetry-breaking process can be highlighted vividly in terms of quantities to characterize electron dynamics. The first breaking z -symmetry indicates the existence of non-zero asymmetric z -vector electronic flux, simply called z -flux, which should arise from the density matrix $\gamma(\mathbf{r}', \mathbf{r})$ those contain b_{1u} symmetry. Recall that $\gamma(\mathbf{r}', \mathbf{r})$ are resulted only from two different Slater determinants composed of the same molecular orbitals except for counterpart, for instance $1b_{1u} \sim 2a_g$ (“ \sim ” denotes orbital interaction), one is $1b_{1u}$ orbital and the other $2a_g$ orbital, which is likely generated mainly between the electronic configurations of excitation $1b_{1u} \rightarrow 2b_{2u}$ and $2a_g \rightarrow 2b_{2u}$ in the present case. Likewise, the z -flux induced by $2b_{2u} \sim b_{3g}$ suggests the presence of interaction between the configurations of $2a_g \rightarrow 2b_{2u}$ and $2a_g \rightarrow b_{3g}$, etc.. At selected time points such as 38 fs, also take $1b_{1u} \sim 2a_g$ for instance, the largest vector of its induced z -flux reaches 4.8×10^{-4} , in atomic units. It turns out that once z -symmetry begins to be a little destroyed, more symmetry-adapted configurations with respect to the degraded point group (from D_{2h} to C_{2v} here) can be involved as the electronic state transforms from B_{2u} to B_2 . Such as arose $1b_{1u}(a_1) \rightarrow 2b_{2u}(b_2)$ configuration after 62 fs, which excites the population of $1b_{1u}(a_1)$ orbital completely, makes a stronger interaction of the z -flux inducer $1b_{1u}(a_1) \sim 2a_g(a_1)$ become possible and the z -symmetry inevitably collapses.

By dissecting the marked areas where transition occurs in other cases, it is found that the nonadiabatic process usually obeys the following procedures: (1) As molecule vibrates, nuclear kinematic interactions generate asymmetric electronic flux. (2) Accumulated asymmetric flux starts

to affect the molecular symmetry at a quasi-symmetric state. (3) Once the symmetry is slightly destroyed, the forbidden interactions turn to be allowed and enhance the flux more. (4) Thus enhanced flux breaks the symmetry to larger extent.

Besides, we demonstrated the time-series of an “assumed instantaneous emission spectrum” by calculating the spectral positions and the associated intensities (oscillator strength times the weight of the eigenstate) as well of B_4 molecule (Fig. 2(b)). Although these spectra do not have quantitative accuracy, we clearly see how the electronic state mixing can evolve in the time scale of nonadiabatic couplings.

It is hoped that the present work serves as a basic building block with which to construct more large-scale quantitative study for nonadiabatic dynamics through symmetry-allowed conical intersections in excited state chemical reactions.

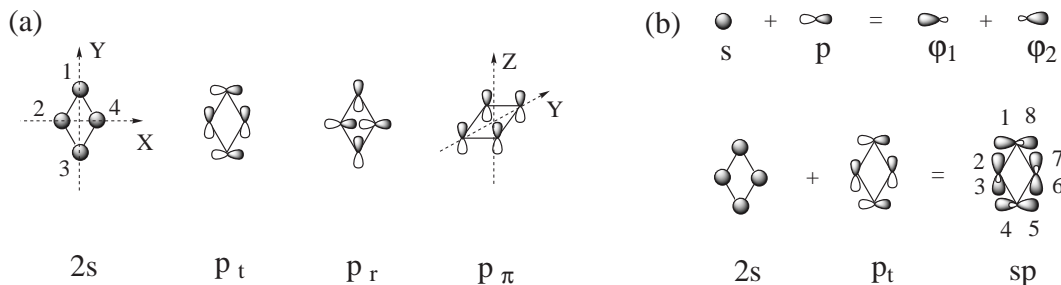


FIG. 1: (a) Bases functions used for the Hückel method. (b) $2s$ - p_t hybridization.

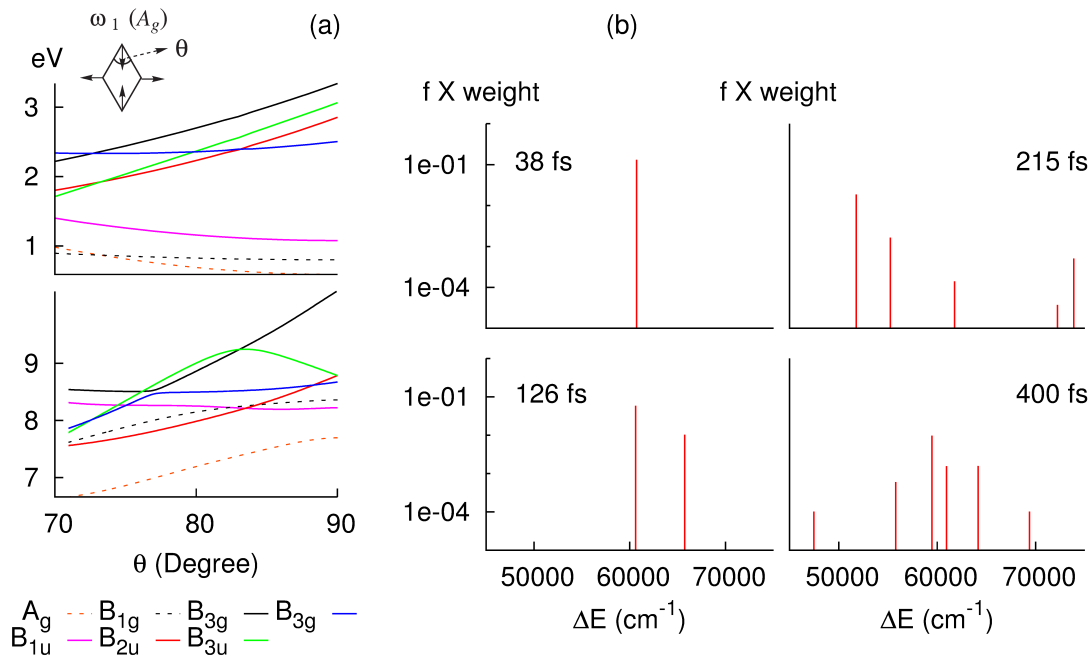


FIG. 2: (a) Excitation energies for the selected excited states by the Hückel theory (top) and the CISD/STO-3G method (down). (b) Spectral representation of the time-evolution of $^1B_{2u}$ state.