Dynamics on Electronic Excitation in Chemical Reaction

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Carrying out simplified theoretical simulations using the time-dependent Schrödinger equation on the basis of the time-dependent density functional theory (for electrons) coupled with the Newtonian equation of motion (for nuclei), we find that a chemical reaction, $Li_2+H_2 \rightarrow 2LiH$, takes place by the double excitation from the highest occupied molecular orbital (HOMO) level to the lowest unoccupied molecular orbital (LUMO) level. Along the reaction path, a level crossing occurs automatically between the highest occupied and lowest unoccupied levels and the electronic excited state changes smoothly into the electronic ground state leaving a kinetic energy of the molecules, i.e., a rapid energy transfer from the electronic excitation to the molecular motion of the order of 10 femto seconds.
Key words: time-dependent Schrödinger equation, spectral method, and a level crossing

1. INTRODUCTION

The electronic excitation opens new reaction channels of chemical reactions. It is interesting to study the chemical reactions at electronic excited states. When we simulate the dynamics on electronic excited states, we can avoid to use the potential energy surface (PES) [1,2] which is the most popular approach nowadays. Instead we can integrate directly the time-dependent *Schrödinger* equation (TDSE) within the framework of the time-dependent density functional (TDDF) theory [3,4]. The merit of doing it is to treat the wavepacket states as well as the steady states. In this paper we focus on the chemical reaction induced by double excitation in a simple system composed of Li_2 and H_2 and carry out the TDSE first-principle molecular dynamics (FPMD) simulation. In what follows, we present an explicit result of the dynamical simulation of $Li_2+H_2 \rightarrow 2LiH$.

2. THEORY

In integrating the TDSE

$$i\frac{\partial}{\partial t}\Psi_j(t)=H(t)\Psi_j(t), \qquad (1)$$

with respect to time, we introduce the spectral method [5]. This spectral method uses the eigenstate $\varphi_k(t)$ and the eigenvalue ε_j of the Hamiltonian $H(t)$, which satisfies

$$H(t)\varphi_k=\varepsilon_k\varphi_k. \qquad (2)$$

Here, $H(t)$ denotes just the electronic part. Since it depends on time, this eigenvalue problem must be solved at each time. Therefore, φ_k and ε_k have also the time dependence, although it is not expressed explicitly. The oscillation of the Hamiltonian $H(t)$ may appear for time which is typically 100-1000 times smaller than the time step for the atomic motion and continue for a time interval of the order of a femtosecond. However, when

the electronic states are not far from steady states, the Hamiltonian would not significantly change in time inside this transient time interval. We expand the wavepackets $\Psi_j(t)$ in terms of the eigenstates $\varphi_k(t)$ at the same time,

$$\Psi_j(t)=\Sigma_k c_{jk}(t)\varphi_k, \qquad (3)$$

where

$$c_{jk}(t)=<\varphi_k \mid \Psi_j(t)>. \qquad (4)$$

Hence, the basic time step Δt can be set as large as the time scale in which the Hamiltonian changes, one may integrate the TDSE as follows:

$$\Psi_j(t+\Delta t)=\Sigma_k c_{jk}(t)\exp(-i\varepsilon_k\Delta t)\varphi_k. \qquad (5)$$

In real numerical treatments, the sum with respect to the eigenstates in Eq. (5) is evaluated only over a finite number of low-lying exited states as well as the ground state. Those low-lying existed states should include also the free-electron continuum states above the vacuum levels. So we use the all-electron mixed basis approach [6-8] which uses plane waves (PW's) together with atomic orbitals (AO's) as basis functions. The all-electron mixed basis approach enables us to represent correctly the free-electron continuum states as well as the bound and resonance states within the all-electron formalism. For the treatment of exchange-correlation terms, we use the local-density approximation (LDA). For the Newtonian equation of motion for nuclei, we use the forces calculated as a derivative of the total energy, as formulated by Ho et al. [9]

3. RESULT AND DISCUSSION

We first consider the case of the electronic ground state. Assuming zero initial velocity, we start the

TDSE-FPMD simulation. The initial atomic geometry of Li$_2$ and H$_2$ molecules are placed to face each other with a distance on the order of the bond length with which the molecules appears in the reaction. Figure 1 shows the time-evolution of atomic motion. The two molecules, Li$_2$ and H$_2$, repel each other with slight interamolecular vibrations forming two isolated molecules. The trajectory is essentially the same as that obtained by the usual Car-Parrinello-type molecular dynamics simulation [4]. The time-evolution of the energy expectation values is shown in Fig. 2.

Next we consider the case of the doubly excited state from the highest occupied molecular orbital (HOMO) level to the lowest unoccupied molecular orbital (LUMO) level at the same initial geometry. The resulting trajectory [Fig. 3] is obviously quite different from the previous Fig. 1. This reaction yields two isolated LiH molecules. The motion of the atoms may be characterized as vibrations along the Li-H bond and repulsion between the LiH molecules. The initial H-H and Li-Li bond are broken very quickly. The balance of the Li-H bond is achieved near its ground-state bond length. The time-evolution of the energy expectation values is shown in Fig. 4 for doubly excited state.
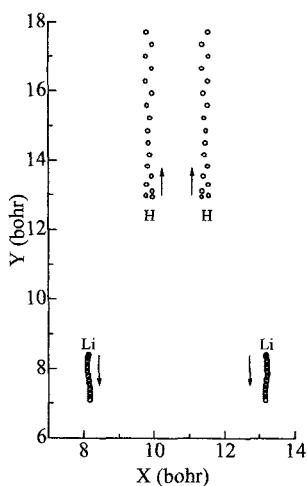

Fig. 1 The time evolution of atomic motion in the simulation starting from the ground state. The abscissa and ordinate represent, respectively, in the X and Y directions
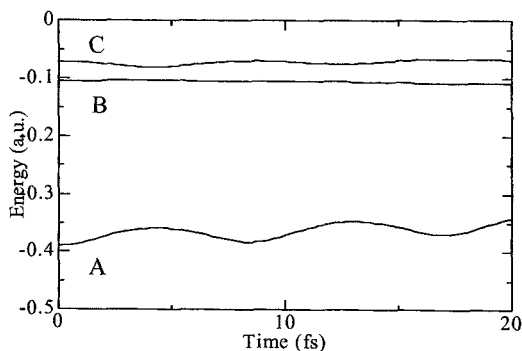

Fig. 2 The time-evolution of the energy expectation values of the valence electrons starting from the ground state. Level B is the highest occupied molecular orbital level. Level C is the lowest unoccupied molecular orbital level.

As seen in Fig. 4, a level crossing occurs between the highest occupied (C) and lowest unoccupied (B) levels approximately 10fs after the initial excitation. Since the present reaction proceeds nearly on the stationary state of the Hamiltonian at each time, it is possible to give a clear physical picture of the present reaction. We may consider only 1s orbital of H and 2s orbital of Li. Then, there are four possible electron levels, A, B, C and D, regardless of the spin multiplicity. First, level A has the lowest energy, representing the fully bonding molecular orbital (MO). Next, intermediate level B represents the bonding Li-Li and H-H and the anti-bonding Li-H MO, while level C represents the anti-bonding Li-Li and H-H and the bonding Li-H MO. Lastly, level D, having the highest energy, is characterized by the fully anti-bonding MO, although it is not shown in Figs. 2 and 4 because it exceeds the upper limit of vertical scale. Obviously there exists a bonding tendency between the Li and H atoms in levels A and C, and an anti-bonding tendency between the Li and H atoms in level B and D. Therefore, in the simulation starting from the ground state, in which level B is occupied and level C is empty, the two Li atoms attract each other and so do the two H atoms, because of the bonding tendency in the occupied levels A and B. On the other hand, in the simulation starting from the doubly excited state, in which level B is empty and level C is occupied, the Li and H atoms attract each other because of the bonding tendency in the occupied levels A and C. In fact, as shown in Fig. 4, levels A and C become closer to be degenerated and anti-bonding empty level B becomes higher when the Li and H atoms make bonds.

As a result of these bonding and anti-bonding tendencies, the level crossing occurs automatically when new molecules are synthesized. The occupied level C, which was originally higher than the empty level B, goes down due to the formation of the Li-H bonds and becomes lower than the empty level B without interlevel hopping. And the electronic energy plus potential energy between nuclei is lowered during this reaction, and the excess energy is all transferred into the kinetic energy of the atoms. In the way, the level crossing plays a key role in the process of the relaxation from the double excitation.
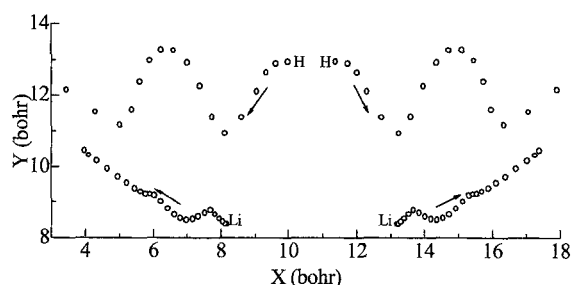

Fig. 3 The time evolution of atomic motion in the simulation starting from the doubly excited state

4. CONCLUSION

In this paper, by integrating the coupled equations of the TDSE-FPMD numerically with respect to time, we found a chemical reactions, Li$_2$+H$_2$→2LiH, in the double excitation. Along the reaction, a level crossing occurs between the HOMO and LUMO levels, according to Fukui's frontier orbital theory and Woodward-Hoffmann law [10-12]. From the present simulation, we can propose

a mechanism for relaxation of the reaction by the double excitation: electronic excited state changes smoothly into the electronic ground state leaving a kinetic energy of the atoms.
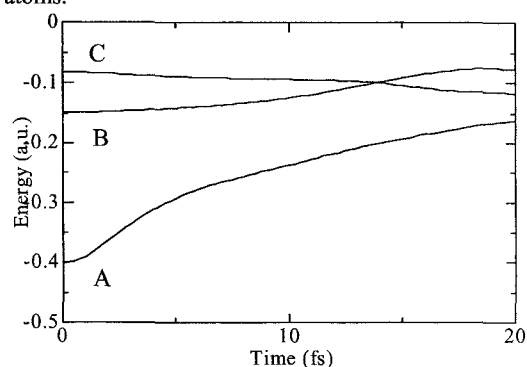

Fig. 4 The time-evolution of the energy expectation values of the valence electrons starting from the doubly excited state. By the double excitation, the electrons move from the highest occupied orbital level to the lowest unoccupied molecular orbital level. Level B is empty and levels A and C are occupied.

5. ACKNOWLEDGEMENT

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