Simulation of a Chemical Reaction, $2\text{LiH} \rightarrow \text{Li}_2 + \text{H}_2$, driven by doubly Excitation

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A direct computer simulation of reaction dynamics at the electronic excited states is not easy to perform, because nonadiabatic equations must be solved as a function of time. Here we present a simple simulation to integrate directly the time-dependent Schrödinger equation within the framework of the time-dependent density functional theory (for electrons) coupled with the Newtonian equation of motion (for nuclei). We find that a chemical reaction, $2\text{LiH} \rightarrow \text{Li}_2 + \text{H}_2$, takes place by the doubly excitation. Along the reaction, a level crossing occurs automatically between the highest occupied and lowest unoccupied levels. The simulation demonstrates a mechanism for relaxation for the reactions driven by doubly excitation: electronic excited state changes smoothly into the electronic ground state leaving a kinetic energy of the atoms.

1. INTRODUCTION

Chemical reactions are related to the dynamics on electronic excitation and attracting much current theoretical interest. It is important to understand the mechanics of chemical reactions. In the simulation, we adopt an approach to integrate directly the time-dependent Schrödinger equation (TDSE) within the framework of the time-dependent density functional (TDDF) theory [1,2]. In this paper, we carry out the TDSE first-principles molecular dynamics (FPMD) simulation and present an explicit result of a chemical reaction $2\text{LiH} \rightarrow \text{Li}_2 + \text{H}_2$, driven by doubly excitation. This work is a counterpart of our previous study of the reverse reaction, $\text{Li}_2 + \text{H}_2 \rightarrow 2\text{LiH}$ [3].

2. THEORY

We introduce the spectral method [4] in order to integrate the TDSE

$$i\frac{\hbar}{\mathcal{E}} \Psi_j(t) = H(t) \Psi_j(t),$$

where $\hbar$ denotes the reduced Planck constant. Here, $H(t)$ denotes just the electronic part. Since it depends on time, this eigenvalue problem must be solved at each time. Therefore, $\Psi_j(t)$ and $\epsilon_j$ have also the time dependence, although it is not expressed explicitly. An oscillation of the wavepackets $\Psi_j(t)$ may appear with a period which is typically 100-1000 times smaller than the time step for the atomic motion. However, when the electronic states are not far from steady states, the Hamiltonian does not change significantly in time, and we can expand the wavepackets $\Psi_j(t)$ in terms of the eigenstates $\phi_k(t)$ at the same time,

$$\Psi_j(t) = \sum c_{jk}(t) \phi_k,$$

where we put

$$c_{jk}(t) = <\phi_k | \Psi_j(t)>.$$

When the basic time step $\Delta t$ is set smaller than the time scale in which the Hamiltonian changes, one may integrate the TDSE (1) as follows:

$$\Psi_j(t+\Delta t) = \sum c_{jk}(t) \exp(-i\epsilon_k \Delta t) \phi_k.$$  

In real numerical treatments, the summation with respect to the eigenstates in Eq. (5) runs over a finite number of low-lying states. Those low-lying states should include also the free-electron continuum states above the vacuum levels. Here we use the all-electron mixed basis approach [5-7] 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. [8].

3. RESULT AND DISCUSSION

Assuming zero initial velocity, we start the TDSE-FPMD simulation. The initial atomic geometry of two $\text{LiH}$ 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 starting from the ground state (the first simulation). The two molecules, $\text{LiH}$, repel each other with slow intermolecular vibrations forming two isolated molecules. The trajectory is essentially the same as that obtained by the usual Car-Parrinello-type molecular dynamics simulation [2].
At the same initial geometry but starting from the doubly excited state in which the two electrons are moved from the highest occupied molecular orbital (HOMO) level to the lowest unoccupied molecular orbital (LUMO) level, we carry out the second simulation. The time-evolution of atomic motion in this case is shown in Fig. 2. The resulting trajectory (Fig. 2) is obviously quite different from the previous Fig. 1. This reaction yields Li₂ and H₂ molecules. The initial Li-H bond is broken very quickly. The time evolution of the energy expectation values is shown in Fig. 3 for the simulation starting from the ground state and in Fig. 4 for the simulation starting from the doubly excited state. Since the present reaction proceeds nearly on the steady 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-H and the anti-bonding Li-Li and H-H MO, while level C represents anti-bonding Li-H and the bonding Li-Li MO. Lastly, level D, having the highest energy, is characterized by the fully anti-bonding MO. Therefore, in the simulation starting from the ground state, in which level B is occupied and level C is empty, the two LiH atoms attract each other 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 atoms attract each other and the H atoms attract each other too, because of the bonding tendency in the occupied levels A and C. In fact, as shown in Fig. 4, H-H bonding level A and H-H anti-bonding level B vibrate according to the H₂ molecular vibration. Since H atoms vibrate strongly along the trajectory [Fig. 2], a level crossing occurs three times in Fig. 4. The occupied level C, which was originally higher than the empty level B, becomes eventually lower than the empty level B due to the formation of the Li-H bonds.

4. CONCLUSION

In this paper, we have carried out the TDSE-FPMD simulation and found that a chemical reaction, 2LiH → Li₂ + H₂, takes place by doubly excitation. As a result of the bonding and anti-bonding tendencies, the level crossing occurs automatically between the HOMO and LUMO, according to Fukui’s frontier orbital theory and Woodward-Hoffmann law [9-11], and the original excited state becomes the ground state when new molecules are synthesized. 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 doubly excitation.

The relation between the present reaction, 2LiH → Li₂ + H₂, and the reverse reaction, Li₂ + H₂ → 2LiH, presented in our previous paper [3] as well as the related reactions between H₂ and F₂ will be reported elsewhere.

![Fig. 1](image1.png)  
*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 coordinates.

![Fig. 2](image2.png)  
*Fig. 2* The time evolution of atomic motion in the simulation starting from the doubly excited state.

![Fig. 3](image3.png)  
*Fig. 3* The time-evolution of the energy expectation values of the electrons starting from the ground state.
Fig. 4 The time-evolution of the energy expectation values of the electrons starting from the doubly excited state.

REFERENCES
[1] E. Runge and E. K. U. Gross, *Phys. Rev. Lett.* **52**, 997 (1984).
[2] see for a review, K. Ohno, K. Esfarjani and Y. Kawazoe, “Computational Materials Science”, Solid-State Sciences, Vol. **129** (Springer-Verlag, Berlin, Heidelberg, 1999). : From Ab Initio to Monte Carlo Methods
[3] Takahiro Sawada, Jian Wu, Yoshiyuki Kawazoe and K. Ohno, *Trans. Mater. Res. Soc. Jpn.* to be published
[4] J. J. Sakurai, “Modern Quantum Mechanics” (The Benjamin/Cummings Publishing Company 1985) Sect. 2.1
[5] K. Ohno, F. Mauri, and S. G. Louie, *Phys. Rev. B* **87**, 1009 (1997).
[6] T. Ohtsuki, K. Ohno, K. Shiga, Y. Kawazoe, Y. Maruyama and K. Masumoto, *Phys. Rev. Lett.* **81**, 967 (1998).
[7] S. Ishii, K. Ohno, Y. Kawazoe, and S. G. Louie, *Phys. Rev. B* **63**, 155104 (2001).
[8] K. M. Ho, C. Elsässer, C. T. Chan and M. Fähnle, *J. Phys.: Condens. Matter* 4, 5189 (1992).
[9] K. Fukui, T. Yonezawa and H. Shingu, *J. Chem. Phys.* **20**, 722 (1952).
[10] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.* **87**, 395 (1965).
[11] J. Simons, “Quantum Mechanics in Chemistry” (Oxford Univ. Press, 1997).