Title	Effects of Non-Adiabatic Transitions on Proton Dynamics(4) Quantum chaos and semiclassical theory in molecular science and nuclear theory, Chaos and Nonlinear Dynamics in Quantum-Mechanical and Macroscopic Systems)
Author(s)	Taniguchi, Akira; Nagai, Yuji; Natsume, Yuhei
Citation	物性研究 (2005), 84(3): 495-496
Issue Date	2005-06-20
URL	http://hdl.handle.net/2433/110203
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

Effects of Non-Adiabatic Transitions on Proton Dynamics

Graduate School of Science and Technology, Chiba University
Akira Taniguchi*, Yuji Nagai†, Yuhei Natsume‡

30 January 2005

Abstract

水素分子では反結合励起状態に置かれた波束はすぐに広がってしまう。これは水素分子が二つの水素に解離することに対応している。しかしながら、準位間遷移のために、波束のほんの少しは結合基底状態に落ちていく。本研究ではプロトン三つと電子一つの系の振る舞いをみた。準位間遷移を考慮に入れて計算した。計算では両側のプロトンを固定し、中央のプロトンの感じる断熱ポテンシャルを求めた。そのポテンシャル準位間の遷移はエネルギー的に接近している中心点で起こっていることがわかった。

It is well confirmed that the wave packet of the hydrogen molecule H_2, which is set at the excited anti-bonding level, spreads quickly. This corresponds to the dissociatioin into two atoms $2H$. However, quite a little part of it falls into the ground bonding level for H_2 because of the transition between energy levels. In the present work, we apply the transitions between levels of adiabatic potentials (AP) to the system which consists of three protons and an electron. In calculation, AP is obtained under the condition that two protons are fixed with distance R_2 as there in Fig1. Resultly, those transitions are occurred at the center point of R_2 where levels of AP get close each other. In calculation, we take transition between levels into account.

1 Hamiltonian and Model

We discuss the model whose Hamiltonian is described as

$$\begin{aligned} H &= \frac{-\hbar^2}{2m}\nabla^2 - \frac{e^2}{r} - \frac{e^2}{|\mathbf{r}-\mathbf{R}_1|} - \frac{e^2}{|\mathbf{r}-\mathbf{R}_2|} \\ &\quad + \frac{e^2}{R_1} + \frac{e^2}{R_2} + \frac{e^2}{|\mathbf{R}_2-\mathbf{R}_1|} - \frac{\hbar^2}{2M}\nabla^2_{\mathbf{R}_1}, \end{aligned}$$

where m and M are masses of the electron and the proton. As shown in Fig1, the distance between the left proton and center proton is R_1. Further, r is the position of the electron.

The solution of the Schrödinger equation is

$$\Psi(\mathbf{r},\mathbf{R}_1,t) = \sum_{n=1}^{3} F_n(\mathbf{R}_1,t)\,\varphi_n(\mathbf{r},\mathbf{R}_1),$$

where $F_n(\mathbf{R}_1,t)$ and $\varphi_n(\mathbf{r},\mathbf{R}_1)$ are wave functions of center proton and the electron. Here, n indicates the AP for this $3H^+$ system. As for the electron, $\varphi_n(\mathbf{r},\mathbf{R}_1)$ is expanded as follows;

$$\begin{aligned} \varphi_n &= A_n(R_1)\phi(\mathbf{r}) \\ &\quad + B_n(R_1)\phi(\mathbf{r}-\mathbf{R}_1) \\ &\quad + C_n(R_1)\phi(\mathbf{r}-\mathbf{R_2}), \end{aligned}$$

where $\phi(\mathbf{r}) = \frac{1}{\sqrt{\pi}}\exp(-r)$, *i.e.* 1s orbital for H atom. In the procedure of adiabatic approximation we get $E_n(R_1)$. Accordingly, $F_n(\mathbf{R}_1,t)$ is obtained in the following expression from the integration of r;

*E-mail: akiragogo@graduate.chiba-u.jp
†E-mail: yuji-ng@phys8.s.chiba-u.ac.jp
‡E-mail: natsume@science.s.chiba-u.ac.jp

$$
\begin{aligned}
i\hbar\dot{F}_n &= \left[\frac{-\hbar^2}{2M}\nabla^2_{R_1} + E_n(R_1)\right] F_n \\
&\quad -\frac{\hbar^2}{2M}\sum_{n'}\left\{2\nabla_{R_1}F_{n'}\cdot\int\varphi^*_n\nabla_{R_1}\varphi_{n'}d\mathbf{r}\right\} \\
&\quad -\frac{\hbar^2}{2M}\sum_{n'}\left\{F_{n'}\int\varphi^*_n\nabla^2_{R_1}\varphi_{n'}d\mathbf{r}\right\}.
\end{aligned}
$$

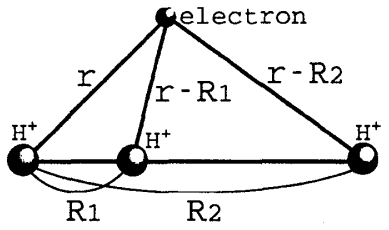

Figure 1: the present system

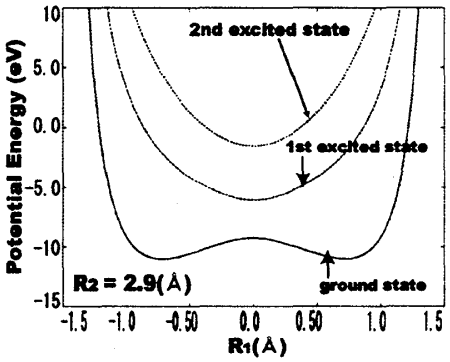

Figure 2: Adiabatic potential vs. R_1

2 Numerical results

The obtained AP vs. R_1 are shown in Fig.2. In those AP , the behavior of wave packets is illustrated in Fig.3, where (a), (b) and (c) are that for ground, 1st excited and 2nd excited states, each other. The transitions of wave packets between three levels are found to be restricted to the center position, where AP get close each other.

Transition probability to second excited state is more than to ground state when initial state is set at the first excited state. We suspect wave packets of an initial state has more energy than difference between those levels.

We would like to point out that the center proton has a tendency to remain at the center point, though the separation to the hydrogen molcule and one hydrogen ion is expected to be found finally. There remains problem of the relationship between present results and the chaotic behavior.

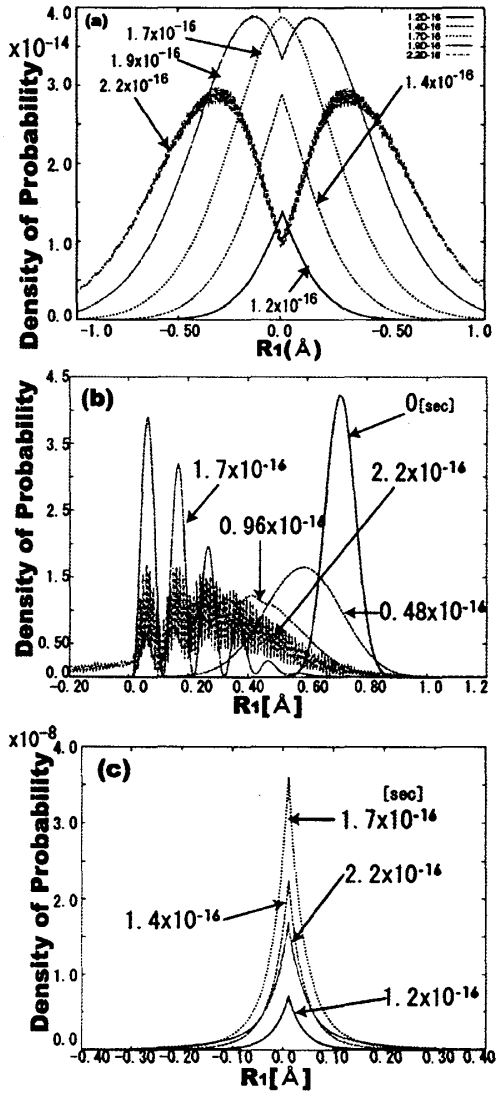

Figure 3: The behavior of wave packets with increasing time in the ground state (a), 1st excited state (b) and 2nd excited state (c) respectively. The initial state is set at first excited state as shown in (b).