<div align="center">論文の内容の要旨</div>

<div align="center">論文題目</div>

Quantum dynamics of H$_2$ molecule described by an electron-nuclear wave function with floating Gaussians

<div align="center">(浮動ガウシアン電子–原子核波動関数を用いた水素分子の量子動力学)</div>

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INTRODUCTION

In intense laser fields, unique phenomena of atoms and molecules can be observed such as tunnel ionization, recollision of ionized electron, Coulomb explosion of multiply charged ions, and molecular dynamics depending on carrier-envelop phase (CEP) of laser pulse. In order to describe such dynamics theoretically, it becomes necessary to treat the electronic motion associated with ionization induced by the interaction with the strong electric field and long time dynamics during and after the duration of excitation laser pulse. Extensive numerical simulations are also required for different laser pulse conditions such as pulse duration, strength, polarization, and CEP. Naturally, the computational time and required memory size for the simulation become much larger than in stationary state calculations, for which various efficient quantum chemistry software are available. In an intense laser field where laser field intensity is in the range of $10^{13} \sim 10^{15}$ W/cm^2, ultrafast proton migration within hydrocarbon molecules has been identified. In order to discuss the correlated motion among electrons and nuclei, it would also be necessary to treat the nuclear motion quantum mechanically.

In the present study, quantal dynamics of H$_2$ molecule in intense laser fields is simulated by combining a coupled coherent states (CCS) description of the orbital functions and an electron-nuclear wave function approach. A CCS is a floating Gaussian and is expressed by

$$\langle \boldsymbol{x}|G_m(t)\rangle = \left(\frac{\gamma_m}{\pi}\right)^{\frac{3}{4}} \exp\left(-\frac{\gamma_m}{2}(\boldsymbol{x}-\boldsymbol{q}_m(t))^2 + \frac{i}{\hbar}\boldsymbol{p}_m(t)(\boldsymbol{x}-\boldsymbol{q}_m(t)) + \frac{i\boldsymbol{p}_m(t)\boldsymbol{q}_m(t)}{2\hbar}\right), \qquad (1)$$

where $\boldsymbol{q}_m(t)$ denotes the center position of the floating Gaussian $|G_m(t)\rangle$, $\boldsymbol{p}_m(t)$ the momentum, and $1/\gamma_m$ the width of $|G_m(t)\rangle$. In the conventional grid approach, the more grid points are needed with the larger spatial range to describe the electronic motion. Therefore, numerical calculations demand growing costs with respect to the computational time and required memory size. In contrast to this situation, the total number of numerical operations to propagate a wave function for a single time step of simulation is independent of the spatial domain for a wave function when the wave function is expressed by using CCSs, where we are able to write differential operations and integrals of orbital functions in analytical forms. Hence the low calculation cost can be achieved by CCS method compared with conventional grid point method.

In the present research, the equations of motion (EOMs) in order to describe the dynamics of the electron-nuclear wave function $\Psi(t)$ are derived. The ground-state wave function of an H_2 molecule is calculated by utilizing the EOMs and the molecular responses to the intense laser fields of different CEPs are investigated.

THEORY

In the non-relativistic quantum mechanics, the action S is defined as a time-integral of the Lagrangian $L(t)$ of the relevant system as follows:

$$S = \int_{t_1}^{t_2} L(t)\, dt, \quad L(t) = \left\langle \Psi(t) \left| i\frac{\partial}{\partial t} - \hat{H}(t) \right| \Psi(t) \right\rangle, \tag{2}$$

where $\hat{H}(t)$ denotes the time-dependent Hamiltonian for the system, in general. We use the atomic unit (a.u.). The EOMs for the parameters $\{\xi_j(t)\}$ used to describe a wave function such as the center positions and the momenta of floating Gaussians and orbital coefficients are derived based on the principle of least action expressed as,

$$\delta S = 0 \quad \Rightarrow \quad \frac{\partial H(t)}{\partial \xi_i(t)} = i\left(\left\langle \frac{\partial \Psi(t)}{\partial \xi_i^*(t)} \middle| \dot{\Psi}(t) \right\rangle - \left\langle \dot{\Psi}(t) \middle| \frac{\partial \Psi(t)}{\partial \xi_i(t)} \right\rangle\right) = \sum_j c_{ij}(t)\, \dot{\xi}_j(t), \tag{3}$$

where $H(t) = \langle \Psi(t)|\hat{H}(t)|\Psi(t)\rangle$ and $\dot{\xi}_j(t) = \partial\xi_j(t)/\partial t$.

In the present study, the wave function $|\Psi\rangle$ of an H_2 molecule is approximated by a product of a two-electron Slater determinant $|\alpha\rangle$ and a two-proton Slater determinant $|\beta\rangle$ as

$$|\Psi\rangle = |\alpha\rangle|\beta\rangle. \tag{4}$$

Here time-dependent orbital function for i-th particle is expressed as a linear combination of CCSs as

$$|i(t)\rangle = \sum_m \mu_m^i(t)|G_m(t)\rangle \quad (1 \le i \le 4), \tag{5}$$

where $\mu_m^i(t)$ denotes a time-dependent orbital coefficient. The indices $i = 1$ and 2 are used for two electrons, and $i = 3$ and 4 for two protons. I derived the analytical expressions of $\partial H/\partial \xi_i$ and c_{ij} in Eq. (3). Then by numerically integrating EOM for $\dot{\xi}_j$ in time, we can obtain the time-dependent dynamics of wave function of Eq. (4). The numerical calculations were performed using program codes I wrote in MATLAB language.

RESULTS AND DISCUSSION

Ground-state electron nuclear wave function

First, the ground-state electron-nuclear wave function of H_2 molecule is prepared using nine CCS function. Both Slater determinants of electrons and protons were set in the singlet configuration. The ground-state wave function can be obtained by optimizing the parameters $\{\xi_j\}$ by an imaginary time propagation (ITP) technique using the unperturbed molecular Hamiltonian. Figure 1 shows the variation of the total energy during the imaginary time

propagation. The total energy was converged to -1.0684 a.u. at $\tau = 500$ a.u. This total energy is slightly lower than -1.0523 a.u. obtained by the previous study in which the TRC-NOMO/HF method is adopted. The slight improvement may be ascribed to the optimization in the position of the Gaussian functions. To start the ITP calculation, initially CCS functions are placed symmetrically with respect to $x = 0$ on the x-axis. The parameters optimized in this ITP were the center positions and the momenta of floating Gaussians and orbital coefficients μ_m^i.
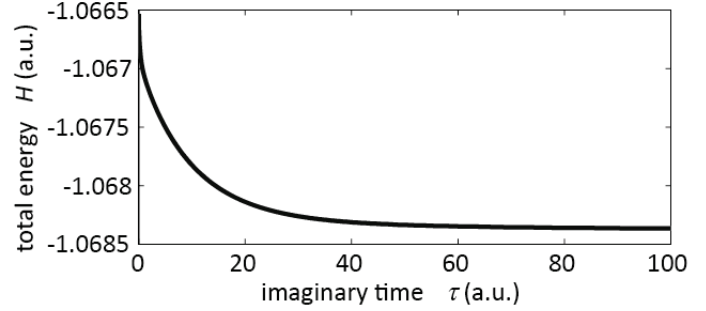
To verify the molecular dynamics obtained from this model, a vibrational period of the ground state of H_2 molecule was estimated in the following manner. By displacing the optimized positions of the respective Gaussian functions by 0.001 a.u. symmetrically with respect to $x = 0$, we can artificially induce a small amplitude molecular vibration since the optimized ground-state is a stationary state. The real time dynamics starting from the displaced configuration are shown in Fig. 2. We can see the several components of vibrational periods for nuclei and electrons. From Fourier transformation it is shown that the vibronic motion of the outer basis of electrons has the frequency component corresponding to the time period of 6.5 a.u. (160 as) and that of the inner basis of electrons has 1.7 a.u. (40 as). Two bases of nuclei have 340 a.u. (8.2 fs), which is consistent with 331 a.u. (8.0 fs) of experimental value of the vibrational period. For the oscillating behaviors for the electronic basis, we can see fast time periods in addition to the same long time periods for nuclear vibration, which may reflect the excitation energy of the electronic states induced by the non-adiabatic coupling between nuclei and electrons.

Figure 1: Variation of the total energy $H = \langle \Psi|H|\Psi \rangle$ in imaginary time. (1 a.u. = 24.19 as)

Figure 2: Variations of the center positions of the Gaussians in real time. (a) Center positions of bases of nuclei. (b) Center positions of bases of electrons.
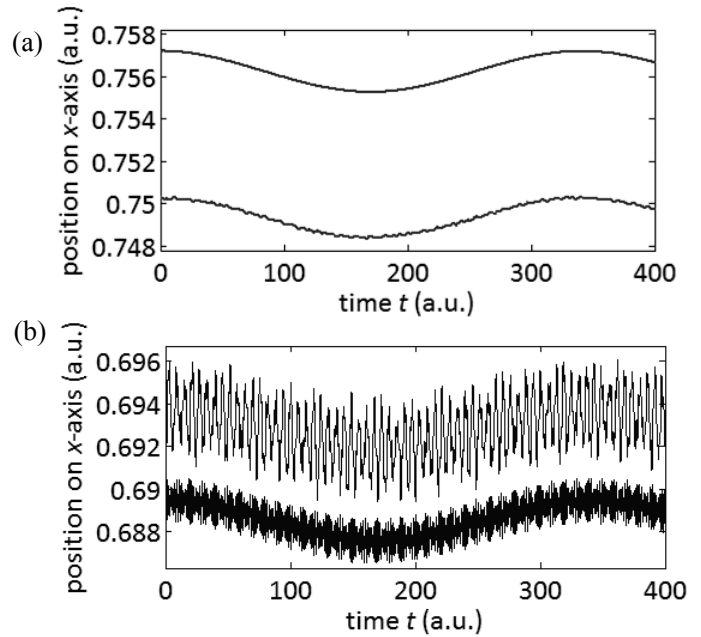
Molecular dynamics in a strong laser field

Next, the molecular dynamics in strong laser fields are examined. We used four CCS functions to describe the orbitals of Eq.(5). Figure3 (a)-(d) show the CEP dependences of the electron and proton dynamics. The laser field $E(t)$ applied to the molecule is expressed as

$$E(t) = E_0 \varepsilon(t)\sin(\omega t + \phi), \tag{6}$$

where E_0, $\varepsilon(t)$, ω, and ϕ denotes the peak intensity, pulse envelope, frequency and CEP respectively. Figure 3 (a) shows the electric field amplitudes adopted in the calculation. Figure 3 (b)-(d) show the time variations of center

positions of Gaussians with CEPs of $\phi = 0, 2.0345,$ and $\pi/2$ respectively. In Figure 3 (b), one electron is ejected at the peak intensity of the pulse and the other electron remains bound in the core. In Figure 3 (c), a single ionization occurs but the recollision of the electron to the bound electron can be observed. This is a characteristic phenomenon observed in intense laser field experiments. Furthermore the double ionization after the recollision can be observed in Figure 3 (d). This double ionization occurs after interaction of two electrons during $t = 50\sim100$ a. u. and can be recognized as a non-sequential double ionization in contrast to a sequential double ionization. From the comparison of Figure 3 (c) and (d), we can see that a small change of the CEP has a large impact on the fate of the molecular ionization.
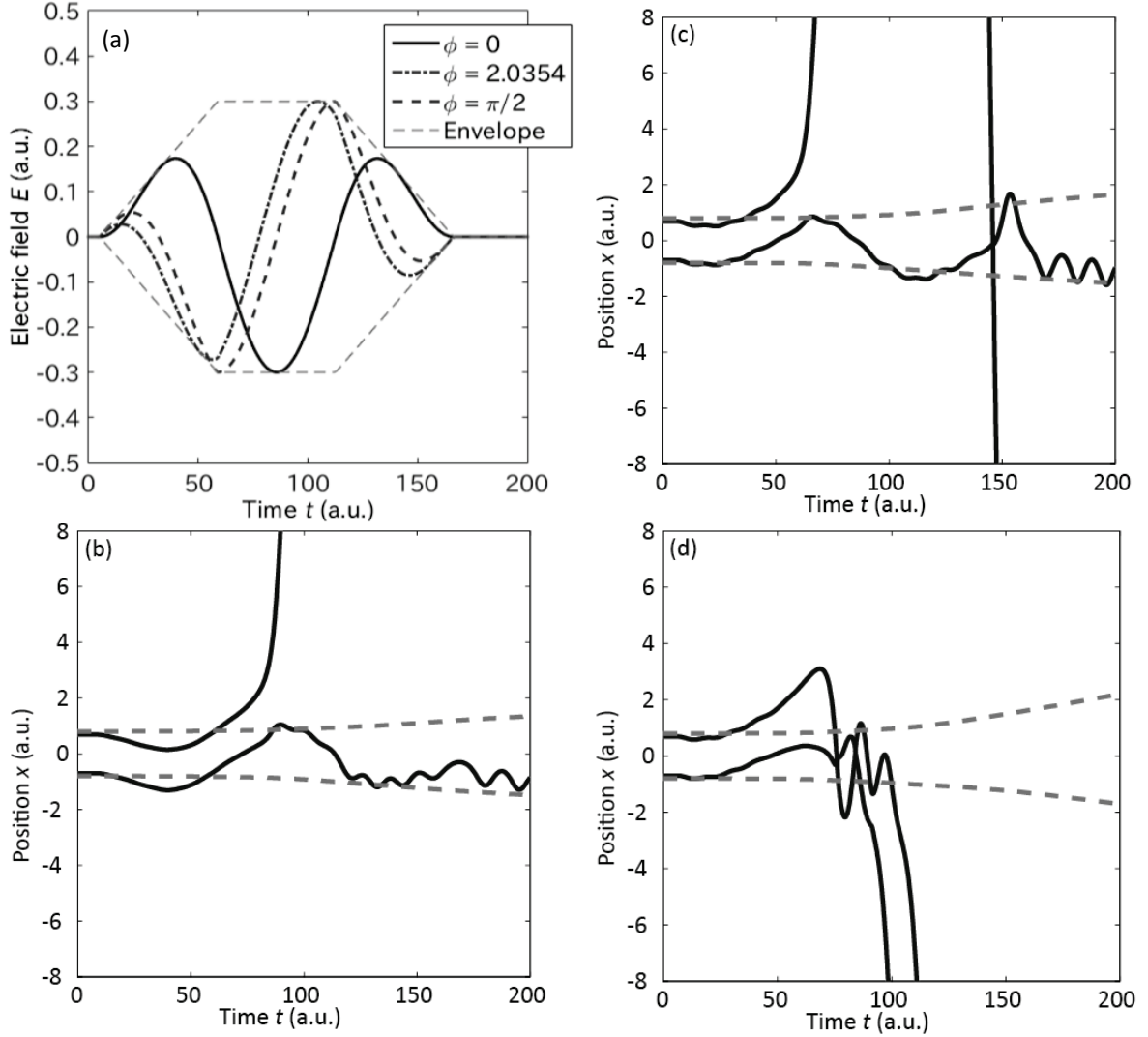
Figure 3: (a): Electric field amplitudes of three pulses adopted in the simulation. Three lines with legends represent carriers and dashed lines represent the envelope. (b): Variations of the center positions of the Gaussian bases with the CEP of $\phi = 0$. (c): Results with the CEP of $\phi = \pi/2$. (d): Results with the CEP of $\phi = 2.0354$ radian. On (b)-(d), solid lines show the center positions of electronic bases and dashed lines show those

CONCLUSION

A time-dependent quantal theory for electron-nuclear wave function using CCSs was developed. We applied the method to describe the electron-proton wave function of an H_2 molecule. From the numerical simulations, we comfirmed that the ground-state energy is consistently evaluated with the previous works and that the CEP of the few cycle strong laser pulse has a large impact on the fate of the molecular ionization.