

## 論文の内容の要旨

### 論文題目

Molecular wave functions of  $H_2$  by multiconfiguration time-dependent Hartree-Fock method  
(多配置時間依存 Hartree-Fock 法による  $H_2$  の分子波動関数)

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### 1. Introduction

In an intense laser field, motions of electrons and nuclei within a molecule are strongly coupled through their interaction with the external electric fields of light, and their coupled motions play an important role in dynamical processes of molecules induced by the intense laser field such as enhanced ionization and ultrafast structural deformation. Because the coupled motions of electrons and nuclei become so complicated in an intense laser field that the molecular wave functions could not be described appropriately by the standard Born-Oppenheimer (BO) approximation. Therefore, for example, when describing ionization processes of  $H_2^+$  induced by an intense near-IR laser field, the Born-Huang (BH) expansion method was adopted for treating coupled motions of an electron and two nuclei beyond the BO approximation. However, in the BH expansion, adiabatic electronic states need to be calculated for all the possible nuclear configurations, which are too demanding even nowadays for general classes of molecules. In order to overcome this difficulty, the multiconfiguration time-dependent Hartree-Fock (MCTDHF) method was extended to describe correlated electron-nuclear dynamics within a molecule.

In this thesis, within the framework of this extended MCTDHF method, I have developed computational codes with which I derive numerically molecular wave functions of a one-dimensional  $H_2$  molecule, and examined the numerical performance of this extended MCTDHF method. Through the comparison of the calculated results with those obtained by the BH expansion method, it was revealed that the MCTDHF method requires approximately two orders of magnitude smaller memory size than the BH expansion method for describing molecular wave functions with the same level of accuracy. It was also confirmed from the calculation of the virial ratios that the

wave functions derived by the MCTDHF method fulfill the virial theorem.

### 【Model and method】

In this thesis, I have chosen a one-dimensional hydrogen molecule,  $H_2$ , as a model molecule. The molecular wave function of this model molecule  $\Phi$  can completely be described by two electron coordinates and one internuclear (proton-proton) distance, and numerically exact wave functions can be obtained for both stationary and time-dependent cases as three dimensional and four (the three coordinates and time) dimensional functions, respectively. Therefore, the performance of a method of approximation such as the extended MCTDHF method and the BH expansion method can readily be evaluated by referring to the numerically exact results.

In the BH expansion, a time-dependent molecular wave function is expressed as

$$\Phi^{\text{BH}}(x_1, x_2, R, t) = \sum_{\mu} \chi_{\mu}(R, t) \Psi_{\mu}(x_1, x_2; R), \quad (1)$$

where  $x_j = (r_j, \sigma_j)$  ( $j = 1$  and  $2$ ) denotes a set of the spatial and spin coordinates of the  $j$ -th electron and  $\chi_{\mu}(R, t)$  denotes the nuclear amplitude in the  $\mu$ -th electronic adiabatic state,  $\Psi_{\mu}$ . On the other hand, in the extended MCTDHF method, a molecular wave function is expanded as

$$\Phi^{\text{MC}}(x_1, x_2, R, t) = \sum_I C_I(R, t) \Phi_I(x_1, x_2, t), \quad (2)$$

where  $C_I(R, t)$  called a CI-vector element denotes the amplitude of the internuclear distance for the  $I$ -th electronic configuration represented by the Slater determinant,  $\Phi_I$ . This CI-vector element corresponds to a CI-coefficient, which depends parametrically on  $R$ , in the standard electronic structure calculations of molecules.

The electronic adiabatic states  $\{\Psi_{\mu}\}$  in the BH expansion are defined at a given internuclear distance  $R$ , and are parametrically dependent on  $R$ , while the electronic spin-orbitals  $\{\varphi_k(x, t)\}$  in the electronic configurations  $\{\Phi_I\}$  in the extended MCTDHF method have no dependence on  $R$ . If we can expand the molecular wave function in Eq.(2) using a complete set of the spin-orbitals,  $\Phi^{\text{MC}}$  becomes an exact wave function. In my thesis work, I have examined the efficiency of the extended MCTDHF method through the comparison of the accuracies achievable by the two methods with a finite expansion length.

For the numerical evaluation, I express all the functions appearing in the calculations by numerical values at respective grid points located on the one dimensional axis. The spatial domain for the electronic coordinate  $r$  is  $[-15 a_0, 15 a_0]$  and the grid spacing is  $\Delta r = 0.2 a_0$ , while the domain of the internuclear distance  $R$  is  $[-5 a_0, 5 a_0]$  and the grid spacing is  $\Delta R = 0.05 a_0$ , where  $a_0$  is the Bohr radius. The differential operations on a function expressed numerically at the grid points are performed by the five-point finite difference method.

In this thesis, I have investigated the properties of the ground state wave function of a one-dimensional  $H_2$ . First, by solving the equations of motion (EOMs) for the extended MCTDHF method, the spin-orbitals and the CI-vector elements in Eq.(2) optimized for the ground state wave function were obtained by the imaginary time propagation starting with their initial trial values. In order to describe the wave function,  $n N_r + n^2 N_R$  grid points are necessary, where  $N_r$  and  $N_R$  denote respectively the grid points for  $r$  and  $R$ , and  $n$  is the total number of independent spatial orbitals included in the expansion of Eq.(2). On the other hand, by the BH expansion, in which  $n N_r N_R + n^2 N_R$  grid points are required, the adiabatic states  $\{\Psi_{\mu}\}$  are calculated by the full-CI method using the

numerical electronic orbitals optimized for the electronic ground state. After calculating the electronic structures, the nuclear amplitudes  $\{ \chi_\mu \}$  were obtained by solving the time-independent Schrödinger equation.

## 【Results and Discussion】

In Fig. 1, the expectation values of the total energy  $E_g(n)$  are plotted as a function of the total number of the grid points required to describe the molecular wave function composed of  $n$  ( $= 1 \sim 5$ ) electronic orbitals. As clearly seen in this figure, the grid points required in the extended MCTDHF method is about two orders of magnitude smaller than the BH expansion, while the expectation value of the total energy converges to the exact value  $E_g^{\text{EX}}$  in a similar manner to each other when  $n$  increases from 1 to 5. This result shows that the extended MCTDHF method reduces the calculation cost significantly without losing the accuracy.

Next, by using the ground state wave functions obtained above, I have calculated the spatial distribution function of electrons  $\rho_e(r)$  and the distribution function of the internuclear distance  $\rho_d(R)$  as shown in Fig. 2 for  $n = 1, 2$ , and 5. When  $n = 5$ , for both of the two expansion methods, the distribution functions  $\rho_e(r)$  and  $\rho_d(R)$  coincide with the exact distributions.

Furthermore, I have examined the accuracy of the extended MCTDHF method by calculating the virial ratio defined as the ratio of the expectation value of the kinetic energy with respect to that of the potential energy. From the exact wave function, we should have the ratio of 2. The calculated virial ratios listed in Table 1 show that they are very close to 2 for all the  $n$  values, showing that the molecular wave function obtained by the extended MCTDHF method satisfies the virial theorem with high accuracy.

I have shown from the present study that the extended MCTDHF method is an accurate and efficient expansion method for describing stationary molecular wave functions. Because this extended MCTDHF method can also be used to describe time-dependent molecular wave functions, the extended MCTDHF method can be regarded as a promising theoretical method by which non-perturbative phenomena of molecules such as those induced by an external laser fields are treated.

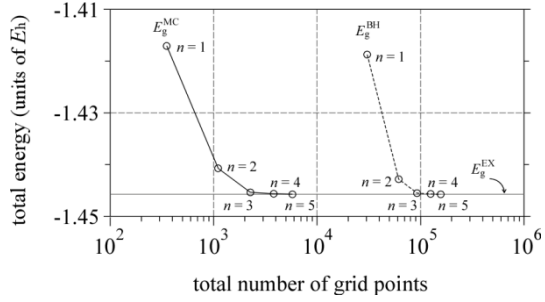


Fig.1. The expectation values of the total energy  $E_g$  by the extended MCTDHF method (solid line), the BH expansion method (dashed line). The numerically exact value  $E_g^{\text{EX}}$  (gray solid horizontal line).

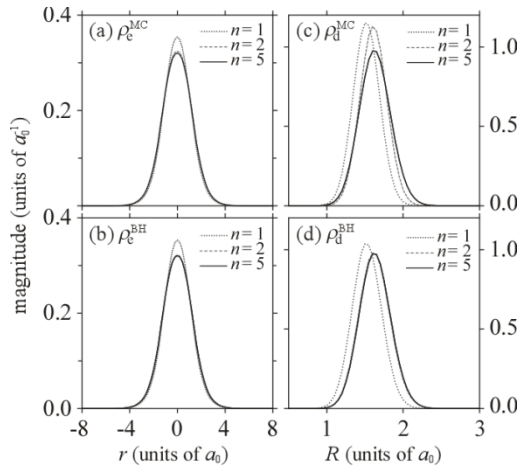


Fig.2. The distribution functions of electrons calculated by the extended MCTDHF method (a) and the BH expansion (b), and the distribution functions for the internuclear distance calculated by the extended MCTDHF method (c) and the BH expansion method (d). Only the results obtained using  $n = 1, 2$ , and 5 are plotted.

Table 1. The  $n$  dependence of the virial ratio calculated by the ground state molecular wave function of a one-dimensional  $\text{H}_2$  obtained by the extended MCTDHF method.

$n$	Virial ratio
1	1.999 930
2	1.999 913
3	1.999 767
4	1.999 562
5	1.999 857