Extended Multi-configuration Time-dependent Hartree-Fock Method for Coupled Electronic and Protonic Motion of Methanol in Intense Laser Fields

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Introduction

◆ Background

The multi-configuration time-dependent Hartree-Fock (MCTDHF) method [1] has been applied to investigate laser induced electronic excitation of molecules.

◆ Research Purpose

In order to describe coupled motion of protons and electrons in hydrocarbon molecules exposed to an intense laser field, we proposed an extended MCTDHF(Ex-MCTDHF) method [2], in which the quantal dynamics of protons and that of electrons are treated on the same footings.

◆ Recent Progress

We numerically implemented a simulation of electro-protonic quantal dynamics of a methanol molecule by Ex-MCTDHF, which shows good convergence in real time propagation.

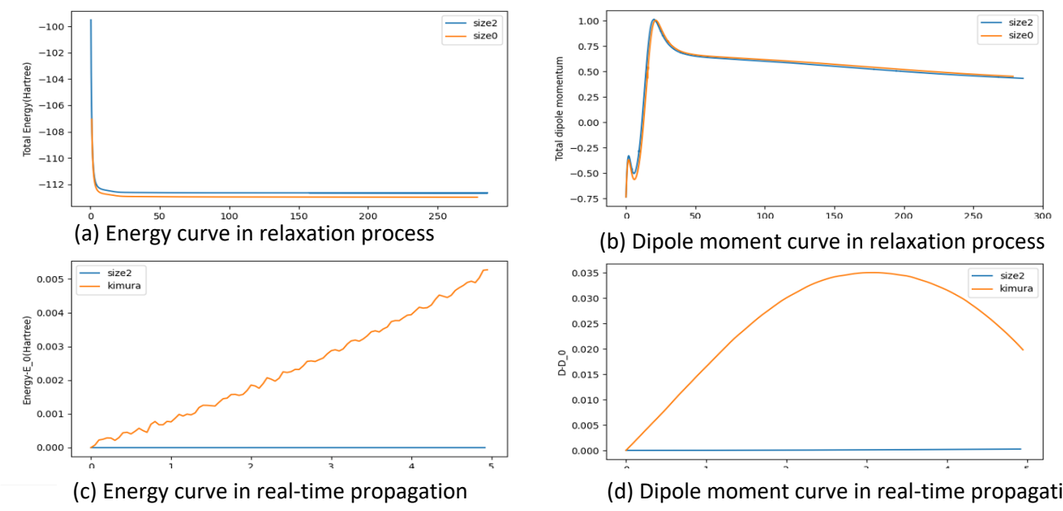
Result and Discussion

◆ Imaginary time propagation

We performed the imaginary time propagation on grid boxes with different number of grid points and find the resultant electro-protonic ground-state wave function exhibits good convergence in the total energy and the induced dipole moment in the real-time propagation, as is showed in **Figure 2**(a,b). The energy is converged, and dipole moment is decreasing slowly, showing the wavefunction is close its to ground state.

◆ Real time propagation

In order to check the convergence of our method, we performed the real time propagation without external laser field. Under this situation, both the energy and dipole moment of the molecule should remain unchanged. As is showed in **Figure 2**(c,d), compared with the previously adopted Lanczos method, we were able to suppress significantly the numerical error in the total energy to 10^{-6} and that in the induced dipole moment to 5×10^{-3}. The significant reduction of the errors in the real-time propagation will allow us to perform accurate calculations of the electro-protonic quantal dynamics in methanol in an intense laser field.



(a) Energy curve in relaxation process
(b) Dipole moment curve in relaxation process
(c) Energy curve in real-time propagation
(d) Dipole moment curve in real-time propagation

Figure 2: Total energy and dipole momentum of methanol in imaginary-time relaxation(a,b) and real-time propagation(c,d). The blue line and the orange line represents the modified method and the original method, respectively.

Method for Molecular Simulation

◆ Time-dependent electro-protonic Ansatz for representing wavefunction

Methanol molecule is represented by the time-dependent electro-protonic ansatz as

$$\Psi(\boldsymbol{x},\boldsymbol{y},t;R)=\sum_J C_J(t)\Phi_{\mathrm{elec}}(\boldsymbol{x},t;R)\Phi_J(\boldsymbol{y},t;R) \qquad (1)$$

where $\boldsymbol{x}$ and $\boldsymbol{y}$ denote the set of spatial and spin coordinates of 18 electrons and 4 protons, respectively. The fixed internuclear distance C-O is represented by R being treated as an adiabatic parameter. The Hartree-Fock amplitude for the electronic system is denoted as $\Phi_{\mathrm{elec}}(t)$ and a Slater determinant for the protonic system as $\Phi_J(t)$.

◆ Grid representation for time-dependent orbitals

The orbitals for protons and electrons are represented by 2-dimensional grids, which can describe the methanol molecule in a 3-dimensional cylindrical coordinate system by adapting Dual Transformation Technique, as is showed in **figure 1**. The parameters for setting the grid box is listed in **table 1**.

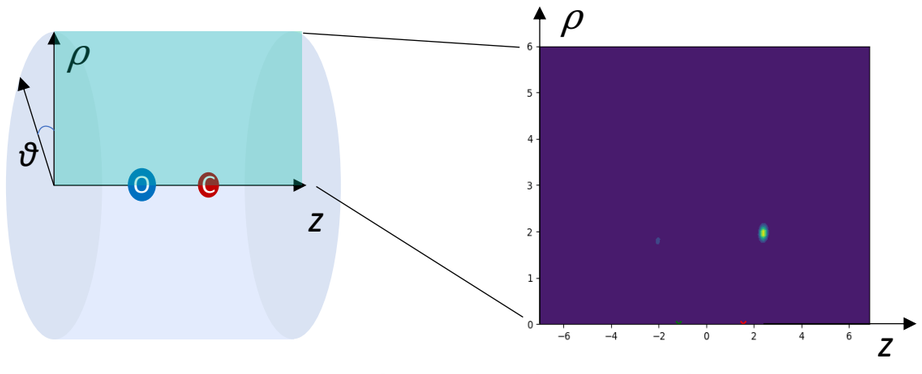


Figure 1: Grid representation for protons' orbitals of methanol molecule

Table 1: Parameters for grid box

Direction	ρ	z
Number of points	70	210
Axis range (a.u.)	0 ~ 6	-7 ~ 7

◆ Time-integration scheme for propagating the wavefunction

We derived the equation of motion(EOM) from Dirac-Frenkel's time-dependent variational principle, and 4th order Runge-Kutta scheme is adapted in propagating methanol's wavefunction both in imaginary time, to obtain the ground-state wavefunction, and real time, to validate the convergence of ground-state we obtained.

Conclusions

- We found a set of optimized settings for performing numerical calculations of electro-protonic dynamics of methanol molecule by the Ex-MCTDHF method.
- The ground state for methanol molecule is obtained and validated by real-time propagation.
- The time-integration scheme is modified from Lanczos method to 4th order Runge-kutta method, to suppress the numerical error significantly, which makes the theoretical study on molecule-laser possible.

Perspectives

Further studies are focused on finding a more efficient way performing numerical calculations. We are also performing the calculations with the laser pulse of different Carrier-Envelop Phases.

References

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[3] T. Kato, K. Yamanouchi, *Phys. Rev. A*, **85**, 034504 -1-5 (2012).