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拡張された時間依存多配置波動関数法によるCH₃OHの電子-プロトン 波動関数の実時間発展

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Real-time propagation of electro-protonic wavefunctions of CH₃OH by extended multiconfiguration time-dependent Hartree-Fock method

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[Abstract] In order to describe theoretically the ultrafast motion of protons within a hydrocarbon molecule induced by an intense laser field, we developed a calculation code of the extended multiconfiguration time-dependent Hartree-Fock (MCTDHF) method, in which both electrons and protons are treated quantum mechanically using electro-protonic wave functions, and perform real-time propagation of the electro-protonic wave functions of CH₃OH exposed to an intense laser field using a parallelized code.

[Introduction] Recent experimental studies on ionization and dissociation processes of hydrocarbon molecules induced by an ultrashort intense laser field revealed that the hydrogen atoms and/or protons migrate rapidly within the hydrocarbon molecules prior to the breaking of skeletal chemical bonds. For example, it was revealed that a hydrogen atom in methyl group in methanol migrates to hydroxy group within 25 fs by the pump-probe coincidence momentum imaging measurements of the Coulomb explosion processes of methanol dication, CH₃OH²⁺, using few-cycle intense near-IR laser pulses [1]. When the ultrafast hydrogen atom migration proceeds, the interatomic potential along the C-O bond should be influenced by the motion of the hydrogen atom, competing with the C-O bond breaking.

For describing theoretically the ultrafast motion of hydrogen atoms and/or protons within a hydrocarbon molecule, we need to treat the motion of hydrogen atoms separately from the heavier atoms such as carbon and oxygen atoms. In 2009, we proposed a method called extended multiconfiguration time-dependent Hartree-Fock (MCTDHF) [2], in which not only the motion of electrons but also the motion of protons are described by time-dependent orbitals, and showed that the ground-state electro-protonic wave function of methanol, CH₃OH, can be derived using the extended MCTDHF method [3].

In order to perform efficiently real-time propagation of orbitals for electrons and protons in CH₃OH, we developed a program code of the extended MCTDHF method, and examined its performance in describing the interaction between the electronic and protonic orbitals and an intense laser field.

[Theory] In the extended MCTDHF method, the molecular wave function of CH₃OH, Φ , is expanded by electro-protonic multiconfiguration wave functions as

$$\Phi(\{x_j\}, \{y_p\}, t; R) = \sum_I \sum_A C_{IA}(t) \Phi_I(\{x_j\}, t; R) \Psi_A(\{y_p\}, t; R), \quad (1)$$

where $x_j = (\mathbf{r}_j, \sigma_j)$ denotes the spatial and spin coordinates of the j -th electron ($1 \leq j \leq 18$), $y_p = (\mathbf{r}_p, \sigma_p)$ denotes the spatial and spin coordinates of the p -th proton ($1 \leq p \leq 4$), R is the inter-nuclear distance between C and O, Φ_I and Ψ_A are the electronic and protonic Slater determinants, respectively, and C_{IA} is a time-dependent configuration interaction (CI) coefficient. The equation of motion of the CI coefficients and spin orbitals are derived based on the Dirac-Frenkel time-dependent variational principle.

[Results and Discussion] For the real-time propagation of the spin orbitals, we apply the split operator technique [4]. First, we write the equation of motion of electronic spin orbitals as

$$i\hbar \frac{\partial}{\partial t} \phi_j(x, t) = \left[h_j(t) + \sum_k V_{kj}(t) \right] \phi_j(x, t), \quad (2)$$

where $h_j(t)$ is an orbital-independent operator and $V_{kj}(t)$ is a non-linear operator that depends on the spin orbitals. When propagating the orbitals from time t to $t + \delta t$ starting from the initial orbital $\phi_j(t)$, we regard h_j and V_{kj} to be time-independent and compute the orbital after the propagation, $\phi_j(t + \delta t)$, as

$$\phi_j(t + \delta t) \approx e^{-\frac{i}{\hbar} h_j(t) \delta t} e^{-\frac{i}{\hbar} \sum_k V_{kj}(t) \delta t} e^{-\frac{i}{\hbar} h_j(t) \delta t} \phi_j(t). \quad (3)$$

The exponential operation of the orbital-independent operators are performed by the Crank-Nicolson method and the exponential operation of the non-linear operators are performed by Lanczos method [5]. Because electrons and protons are treated in a parallel manner in the electro-protonic Hamiltonian, we propagate the protonic spin orbitals using the same algorithm adopted for the electronic orbitals.

In order to parallelize the calculation code, we use the library of OpenMP. Using the calculation times, $T(n)$, required when the number of threads n takes the values of $n = 1, 2$, and 4, we obtain the parallelization ratio, p , of $p = 0.92$ for the imaginary-time propagation by a least-squares fit to the Amdahl's law written as

$$T(n) = \left(\frac{p}{n} + 1 - p \right) t_1, \quad (4)$$

where t_1 is the calculation time when $n = 1$. When $n = 8$, for example, the calculation time of the imaginary-time propagation can be 5.1 times shorter than when $n = 1$. The calculation code of real-time propagation is also parallelized in the same manner as in the imaginary-time propagation, and the real-time propagation of the electro-protonic wave functions of CH₃OH exposed to an intense laser field is performed using the parallelized code.

[References]

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