

Natural Orbitals and Potential Curves within the Framework of Extended Multi-configuration Time-dependent Hartree-Fock Method

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Abstract: The extended multi-configuration time-dependent Hartree-Fock method is proposed to calculate time-dependent wave functions. By constructing the ground-state wave function of one-dimensional H_2 by imaginary time-propagation, the natural orbitals and the potential energy curves were derived.

OCIS codes: (000.1570) Chemistry; (020.5580) Quantum electrodynamics

1. Introduction

It is reported that a hydrogen molecule dissociates when it is exposed to an intense laser field (790 nm, 3×10^{14} W/cm², 14 fs) [1]. The energy supplied from the laser-molecule interaction comes from the interaction between two electrons and the laser field, which then induces the nuclear motion on the potential energy curves. In other words, the energy given to the electronic system by the external fields is converted to the nuclear kinetic energy, which could be used for the subsequent vibrational excitation and/or dissociation. Therefore, a method to describe the coupled motions of electrons and protons is necessary to explain the dissociation process of a hydrogen molecule in an intense laser field.

As a method to describe the coupled motions of electrons and protons quantum mechanically, the extended multi-configuration time-dependent Hartree-Fock (MCTDHF) method was proposed [2]. It is reported that the extended MCTDHF method needs the smaller memory size to describe the molecular wave function compared to the conventional Born-Huang expansion method [3]. On the other hand, the interpretation of the calculated molecular wave functions obtained by the extended MCTDHF method has not been established probably because the extended MCTDHF method does not use the notion of adiabatic states.

In the present study, we propose a method to calculate natural orbitals and potential curves by the extended MCTDHF method, and demonstrated its applicability by deriving natural orbitals and potential curves of the ground-state molecular wave function of a one-dimensional hydrogen molecule.

2. Natural orbitals

Within the extended MCTDHF method, the molecular wave function of a one-dimensional hydrogen molecule is written using a multiconfiguration expansion as

$$\Psi^{\text{MC}}(x_1, x_2, R, t) = \sum_I C_I(R, t) \Phi_I(x_1, x_2, t), \quad (1)$$

where $x = (r_j, \sigma_j)$ denotes the spatial and spin coordinates of the j th electron, and R the internuclear distance. The function $C_I(R)$ represents an amplitude of the nuclear motion associated with an electronic Slater determinant Φ_I and is called configuration interaction (CI) vector. The electronic orbitals in the determinant Φ_I do not depend on the variable R differently from the conventional electronic structure theory. The electronic orbitals and CI-vectors optimized for the ground state can be determined by the imaginary time propagation using the equations of motion for the electronic orbitals and CI-vectors in real time, which are derived from the Dirac-Frenkel time-dependent variational principle [2,3].

The first order reduced density matrix for the wave function of Eq. (1) is written as

$$\rho^{\text{MC}}(r, r') = \sum_{km}^{\text{occ}} \sum_{\sigma=\pm 1/2} \sum_{\sigma'=\pm 1/2} \phi_k^*(x) \langle \Psi^{\text{MC}} | \hat{a}_k^\dagger \hat{a}_m | \Psi^{\text{MC}} \rangle \phi_m(x'), \quad (2)$$

where \hat{a}_k represents the Fermi annihilation operator of the k th spin-orbital, ϕ_k , and \hat{a}_k^\dagger the Fermi creation operator of ϕ_k . Natural orbitals are defined as the orbitals with which the hermitian matrix of $A_{km} = \langle \Psi^{\text{MC}} | \hat{a}_k^\dagger \hat{a}_m | \Psi^{\text{MC}} \rangle$ is diagonalized. The shapes of the natural orbitals obtained for the ground-state wave function of a one-dimensional hydrogen molecule are shown in Fig. 1. The ground-state wave function is calculated by using five spatial orbitals.

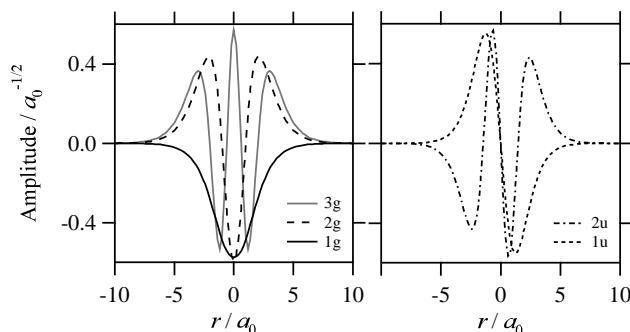


Fig. 1. The natural orbitals obtained from the ground-state wave function of Eq. (1) calculated by using five spatial orbital functions are plotted. In the left panel (a) the orbitals with the *gerade* symmetry are plotted, and in the right panel (b) the orbitals with the *ungerade* symmetry are plotted.

3. Potential energy curves

The function $C_J(R,t)$ is determined by the following equation in the extended MCTDHF method [2],

$$i\hbar \frac{\partial}{\partial t} C_J(R,t) = \left[-\frac{\hbar^2}{2\mu_r} \frac{\partial^2}{\partial R^2} + W_{pp}(R) \right] C_J(R,t) + \sum_J \langle \Phi_J(t) | \hat{H}_e(R,t) + \hat{H}_{mp} | \Phi_J(t) \rangle C_J(R,t), \quad (3)$$

where μ_r denotes the reduced mass for the protons, $W_{pp}(R)$ the soft Coulombic interaction between protons [4], $\hat{H}_e(R)$ the electronic Hamiltonian including the interaction of electrons with an external field, and \hat{H}_{mp} the mass-polarization term. When the electronic states are determined for each internuclear distance R so that the hermitian matrix $V_{JJ}(R,t) = \langle \Phi_J | \hat{H}_e(R,t) + \hat{H}_{mp} | \Phi_J \rangle$ in Eq. (3) is diagonalized, the eigenvalue, $V_J(t; R)$, can be regarded as the potential energy for the J th electronic state similar to the conventional adiabatic potential energy.

The value of $V_J(t; R)$ calculated for the ground-state wave function of a one-dimensional hydrogen molecule is plotted in Fig. 2, where the ground-state wave function is calculated using five spatial orbitals. The potential energy curve with the lowest energy value has the minimum point at around $R = 1.6 a_0$, which is the expectation value of the internuclear distance.

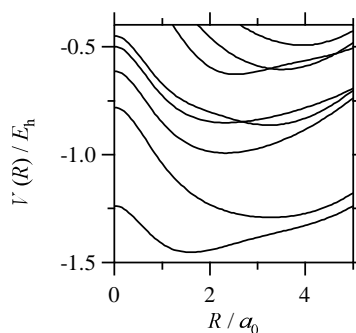


Fig. 2. The potential energy curves obtained from the ground-state wave function of Eq. (1) calculated by using five spatial orbital functions are plotted.

When the wave function is propagated in real time, we expect that the time evolution of the wave function can be interpreted in terms of (i) the idea of nonadiabatic transitions among electronic states and (ii) the shape of the time-dependent potential energy curves for the nuclear motion.

4. References

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