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Extended multiconfiguration theory applied to H_2^+

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[Abstract] The extended multiconfiguration time-dependent Hartree-Fock (Ex-MCTDHF) method is applied to the simulation of strong field-induced dissociation of a hydrogen molecular ion. In the Ex-MCTDHF method, the total electro-protonic wave function is written as a sum of products of electronic and protonic time-dependent wave functions. Differently from the commonly adopted Born-Oppenheimer (BO) approximation, the electronic wave functions have no parametric dependence on the internuclear distance. It is shown that the Ex-MCTDHF method is well suited to describe not only laser-induced ionization of H_2^+ but also laser-induced dissociation of H_2^+ into H + H^+ fragments and vibrational excitations in bound H_2^+. The results obtained by the Ex-MCTDHF method are compared with those obtained by solving the time-dependent Schrödinger equation directly on a three-dimensional grid and with those obtained with the BO approximation.

[Introduction] The standard theoretical method to simulate molecules exposed to an intense laser pulse is the Born-Oppenheimer (BO) approximation, in which the total time-dependent wave function Ψ is expanded as

$$\Psi(\boldsymbol{r}, \boldsymbol{R}, t) = \sum_{n=1}^{K} \chi_n(\boldsymbol{R}, t)\phi_n(\boldsymbol{r}; \boldsymbol{R}). \quad (1)$$

In Eq. (1), $\boldsymbol{R}$ denotes the collective coordinate of the nuclei in the molecule, $\boldsymbol{r}$ denotes the electronic coordinates, $\chi_n(\boldsymbol{R}, t)$ is the n-th time-dependent nuclear wave function ($n = 1, 2, \ldots, K$), and $\phi_n(\boldsymbol{r}; \boldsymbol{R})$ is the n-th electronic wave function that depends parametrically on $\boldsymbol{R}$. However, for polyatomic molecules having many vibrational degrees of freedom, it would be a formidable task to compute the electronic states $\phi_n(\boldsymbol{r}; \boldsymbol{R})$ at each value of $\boldsymbol{R}$. Furthermore, when we simulate an ionization process, we need to include continuum electronic functions $\phi_\varepsilon(\boldsymbol{r}; \boldsymbol{R})$ having an excess energy ε in the expansion in Eq. (1), which the BO approximation could not accommodate appropriately.

An alternative ansatz for the total time-dependent wave function is [1],

$$\Psi(\boldsymbol{r}, \boldsymbol{R}, t) = \sum_{n=1}^{K} \chi_n(\boldsymbol{R}, t)\phi_n(\boldsymbol{r}, t), \quad (2)$$

where the electronic wave functions $\phi_n(\boldsymbol{r}, t)$ depend on time t, but do not depend on $\boldsymbol{R}$. The time-dependence of $\phi_n(\boldsymbol{r}, t)$ means that the electronic wave functions can vary their amplitude in response to the laser pulse, which facilitates the simulation of ionization. In addition, it is unnecessary to prepare a set of electronic states at each value of $\boldsymbol{R}$. The MCTDHF method based on the ansatz (2) is referred to as the Ex-MCTDHF method [1], because it is a variation of the original MCTDHF method [2,3] extended so that it can include nuclear motion.

[Methods] We apply the Ex-MCTDHF method to the simulation of H_2^+ exposed to an intense laser pulse. In the case of H_2^+, we have $\boldsymbol{R} = R$ in Eq. (2), with R being the internuclear distance, and $\boldsymbol{r} = (\rho, z)$ is the cylindrical coordinates of the electron. Both the molecular axis

and the electric field vector of the laser pulse are assumed to be parallel to the z-axis. In the Ex-MCTDHF method, the equations of motion satisfied by $\chi_n(R,t)$ and $\phi_n(\rho,z,t)$ are derived from the time-dependent variational principle. Orthonormality $\langle\phi_n|\phi_m\rangle = \delta_{nm}$ of the electronic wave functions is added as a constraint.

For comparison, we also carried out simulations by the BO approximation [Eq. (1)] as well as by a 3D grid method, where the time-dependent Schrödinger equation is solved directly on a 3D grid. In the BO method, the ground $1s\sigma_g$ and the first excited $2p\sigma_u$ electronic states of H_2^+ were adopted in the expansion of the wave functions.

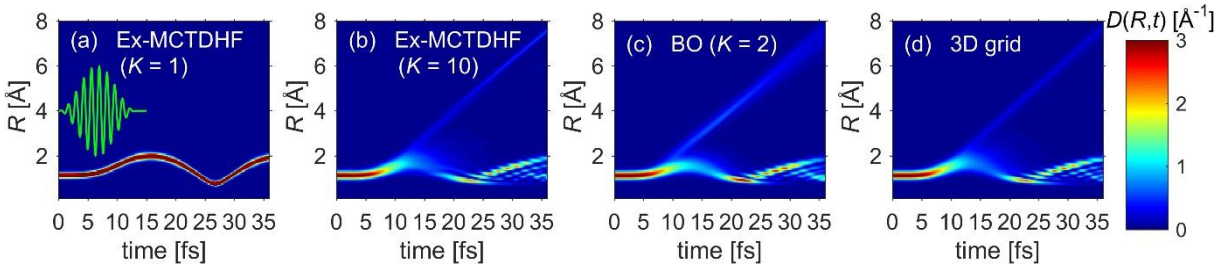

Fig. 1. Protonic density $D(R,t) = R^2\int \rho d\rho z|\Psi(\rho,z,R,t)|^2$ for H_2^+ exposed to an intense laser pulse. Results obtained with the Ex-MCTDHF method with (a) $K = 1$ and (b) $K = 10$. (c) Results obtained within the BO approximation. (d) Results obtained with the direct grid method. The time variation of the laser field is indicated with a green line in (a).

[Results and Discussion] The result of a simulation of H_2^+ exposed to a laser pulse with the wavelength of 400 nm, the total pulse width of 13 fs and the peak intensity of 5×10^{14} W/cm^2 is shown in Fig. 1. We can see that the Ex-MCTDHF method with only one configuration $(K = 1)$ does not reproduce the bifurcation of the vibrational wave packet into a dissociating component in which the average value $\langle R\rangle$ of the internuclear distance increases with increasing time and a component representing vibrational excitation for which $\langle R\rangle$ oscillates within the molecular domain. When K is increased to $K = 10$ a good agreement is reached between the results obtained by the Ex-MCTDHF method and those obtained by the 3D grid method, which is consistent with the earlier studies in which the motion of an electron was restricted to one dimension [4]. By comparing Fig. 1(c) and Fig. 1(d), we can see that the results obtained by the BO method with $K = 2$ and those obtained by the 3D grid method are in good agreement with each other.

In order to further assess the performance of the Ex-MCTDHF method, we also calculated the total ionization probability P_{ion} of H_2^+ for the same laser pulse as used in the simulation shown in Fig 1. We obtain P_{ion}(Ex-MCTDHF) ≈ 0.19, which agrees well with P_{ion}(3D grid) ≈ 0.17 obtained by the 3D grid method. It should be noted that ionization cannot be described by the BO approximation, and consequently, P_{ion} cannot be calculated in the BO approximation.

In summary, we showed that the Ex-MCTDHF method can be used to simulate both dissociation and ionization of molecules induced by an intense laser pulse.

[References]

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