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Time-dependent intershell correlation in a laser-driven beryllium atom

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[Introduction]

Electron correlation is an important concept in quantum chemistry, and has been thoroughly studied for stationary states of atoms and molecules. On the other hand, much less attention has been given to the issue of time-dependent electron correlation. In this contribution, we propose a new way of analyzing the time-dependent correlation between pairs of electrons in many-electron systems having an even number of electrons. We do this by introducing an approximate method to solve the time-dependent Schrödinger equation (TDSE) called the time-dependent geminal (TDG) method. In this method, the total wave function is written as an antisymmetrized product of geminals, where a geminal is a two-electron orbital represented as a function of the coordinates of two electrons [1]. In this TDG method, electrons within a geminal can be fully correlated (intrapair correlation), but the interaction between electrons belonging to different geminals is included on a mean-field level only.

In the present study, we examine time-dependent electronic state dynamics of Be exposed to an external laser field by the three different methods: (i) the TDG method introduced in the present study, (ii) the fully correlated multiconfiguration time-dependent Hartree-Fock (MCTDHF) method [2, 3], and (iii) the uncorrelated time-dependent Hartree-Fock (TDHF) method. By comparing the results obtained by these three methods, we discuss the importance of the intershell correlation in a beryllium atom, Be, driven by an external laser field.

[Theoretical method]

The wave function ansatz in the TDG method is written as an antisymmetrized product of geminals,

$$\Psi(x_1, x_2, x_3, x_4, t) = \hat{A}\Lambda_1(x_1, x_2, t)\Lambda_2(x_3, x_4, t), \quad (1)$$

where $x_j = (\boldsymbol{r}_j, s_j)$ is the combined spatial and spin coordinate of the j-th electron (j = 1,…,4) of a four-electron system of Be. We furthermore assume that the geminals are strongly orthogonal, that is, $\int dy \Lambda_1^*(x_1, y, t)\Lambda_2(x_2, y, t) = 0$ for all x_1, x_2, and t. In order to practically deal with the geminals $\Lambda_\mu(x_1, x_2, t)$, we expand each geminal in terms of time-dependent spatial orbitals $\phi_j(\boldsymbol{r}, t)$ as

$$\Lambda_\mu(x_1, x_2, t) = \sum_{jk} C_{jk}^{\mu}(t)\phi_j(\boldsymbol{r}_1, t)\phi_k(\boldsymbol{r}_2, t)\sigma_0(s_1, s_2), \quad (2)$$

where $\sigma_0(s_1, s_2)$ is a singlet spin wave function. The equations of motion for the coefficients $C_{jk}^{\mu}(t)$ and the orbitals $\phi_j(\boldsymbol{r}, t)$ are derived by applying the Dirac-Frenkel variational principle. The equation of motion for the coefficients $C_{jk}^{\mu}(t)$ resembles the TDHF equation, and the equation of motion for the orbitals $\phi_j(\boldsymbol{r}, t)$ is similar to the corresponding equation in the MCTDHF method.

[Results]

We have implemented the TDG method for Be exposed to a strong laser field. In Fig. 1, we show the

induced dipole moment of Be exposed to a few-cycle laser field with a peak intensity of 5×10^{13} W/cm^2 and a wavelength of 400 nm. It is found that the TDG method performs much better than the TDHF method, and almost perfectly reproduces the MCTDHF curve. Therefore, we can say that intershell correlation is not important in the interaction of Be with long-wavelength laser light.

We have also simulated the interaction of Be with short-wavelength (10 nm) radiation. The energy of one 10-nm photon is $\hbar\omega \approx 122$ eV, which is close to the core electron's binding energy $\epsilon_{1s} \approx 129$ eV (as estimated by Koopman's theorem). After the absorption of one 10 nm photon, Be is excited to an excited state, for which configuration interaction needs to be taken into account. However, since the TDG wave functions are composed of the configurations of the type $\|\phi_{j_1}\bar{\phi}_{k_1}\phi_{j_2}\bar{\phi}_{k_2}\|$, where the orbitals ϕ_{j_1}, ϕ_{k_1} are the orbitals in the geminal Λ_1, and ϕ_{j_2}, ϕ_{k_2} the orbitals in the geminal Λ_2, the TDG method may not be suited to treat the configuration interaction.

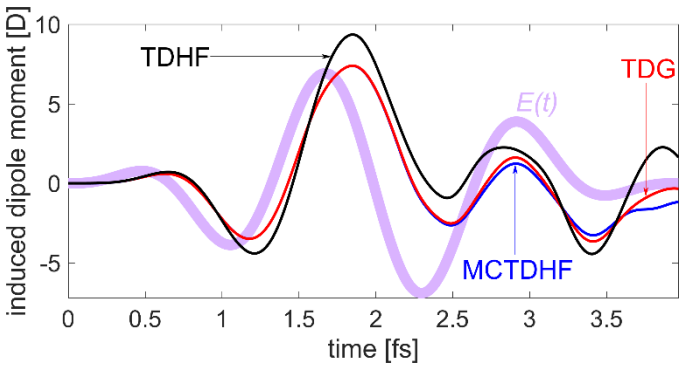

Figure 1. Induced dipole moment of Be exposed to a 5×10^{13} W/cm^2, 400 nm laser pulse. The TDG method is compared with the MCTDHF and the TDHF methods. The amplitude $E(t)$ of the laser field is shown on an arbitrary scale as a thick line.

[Summary]

We have introduced the time-dependent geminal method, which can be used to study time-dependent intershell correlation in the laser-driven atoms, and have demonstrated the applicability of the method by simulating the electronic structure of Be in a strong laser field. The TDG method performs well in the case of excitation by a 400 nm laser pulse, where the intershell correlation does not play a primary role. However, the TDG method fails in describing the electronic structure driven by a 10 nm laser pulse, suggesting that intershell correlation is crucial when Be interacts with the shorter wavelength light.

[References]

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