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Introduction. In order to theoretically simulate the electronic dynamics of a many-electron atom or a molecule in an intense laser field, we need to solve the time-dependent Schrödinger equation (TDSE). The TDSE in principle provides an *ab initio* description of the correlated electron motion, however, solving the TDSE numerically is very demanding.

A powerful method to calculate an approximate solution of the TDSE is the multi-configuration time-dependent Hartree-Fock (MCTDHF) method [1,2]. In this method, the time-dependent wave function is written as a superposition of time-dependent Slater determinants constructed from time-dependent spin orbitals. Although the MCTDHF method is a versatile method, its application has so far been limited to few-electron systems. This is because the number of Slater determinants included in the expansion of the wave function becomes very large. Therefore, several attempts have been made recently to reduce the length of the expansion by omitting certain subsets of determinants [3–5]. In this contribution, we propose an alternative method to simplify the MCTDHF method without restricting the number of determinants, i.e., we keep the intact full configuration interaction (CI) space while making an approximation for the CI coefficients themselves.

Theoretical method. In MCTDHF, the total wave function is written as

$$\begin{aligned}\Psi(t) &= \sum_{IJ} C_{IJ}(t) \Phi_{IJ}(t) \\ &= \sum_{IJ} C_{IJ}(t) |\phi_{I_1}(t)\alpha \cdots \phi_{I_{N/2}}(t)\alpha \phi_{J_1}(t)\beta \cdots \phi_{J_{N/2}}(t)\beta|,\end{aligned}\tag{1}$$

where we assumed a system having an even number N electrons with the same number $N/2$ of α and β electrons. The sum over I and J in Eq. (1) goes over all possible determinants that can be constructed from a given number of M spatial orbitals ϕ_k . Thus, C_{IJ} is an $L \times L$ matrix, where $L = M! / [(M - N/2)! (N/2)!]$. L grows extremely rapidly with increasing M and N . We now propose to approximate the matrix C_{IJ} as a product of three smaller matrices,

$$C_{IJ}(t) \approx \sum_{\mu, \nu=1}^K \lambda_{\mu\nu}(t) B_{I\mu}(t) B_{J\nu}(t),\tag{2}$$

where the summation with respect to μ and ν goes over the range $1 \leq \mu, \nu \leq K$. When K is set to be L , the factorization recovers the exact CI matrix. The exact CI matrix contains L^2 parameters, but the approximate form (2) requires only $K(K + L)$ parameters. Therefore, we can drastically reduce the number of parameters required to construct the CI matrix, provided that $K \ll L$. We stress that, although the CI coefficients are approximately calculated, *all* configurations (determinants) are included in the wave function expansion. The factorization of Eq. (2) has the same structure as a multi-configuration approximation for the wave functions for two-electron systems. Therefore,

equations of motion for $\lambda_{\mu\nu}(t)$ and $B_{I\mu}(t)$ are derived via the Dirac-Frenkel time-dependent variational principle.

Results. We have applied the MCTDHF method with the approximation (2) (hereafter called the “factorized CI” method) to various atomic and molecular model systems, where the electrons are restricted to move in one spatial dimension. In Fig. 1, we show the induced dipole moment $\langle\Psi| -e \sum_{i=1}^N x_i |\Psi\rangle$ of an H_4 molecule exposed to a three-cycle, 800 nm, 9×10^{13} W/cm² laser field. The internuclear distance R between neighboring H atoms was assumed fixed to $R = 2.1$ Å. We compare three different approximations: (i) time-dependent Hartree-Fock (TDHF), which implies that the wave function is described by one single closed-shell Slater determinant, (ii) the standard MCTDHF method with $M = 8$ spatial orbitals (this implies that there are $L^2 = 784$ Slater determinants), and (iii) the factorized CI approximation to the MCTDHF equations, with different values of the cut-off parameter K .

As is well known, the TDHF is inadequate for the description of ionization dynamics due to the restriction that the same spatial orbital needs to be used for pairs of electrons. We can see in Fig. 1 that the factorized CI method with $K = 1$ is very similar to the TDHF method, even though all configurations are included in the wave function expansion. To reproduce the time-dependent dipole moment of the full MCTDHF method, a range parameter of $K = 9$ is required.

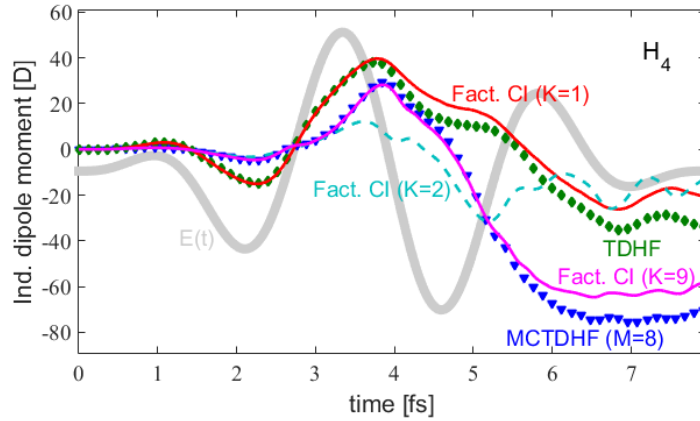


Figure 1. Induced dipole moment of an H_4 molecule exposed to an intense, few-cycle laser field. Shown are the results of the TDHF approximation, the MCTDHF approximation, and the factorized CI approximation, with $K = 1, 2, 9$. The laser field $E(t)$ (on an arbitrary scale) is indicated as a thick, grey line.

We have also applied the factorized CI approximation to one-dimensional Be and C atoms, and obtained similar results for the induced dipole moments. We conclude that the factorized CI method seems promising for extending the MCTDHF method to large, many-electron systems such as heavy atoms or hydrocarbon molecules.

References.

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