

Solving the time-dependent many-electron Schrödinger equation

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Introduction

The behavior of electrons in atoms and molecules is governed by the time-dependent Schrödinger equation (TDSE)

$$i\hbar \frac{\partial \Psi}{\partial t} = H(t)\Psi, \quad (1)$$

where i is the imaginary unit, \hbar is the reduced Planck constant, $H(t)$ is the Hamiltonian operator, and Ψ is the wave function of the system. Ψ is a complex, scalar function depending on $3N$ spatial coordinates and on time, $\Psi = \Psi(\mathbf{x}_1, \dots, \mathbf{x}_N, t)$, where N is the number of electrons. $\mathbf{x}_j = (\mathbf{r}_j, \omega_j)$, where \mathbf{r}_j is the spatial coordinate of electron j , and ω_j is the spin coordinate. An electronic wave function must satisfy the Pauli principle: $\Psi(\mathbf{x}_1, \dots, \mathbf{x}_j, \dots, \mathbf{x}_k, \dots, \mathbf{x}_N, t) = -\Psi(\mathbf{x}_1, \dots, \mathbf{x}_k, \dots, \mathbf{x}_j, \dots, \mathbf{x}_N, t)$, or in other words, the wave function must change its sign upon interchange of two electrons.

In principle, the wave function Ψ contains the complete information of the atom or molecule under study. Any measurable quantity can be extracted from Ψ . Therefore, the most direct way of studying the time-dependent behavior of an atom or molecule based on first principles is to solve the TDSE.

The Hamiltonian operator $H(t)$ in equation (1) is a differential operator containing single-electron terms operating on one electronic coordinate, and two-electron Coulomb potential terms depending on the distance between two electrons,

$$H(t) = \sum_{j=1}^N \left(-\frac{\hbar^2}{2m_e} \frac{\partial^2}{\partial \mathbf{r}_j^2} + V(\mathbf{r}_j) + U(\mathbf{r}_j, t) \right) + \frac{e^2}{4\pi\epsilon_0} \sum_{j=1}^N \sum_{k>j}^N \frac{1}{|\mathbf{r}_j - \mathbf{r}_k|}. \quad (2)$$

In equation (2), m_e is the mass of an electron, e is the elementary charge, ϵ_0 is the permittivity of the vacuum, $V(\mathbf{r})$ is a potential formed by the nucleus (nuclei) of the atom (molecule), and $U(\mathbf{r}, t)$ is a time-dependent potential originating from the interaction with an external time-dependent field, for example a laser field.

The TDSE (1) is a partial differential equation in $3N$ spatial plus one temporal variable. Since the derivative with respect to time t is of the first order, the TDSE is an initial value problem in which an initial wave function $\Psi_0 = \Psi(t=0)$ needs to be given. Given Ψ_0 , we will find $\Psi(t)$ for $0 \leq t \leq T$, where T is determined by the longest timescale of the problem, for example, the temporal width of a laser pulse. This kind of formulation is different from formula in traditional quantum chemistry¹, in which we find approximate solutions to the eigenvalue problem $E\Psi =$

¹ A. Szabo and N. S. Ostlund, “Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory”, Dover Publications, New York (1996).

$H'\Psi$, where H' is a time-independent Hamiltonian operator.

Solving the TDSE numerically is a difficult task because of its high dimensionality. A simple approach of discretizing equation (1) is to represent the wave function on a mesh with n grid points in each spatial dimension. If we let the grid points be given by $\mathbf{r}^{(klm)} = (x^{(k)}, y^{(l)}, z^{(m)})$, $k, l, m = 1, \dots, n$, the discretized wave function becomes

$$\Psi_{k_1 l_1 m_1 \dots k_N l_N m_N} = \Psi \left(\mathbf{r}_1^{(k_1 l_1 m_1)}, \dots, \mathbf{r}_N^{(k_N l_N m_N)} \right), \quad (3)$$

where we neglect the spin coordinates for simplicity. We see that the discretized wave function on the left hand side of equation (3) is an array of n^{3N} complex numbers. For the description of a laser-driven atom, we have to take $n > 100$ in most cases. Thus, even for a two-electron system with $N = 2$, the discretized wave function is represented by at least $100^6 = 10^{12}$ complex numbers, which is too large to store in memory. Therefore, we have to consider approximate methods to solve the TDSE.

Multiconfiguration time-dependent Hartree-Fock method

In the multiconfiguration time-dependent Hartree-Fock (MCTDHF) method², the wave function is expanded as a linear combination of Slater determinants Φ_I , which is also called configurations,

$$\Psi(t) = \sum_I C_I(t) \Phi_I(t), \quad (4)$$

where $I = (I_1, \dots, I_N)$ is a multi-index, and

$$\Phi_I(t) = \det[\chi_{I_1}(t) \dots \chi_{I_N}(t)] \equiv \frac{1}{\sqrt{N!}} \sum_{j_1, \dots, j_N} \varepsilon_{j_1 \dots j_N} \chi_{j_1}(x_1, t) \dots \chi_{j_N}(x_N, t). \quad (5)$$

In equation (5), $\varepsilon_{j_1 \dots j_N}$ is an anti-symmetric Levi-Civita symbol, and $\chi_j(x, t) = \phi_j(\mathbf{r}, t) \sigma(\omega)$ is a spin-orbital, which is a scalar function depending on one coordinate only, and $\phi_j(\mathbf{r}, t)$ is a spatial orbital. For a spin-up electron, $\sigma = \alpha$, and for a spin-down electron $\sigma = \beta$. The coefficients C_I are called configuration-interaction (CI) coefficients. By inserting the ansatz (5) into the Dirac-Frenkel variational equation,

$$\int dx_1 \dots dx_N \delta \Psi^*(t) \left[H(t) - i\hbar \frac{\partial}{\partial t} \right] \Psi(t) = 0, \quad (6)$$

where $\delta \Psi(t)$ is a small variation of the wave function with respect to the variation of C_I or ϕ_j , we can derive time-dependent equations for the coefficients C_I and the spatial orbitals ϕ_j .

² J. Zanghellini, M. Kitzler, C. Fabian, T. Brabec, and A. Scrinzi, "An MCTDHF approach to multielectron dynamics in laser fields," *Laser Phys.* **13**, 1064 (2003); T. Kato and H. Kono, "Time-dependent multiconfiguration theory for electronic dynamics of molecules in an intense laser field," *Chem. Phys. Lett.* **392**, 533 (2004).

The equations (4) and (5) have two interesting properties: (i) By the definition of equation (5), we see that a Slater determinant always satisfies the Pauli principle. This means that two orbitals in one Slater determinant cannot be equal to each other. (ii) Both the coefficients C_I and the Slater determinants Φ_I in equation (4) are time-dependent. The time-dependence of both C_I and Φ_I means that our ansatz for the wave function is very flexible in the sense that the spatial orbitals ϕ_j in the Slater determinants Φ_I can vary in response to the change in the time-dependent potential $U(\mathbf{r}, t)$ [see equation (2)]. The time-dependent equations of motion for $C_I(t)$ and $\phi_j(\mathbf{r}, t)$ are a set of coupled, non-linear equations, in contrast to the original TDSE (1), which is linear with respect to Ψ .

Then, we need to set the number of determinants we include in the sum (4). In the original formulation of MCTDHF², all the determinants that can be generated from a given set of spin-orbitals are included in the sum. For example, if we have six spin-orbitals and $N = 3$ electrons, we can construct $\binom{6}{3} \equiv \frac{6!}{(6-3)!3!} = 20$ different Slater determinants. The number of possible determinants grows extremely rapidly with the number of electrons N . If we assume that $2N$ spin-orbitals are needed for an accurate representation of the wave function, we can construct $\binom{2N}{N} \approx 4^N / \sqrt{\pi N}$ determinants. This exponential scaling with N makes it extremely demanding to apply the MCTDHF method to many-electron systems. Thus, in most cases, few-electron systems such as Be (four electrons)³ and LiH (four electrons)⁴ have been treated with the MCTDHF method. In the most extensive calculation, a wave function for 15 electrons was constructed by 12 spatial orbitals for a NO molecule⁵, resulting in a total of 392,040 Slater determinants in the sum (4).

Factorized CI method

We have suggested a way to overcome the unfavorable exponential scaling of the MCTDHF method⁶, called the factorized CI method. In this method, we first assume that the array of CI coefficients is arranged as a matrix, C_{IJ} . This can be achieved by using the index I to label the spatial orbitals for the up-spin (α) electrons, and J for the down-spin (β) electrons. If we assume a system with equal number $N/2$ of up-spin and down-spin electrons, then a general determinant can be written as $\Phi_{IJ} = \det[\phi_{I_1}\alpha \cdots \phi_{I_{N/2}}\alpha \phi_{J_1}\beta \cdots \phi_{J_{N/2}}\beta]$. If we assume that we have M spatial orbitals ϕ_j ($j = 1, \dots, M$), then C_{IJ} is an $L \times L$ matrix, with $L = \binom{M}{N/2}$. For a spin singlet state,

³ D. J. Haxton, K. V. Lawler, and C. W. McCurdy, “Single photoionization of Be and HF using the multiconfiguration time-dependent Hartree-Fock method,” *Phys. Rev. A* **86**, 013406 (2012).

⁴ M. Nest, F. Remacle, and R. D. Levine, “Pump and probe ultrafast electron dynamics in LiH: a computational study,” *New J. Phys.* **10**, 025019 (2008).

⁵ D. J. Haxton and C. W. McCurdy, “Ultrafast population transfer to excited valence levels of a molecule driven by x-ray pulses,” *Phys. Rev. A* **90**, 053426 (2014).

⁶ E. Lötstedt, T. Kato, and K. Yamanouchi, “Decomposition of the configuration-interaction coefficients in the multiconfiguration time-dependent Hartree-Fock method,” *J. Chem. Phys.* **144**, 154111 (2016).

C_{IJ} is symmetric, $C_{IJ} = C_{JI}$. We now assume that the coefficient matrix C_{IJ} can be written as a matrix product,

$$C_{IJ}(t) = \sum_{\mu, \nu=1}^K B_{I\mu}(t) \lambda_{\mu\nu}(t) B_{J\nu}(t), \quad (7)$$

where \mathbf{B} is an $L \times K$ matrix, $\boldsymbol{\lambda}$ is a $K \times K$ matrix, and K is an expansion length parameter satisfying $1 \leq K \leq L$. We use bold upright font to denote matrices, and normal italic font to denote the matrix elements, for example $(\mathbf{B})_{I\mu} = B_{I\mu}$. As explicitly indicated in equation (7), both \mathbf{B} and $\boldsymbol{\lambda}$ depend on time. Dynamical equations governing the time-dependence of $\mathbf{B}(t)$ and $\boldsymbol{\lambda}(t)$ can be derived by applying the Dirac-Frenkel variational principle.

The efficiency of the factorization (7) depends on how many terms we have to include in the expansion. We then need to know how large the expansion parameter K has to be to obtain a converged result. Writing the equation (7) in matrix form, $\mathbf{C} = \mathbf{B}\boldsymbol{\lambda}\mathbf{B}^t$, where \mathbf{B}^t denotes the transpose of a matrix \mathbf{B} , it becomes clear that \mathbf{C} is invariant under the unitary transformation of $\mathbf{B} \rightarrow \mathbf{B}\mathbf{U}^\dagger$, and $\boldsymbol{\lambda} \rightarrow \mathbf{U}\boldsymbol{\lambda}\mathbf{U}^t$, where \mathbf{U} is a unitary matrix. If we choose \mathbf{U} so that $\mathbf{U}\boldsymbol{\lambda}\mathbf{U}^t$ becomes a diagonal matrix, we see that the factorization (7) is closely related to the eigenvalue decomposition of \mathbf{C} . Thus, if \mathbf{C} has only a few large, dominant eigenvalues, the ansatz (7) will be efficient. Whether this is the case or not depends on the atomic or molecular system under study. In general, we cannot judge the efficiency of the expansion (7) until we perform explicit numerical simulations.

The strength of the factorized CI method is that the number of parameters required for constructing the matrix C_{IJ} of CI coefficients is $K(L + K)$, which can be much smaller than L^2 , which is the number of parameters needed in the MCTDHF method, provided that K is sufficiently small, $K \ll L$, for achieving the convergence.

Numerical implementation of MCTDHF and factorized CI

We have implemented the MCTDHF equations and the factorized CI equations⁶ in Fortran. In the implementation, we restrict the electrons to move along one spatial dimension only. Although an atom or a molecule is a three-dimensional system, this restriction to one spatial dimension is reasonable as long as it interacts with an intense external electric field, since the electrons move mainly along the direction of the field. In one dimension, the Coulomb potential must be modified at short distances because of the singularity at the limit of zero interparticle separation. We employ a soft-core potential⁷, $V_{\text{sc}}(r) \propto (r^2 + \alpha^2)^{-1/2}$, in place of the Coulomb potential, which is a common choice when we treat the intense laser-matter interaction. The soft-core parameter α is taken to be $\alpha = \alpha_0$, where $\alpha_0 \approx 0.53 \times 10^{-10}$ m denotes the Bohr radius.

The spatial orbitals are discretized on a uniform mesh $r^{(q)}$, $q = 1, \dots, q_{\text{max}}$, such that $\phi_j(r^{(q)}) = \phi_{qj}$. The mesh spacing is $\Delta r = r^{(q+1)} - r^{(q)} = 0.1\alpha_0$, $r^{(1)} = -300\alpha_0$, and $r^{(q_{\text{max}})} = 300\alpha_0$, which means that the number of grid points is $q_{\text{max}} \approx 6000$. Second-order derivatives are obtained using a seven-point finite difference formula.

⁷ J. Javanainen, J. H. Eberly, and Q. Su, "Numerical simulations of multiphoton ionization and above-threshold electron spectra," Phys. Rev. A **38**, 3430 (1988).

As we see in traditional, stationary-state quantum chemistry, the bottleneck of the computation is the numerical evaluation of the two-electron integrals. In the present one-dimensional model the two-electron integrals g_{ijkl} are expressed as

$$g_{ijkl} = \iint dr dr' \frac{\phi_i^*(r)\phi_j(r)\phi_k^*(r')\phi_l(r')}{\sqrt{(r-r')^2 + \alpha^2}} \approx \Delta r^2 \sum_{p,q} \frac{\phi_{pi}^*\phi_{pj}\phi_{qk}^*\phi_{ql}}{\sqrt{(r^{(p)}-r^{(q)})^2 + \alpha^2}}. \quad (8)$$

The sum in (8) is performed in two steps. First $\varphi_{pij} = \phi_{pi}^*\phi_{pj}$ and $w_{pkl} = \Delta r \sum_q \varphi_{qkl} [(r^{(p)} - r^{(q)})^2 + \alpha^2]^{-1/2}$ are calculated, and second the sum $g_{ijkl} = \Delta r \sum_q \varphi_{qij} w_{qkl}$ is taken. In the actual program, the calculation of φ_{pij} and w_{pkl} is performed in parallel using the OpenMP library. This means that w_{pij} and $w_{pi'j'}$ for two different indices ij and $i'j'$ are calculated simultaneously on different computational cores.

In order to propagate the MCTDHF wave function forward in time, we have to solve the following coupled equations for C_{IJ} and ϕ_j ,

$$i\hbar \frac{dC_{IJ}}{dt} = \sum_{I'J'} H_{IJ I'J'} C_{I'J'}, \quad (9)$$

$$i\hbar \frac{d\phi_{pj}}{dt} = \sum_q h_{pq} \phi_{qj} + E(t) f_p \phi_{pj} + \sum_{q,k} \Lambda_{pj qk} \phi_{qk}, \quad (10)$$

where $H_{IJ I'J'} = H_{IJ I'J'}(\phi, t)$ is a four-dimensional functional of the orbitals and time, h_{pq} is a time-independent matrix, f_p is a time-independent vector, and $E(t)$ is a scalar function of time. The time-dependent matrix h_{pq} is the discretized version of the single-electron operator $-(\hbar^2/2m_e)\partial^2/\partial r^2 + V(r)$, while $E(t)f_q = U(r^{(q)}, t)$ is the time-dependent potential $U(r, t)$ in equation (2) evaluated at the grid points. $\Lambda_{pj qk} = \Lambda_{pj qk}(\phi, C, t)$ is a time-dependent four-dimensional functional of the orbitals and the CI coefficients. More detailed descriptions on these functionals can be seen in reference 6.

The equations (9) and (10) are non-linear equations since $H_{IJ I'J'}$ depends on the orbitals ϕ_{pj} , and $\Lambda_{pj qk}$ depends on the orbitals and on C_{IJ} . To solve the equations (9) and (10), we linearize them by assuming that the arrays \mathbf{H} and $\mathbf{\Lambda}$ can be regarded to be constant over a short time interval Δt . We then approximate the solution at $t + \Delta t$ by

$$\mathbf{C}(t + \Delta t) \approx \exp(-i\tau\mathbf{H})\mathbf{C}(t), \quad (11)$$

$$\begin{aligned} &\boldsymbol{\phi}(t + \Delta t) \\ &\approx \exp\left(-\frac{i\tau E(t)\mathbf{f}}{2}\right) \exp\left(-\frac{i\tau\mathbf{h}}{2}\right) \exp(-i\tau\mathbf{\Lambda}) \exp\left(-\frac{i\tau\mathbf{h}}{2}\right) \exp\left(-\frac{i\tau E(t)\mathbf{f}}{2}\right) \boldsymbol{\phi}(t), \end{aligned} \quad (12)$$

where $\tau = \Delta t/\hbar$, and we have used matrix notation. The array \mathbf{H} contains L^4 matrix elements, and therefore, \mathbf{H} is too large to be stored in memory. However, without storing \mathbf{H} , the operation of \mathbf{H} on \mathbf{C} , $(\mathbf{H}\mathbf{C})_{IJ} = \sum_{I'J'} H_{IJ I'J'} C_{I'J'}$, can be efficiently implemented using a number of operations proportional to L^2 . The exponential in equation (11) is therefore evaluated by the Lanczos algorithm⁸: First, k orthonormal

⁸ R. J. LeVeque, "Finite Difference Methods for Ordinary and Partial Differential Equations," Society for Industrial and Applied Mathematics, Philadelphia (2007).

vectors $\mathbf{v}_1, \dots, \mathbf{v}_k$ spanning the same space as the matrix products $\mathbf{C}, \mathbf{H}\mathbf{C}, \mathbf{H}^2\mathbf{C}, \dots, \mathbf{H}^{k-1}\mathbf{C}$ are generated, and the matrix elements $A_{ij} = \mathbf{v}_i^\dagger \mathbf{H} \mathbf{v}_j$ are calculated. We let $\mathbf{v}_1 = \mathbf{C}$. Then, we make the approximation $\mathbf{C}(t + \Delta t) \approx \sum_j b_j \mathbf{v}_j$, with $\mathbf{b} = \exp(-i\tau\mathbf{A})\mathbf{b}_0$, $\mathbf{b}_0 = (1, 0, \dots, 0)^t$.

For the orbital equation (12), we note that the calculation of the operation on Φ by the exponential involving \mathbf{f} is trivial, since \mathbf{f} is a diagonal matrix. The exponential including \mathbf{A} is calculated with the Lanczos method, similarly to the equation (11). For the exponential containing \mathbf{h} , it is advantageous to use the Crank-Nicolson method⁸, which is unconditionally stable for any value of Δt . Because of this stability, it becomes possible to use longer time steps Δt and thereby shorten the time needed for the simulation. In the implicit Crank-Nicolson method, we obtain an approximation to the expression $\mathbf{y} = \exp(-i\tau\mathbf{h})\mathbf{y}_0$ by solving the implicit equation $(1 + i\tau\mathbf{h}/2)\mathbf{y} = (1 - i\tau\mathbf{h}/2)\mathbf{y}_0$.

In the case of the factorized CI method, the equation (9) for the CI coefficients is replaced with two equations, that is, one for the $\boldsymbol{\lambda}$ matrix, and the other for the \mathbf{B} matrix. The equation for the spatial orbitals is the same as that in the MCTDHF method, equation (10). The equations for $\boldsymbol{\lambda}$ and \mathbf{B} are also solved by treating the non-linear parts as constant over a short time step, and by approximating exponentials with the Lanczos method.

Results and discussion

As a first test of the factorized CI method, we have simulated a 1D model of an H_4 molecule interacting with a short intense laser pulse. The H_4 molecule is considered to be linear, consisting of four H atoms placed equidistantly on a straight line

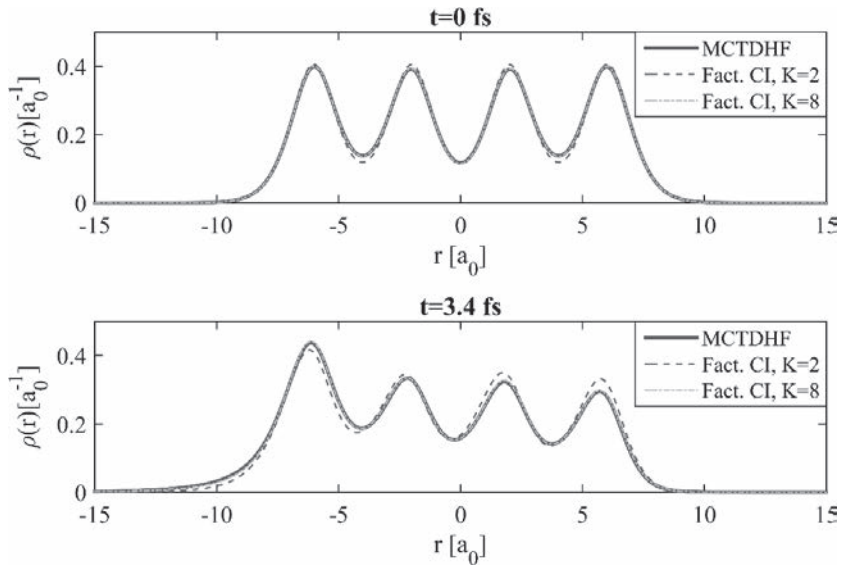


Figure 1. Electron density $\rho(r)$ at different times.

The top panel shows the one-electron density before the interaction with the laser field at $t = 0$, while the bottom panel shows the distorted one-electron density during the interaction with the laser field. In both panels, the solid curve (MCTDHF) and the dash-dotted curve (Fact. CI, $K=8$) almost perfectly overlap. $a_0 \approx 0.53 \times 10^{-10}$ m denotes the Bohr radius.

with an internuclear separation of $4a_0$. In the simulation, we employ a laser field having a wavelength of 800 nm, a duration of 3 optical cycles, and a peak electric field amplitude of 25 GV/m. A total number of spatial orbitals employed in the calculation is $M = 10$. Since a time-dependent wave function depends on N spatial variables and on time, it cannot be visualized directly. Some kind of reduced quantities must be calculated for the visualization. A very useful observable may be the one-electron density $\rho(r)$ defined as

$$\rho(r, t) = N \int d\omega_1 dx_2 \cdots dx_N |\Psi(x_1, \dots, x_N, t)|^2, \quad (13)$$

where $x_j = (r_j, \omega_j)$. The one-electron density $\rho(r, t)$ is a measure of the probability of finding an electron at a particular place in space. More precisely, the quantity $\Delta r \rho(r, t)/N$ is the probability of finding an electron in a small range Δr around the point r at time t . Conventionally $\rho(r, t)$ is normalized so that $\int dr \rho(r, t) = N$.

In Figure 1, we show the one-electron density at two instants in time, i.e., (i) at $t = 0$ (before the interaction with the laser pulse) and (ii) at $t = 3.4$ fs (during the interaction). The one-electron density distorted by the interaction with the laser field can clearly be seen in the bottom panel of Figure 1. The larger electron density in the negative r area ($r < 0$) than in the positive r area ($r > 0$) found in Figure 1 shows that H_4 is polarized by the laser field. It can also be seen in Figure 1 that the factorized CI approximation is a good approximation for the density $\rho(r)$ even at $K = 2$. When $K = 8$, the one-electron density obtained by the factorized CI approach shown by a dash-dotted line perfectly overlaps with the reference MCTDHF curve. We thus confirm that the results obtained by the factorized CI method converge to those obtained by the MCTDHF method at $K = 8$. Further comparisons of the performance of the factorized CI method with the MCTDHF method can be found in reference 6.

To what extent polarization is induced in many-electron systems by an external laser field depending on the laser parameters such as wavelength, peak electric field amplitude, and pulse width is currently an open problem in the atomic, molecular, and optical physics community. It is expected that the application of computational methods like the MCTDHF method and the factorized CI method, which have been developed to solve time-dependent problems, will contribute to our further understanding of laser-driven electron-electron interaction.

Future developments

One important subject for future investigation is the efficient parallelization of the MCTDHF codes. A fully parallelized MCTDHF code is crucial for the extension of the MCTDHF method to three-dimensional atoms and molecules with more than 10 electrons.

Concerning the factorized CI method, another issue we need to investigate is the issue of the non-conservation of spin. As shown in reference 6, the factorized CI equations of motion do not conserve the expectation value of the total spin operator. Although this property does not seem to have a large influence on the electron dynamics under the influence of an intense external light field, and the effect of spin non-conservation is usually small, it would be desirable to develop a

factorization method further so that the expectation value of the total spin is conserved.

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