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Time and intensity dependence of total ionization of helium studied with the multi-configuration time-dependent Hartree–Fock method

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ABSTRACT

We have demonstrated the use of the multi-configuration time-dependent Hartree–Fock (MCTDHF) method to compute total ionization probabilities of a 3-dimensional (3D) model helium atom interacting with a strong laser field. The time dependence and the intensity dependence of the total ionization probabilities of helium are investigated by using the MCTDHF method. The MCTDHF results are consistent with the previous theoretical expectations by directly solving the time-dependent Schrödinger equation.

1. Introduction

The multi-configuration time-dependent Hartree (MCTDH) theory for studying the multi-body dynamics of (distinguishable) nuclei has been developed [1–5] since 1990s and has attracted considerable attention. Based on the MCTDH method, the multi-configuration time-dependent Hartree–Fock method (MCTDHF) has been proposed and a great success has been made [6–33]. The MCTDHF method, which solves the time-dependent Schrödinger equation (TDSE) using the complete active space self-consistent field (CASSCF) scheme, is the extension of the time-dependent Hartree–Fock (TDHF) approach. This method can exactly describe the correlated multi-electron dynamics in strong laser field and thus can be used to study the interaction between laser and atoms or molecules. In order to investigate the correlated dynamics of multi-electron systems, Zanghellini et al. developed an MCTDHF approach to deal with multi-electron dynamics in strong laser fields [6,7] and they concluded that the method provides a good approximation of time-dependent multi-electron wave-functions and is able to deal with the correlated dynamics of multi-electron systems in strong laser fields [8]. Subsequently the second-quantization formalism of the MCTDHF theory was expanded by Kato and Kono [9]. In 2005, Nest and Klamroth further developed a MCTDHF method by using atomic basis functions [10], after that they have applied the method to study the electronically excited states of molecules [11] and ultrafast electron dynamics in LiH [12,13].

Recently, there has been great progress in the development of the MCTDHF methods. Alon et al. [14–16] have developed a unified and compact form of the MCTDH theory to specify for systems of identical particles (MCTDHF for fermions, MCTDHB for bosons). Then the same group [17] has developed a multi-configurational time-dependent Hartree method for systems with particles conversion, thus extending the scope of the available and successful multi-configurational time-dependent Hartree methods, which were solely formulated for and applied to systems with a fixed number of particles, to a broader class of physical systems and problems. Following this work the accurate multi-boson long-time dynamics in triple-well periodic traps were studied [18]. The MCTDHF working equations for a multi-configurational expansion with fixed coefficients and specialize to the case of general open-shell states have been derived by Miranda et al. [19]. And the mathematical analyses of the MCTDHF equations have been presented in Refs. [20,21]. The MCTDHF method was also applied to study the two-photo ionization of helium by Hochstuhl and Bonitz [22]. The MCTDHF method capable of treating the coupled electron–nuclear dynamics in diatomic molecules has also been developed [23–25]. In the present article, we have demonstrated the use of the MCTDHF method to compute intensity dependence and time dependence of total ionization probabilities of a helium atom exposed to an external laser field, for the purpose to verify

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the effectiveness of the MCTDHF method to deal with systems interacting with laser fields [34–36]. Our MCTDHF results from propagation in real time are in good agreement with other previous theoretical reports.

2. Theory

The MCTDHF methodology here employed is standard, and the details can be found in Refs. [1–5,9,10,15]. Here we only give some brief aspects of the method. In MCTDHF, the *N*-electron wave function is a linear combination of time-dependent Slater determinants,

$$\Psi(\vec{x}_1,\vec{x}_2,\ldots\vec{x}_N,t) = \frac{1}{\sqrt{N!}}\sum_J A_J(t)|\chi_{j_1}(\vec{x}_1,t)\ldots\chi_{j_N}(\vec{x}_N,t)| = \frac{1}{\sqrt{N!}}\sum_J A_J(t)|J,t\rangle \quad (1)$$

The coefficient A_J and the spin–orbitals $\chi_{j_1}(\vec{x}_1,t)$ are time-dependent. The capital letter J is a composite index which enumerates the number of spin–orbitals NUM appearing in the determinant, and $\vec{x}_i = (\vec{r}_i, s_i)$ is a composite variable for the position $\vec{r}_i$ and the spin coordinate s_i. The corresponding equations of motion $A_J(t)$ and $\chi_{j_1}(\vec{x}_1,t)$ are as follows:

$$i\frac{dA_J}{dt} = \frac{1}{N!}\sum_L \langle J|H|L\rangle A_L, \quad (2)$$

$$i\frac{d\chi}{dt} = (1-P)\rho^{-1}\langle H\rangle\chi. \quad (3)$$

where H is the Hamiltonian describing the N-electrons system that interacts with the strong laser field. The numerical time-dependent $A_J(t)$ and $\chi_{j_1}(\vec{x}_1,t)$ can be obtained by solving Eqs. (2) and (3).

3. Calculation aspects

The Cartesian coordinate system is employed in the present calculations (atomic units have been used throughout, unless stated otherwise). The spatial coordinates of the helium atom are (000) and the atomic basis set is 6-311G (2df, 2pd) [37] which is comprised of 14 Cartesian atomic orbitals. In order to correctly depict the wave-function far away from nuclei, more than one basis set are used in the MCTDHF calculation. That is, there is one set of basis set (6-311G (2df, 2pd)) centered at the original point with coordinates (000), and there are also two sets of basis set (6-311G (2df, 2pd)) centered at the points with coordinates (006) and (00−6). The laser field is linearly polarized along the Z axis.

In the Hartree–Fock calculations performed by using the Molpro *ab initio* program [38], two dummy atoms with coordinates (006) and (00−6) (with the basis function = 6-311G (2df, 2pd) and without charges) are also used, leading to a total number of 42 basis functions in the calculations.

The working equations of MCTDHF are solved by using the Runge–Kutta integrator method with our developed MPI source code. This MPI source code for solving the MCTDHF working equations is available upon request.

4. Results and discussions

In order to simulate the dynamics of a helium atom interacting with a laser field, the ground state wave-function of helium atom is indispensable. In MCTDHF, the system wave-function is determined when the time-dependent coefficients $A_J(t)$ and time-dependent spin orbitals $\chi_{j_1}(\vec{x}_1,t)$ are available. First of all, we have obtained the information of the ground state of helium through the propagation in imaginary time in the absence of an external laser field. In order to solve the differential equations of Eqs. (2) and (3), the initial values $A_J(t=0)$ and $\chi_{j_1}(\vec{x}_1,t=0)$ must be set in advance. The initial coefficients A_J are identical to each other and are set to $1/\sqrt{N}$ for $J = (1,2,\ldots N)$. We have initialized the spatial orbitals through diagonalization of single electron hamiltonian h or Fock operator matrix $F = h + p * G$. The G operator represents the two-electrons integrals and p indicates the Hartree–Fock density matrix, $p_{\mu\upsilon} = \sum_{ij} c^*_{i\mu} c_{j\upsilon}$. To obtain the atomic orbital integrals and the Fock operator matrix, we have carried out Hartree–Fock (HF) calculation by using the Molpro 2010 [38] or Gamess [39] program package. The Slater-type function can also be employed as basis set by means of the SIMILES2007 program package [40–42]. We choose 12 spin orbitals for the two active electrons system giving rise to 66 singlet determinants. Our obtained ground energy of helium is about −2.8951277 hartree, which is close to the full configuration interaction results calculated by Molpro [38].

We then further investigated the interaction between a laser pulse and the helium atom after the accurate ground state wave function has been obtained. In our calculation, the $\sin^2$ temporal shape laser pulse with the expression of $E\sin^2(\pi t/\tau)\cos(\omega t)$ is used. Fig. 1 shows the total ionization probability versus electric field strength ε for a six-cycle laser pulse with a $\sin^2$ temporal shape and a central frequency $\omega = 5$ a.u. (atomic units). This set of parameters and pulse shape has been chosen so as to match those employed in the calculation by Birkeland et al. [43]. The probabilities of finding the two electrons in bound states are expressed as $\sum_{j_1 j_2} P_{j_1 j_2} = \sum_{j_1 j_2} |\langle \chi_{j_1}\chi_{j_2}|\Psi(\vec{x}_1,\vec{x}_2,t)\rangle|$ [44,45]. Then we can get the total ionization probability by $P^{tot} = 1 - \sum_{j_1 j_2} P_{j_1 j_2}$. Comparing with the results calculated by directly solving the 5 + 1 dimensional time-dependent Schrödinger equation (TDSE) [43], the present MCTDHF total ionization probabilities as a function of the laser intensity are in general agreement with the theoretical reports in Ref. [43]. At the four electronic field strengths ($\varepsilon = 0.01, 0.05, 0.75, 1.0$ a.u.), it is found that the MCTDHF results are slightly smaller than the available TDSE results. This may be due to the limitation of the atomic basis functions. The other three points at the electronic field strengths of $\varepsilon = 0.1, 0.25, 0.5$ a.u. are from our theoretical prediction. In order to get more information about the ionization process, we present, in Fig. 2, the results of time evolution of total ionization probability at six different electronic field strengths ($\varepsilon = 0.01, 0.05, 0.1, 0.25, 0.5, 1$ a.u.). This figure shows that the time dependence of ionization probabilities oscillates obviously because of the "rescattering" of the wave packets driven back by the laser pulse with $\sin^2$ temporal shape

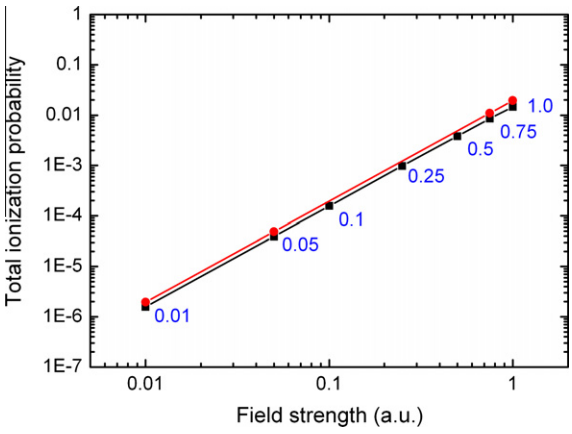

Fig. 1. Total ionization probabilities of helium versus electric field strength (in atomic units) for 6-cycle laser pulse with $\hbar\omega = 136$ eV ($\omega = 5$ a.u.). The solid circles denote the results of 5 + 1 dimensional time-dependent Schrodinger equation (TDSE), and the solid squares denote the present results calculated by using MCTDHF method.