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Classical dynamics of H_2^+ in an intense laser field by using the symplectic method

Shi-Xing Liu* and Ya-Qiu Lang

Department of Physics, Liaoning University, Shenyang 110036, People's Republic of China
E-mail: lsx197783@yahoo.com.cn

Xue-Shen Liu and Pei-Zhu Ding

Institute of Atomic and Molecular Physics, Jilin University, Changchun 130012, People's Republic of China

Yue-Ying Qi

School of Electrical Engineering, Jiaxing University, Jiaxing 314001, People's Republic of China

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The classical dynamics of 1D H_2^+ in an intense field are discussed. The initial conditions are chosen at random in the field-free case, and then the Hamiltonian canonical equations of H_2^+ system in the intense laser field are solved numerically by mean of the symplectic method under these initial conditions. The probabilities of survival, dissociation, ionization, and Coulomb explosion of H_2^+ system in the intense laser field are obtained for different laser intensity based on the classical theory.

KEY WORDS: symplectic method, Coulomb explosion, dissociation, ionization

1. Introduction

With the development of the ultrashort intense laser technology, it is possible to observe the transient process of atoms or molecules in an intense laser pulse, which brings on the development of modern laser chemistry, for example, the femtosecond chemistry may makes people carry through the tracking exploration of molecular process on the femtosecond scale. These requirements on experiment promote the theory research of the dynamic process of the interaction of atoms or molecules in ultrashort intense laser pulse, and make the dynamic process of atoms or molecules in ultrashort intense laser pulse become one of the very active research fields now [1]. For the study of dynamic process of atoms in intense laser fields, people usually solve numerically the electronic

*Corresponding author.

time-dependent Schrödinger equation, which is based on the effect of Coulomb and laser fields [2, 3]. But it is still impossible to numerically solve the time-dependent Schrödinger equation for many-atom molecules system or multi-electron atoms under the intense laser field even though the best computer today is used [4]. So the classical theory is used to study the dynamic behaviors of the molecules in the intense laser fields, such as the stabilization of a molecule in superintense high-frequency laser field [5], ionization, Coulomb explosion [6], and the high-harmonic generation of atom or small molecule in the strong laser field [7], etc., these applications based on the classical theory are very successful.

In this paper, we study the interaction of 1D H_2^+ in ultrashort intense laser pulse by using the classical theory, and discuss the dynamical processes of survival, dissociation, ionization, and Coulomb explosion of H_2^+ for different laser intensity. In next section, we summarize the classical model of H_2^+ system, and give the classical Hamiltonian canonical equation of H_2^+ system and the criterion of four dynamic processes (survival, dissociation, ionization, and Coulomb explosion). In section 3, we illustrate that how to choose the initial conditions in the field-free case, and construct the symplectic scheme tailored to the time-dependent Hamiltonian function including explicitly time. We also describe the probabilities of survival, dissociation, ionization, and Coulomb explosion of H_2^+. In section 4, the time-evolution of survival, dissociation, ionization, and Coulomb explosion of H_2^+ for different intensity of laser fields is discussed.

2. Classical model of H_2^+ in intense laser

The two protons and electron in H_2^+ system can be regarded as the classical particles based on the classical theory. The system of H_2^+ is regarded as a three-body system of classical mechanics. The forces are the Coulomb force, which is determined by the particles, and the external laser field $E(t) = E_0 f(t) \sin \omega_0 t$. The classical movement of system is described by the Hamiltonian canonical equation. We presume that the laser electric field is along the direction of two protons and adopt the 1D model in which the electron is collinear with two protons. Thus the Hamiltonian function of H_2^+ in external intense laser fields can be written as

$$H(P, p; x, R, t) = \frac{P^2}{2\mu_\mathrm{p}} + \frac{p^2}{2\mu_\mathrm{e}} + V_c(x, R) + V_\mathrm{ex}(x, t), \tag{1}$$

where $\mu_\mathrm{p} = m_\mathrm{p}/2$, $\mu_\mathrm{e} = 2m_\mathrm{e}m_\mathrm{p}/(2m_\mathrm{p} + m_\mathrm{e})$ are the reduced masses, $m_\mathrm{p}, m_\mathrm{e}$ are the proton and electron masses, respectively. R is the internuclear distance of two protons and P is its corresponding conjugated momentum, while x is the distance between electron and the center of the mass of two protons and p is its corresponding conjugated momentum. The Coulomb interaction between the electron and the protons is

$$V_c(x, R) = \frac{1}{R} - \frac{1}{|x - R/2|} - \frac{1}{|x + R/2|}, \tag{2}$$

and the interaction potential with the external laser field is [7]

$$V_{\text{ex}}(x, t) = -\sigma x E(t), \qquad \sigma = 2\left(m_{\text{p}} + m_{\text{e}}\right)/\left(2m_{\text{p}} + m_{\text{e}}\right). \tag{3}$$

There exist the singularities in the bare Coulomb potential (2), which will induce the numerical integration unstable. Such singularities can be removed by using the regularized coordinates. The usual remedy is to use a screened Coulomb potential [7]

$$V_{\text{sc}}(x, R) = \frac{1}{R} - \frac{1}{\sqrt{(x - R/2)^2 + q_{\text{e}}}} - \frac{1}{\sqrt{(x + R/2)^2 + q_{\text{e}}}}, \tag{4}$$

where parameter q_{e} (we choose $q_{\text{e}} = 1.0$ a. u.) is the screened parameter of 1D Coulomb potential. Thus the Hamiltonian function (1) changes to

$$H(P, p; x, R, t) = \frac{P^2}{2\mu_{\text{p}}} + \frac{p^2}{2\mu_{\text{e}}} + V_{\text{sc}}(x, R) + V_{\text{ex}}(x, t) \tag{5}$$

and the Hamiltonian canonical equation of H_2^+ system can be written in the form

$$\begin{aligned} \frac{\mathrm{d}p}{\mathrm{d}t} &= -\frac{\partial V_{\text{sc}}}{\partial x} - \frac{\partial V_{\text{ex}}}{\partial x} = -f_1(x, R, t) & \frac{\mathrm{d}x}{\mathrm{d}t} &= \frac{p}{\mu_e} = g_1(p), \\ \frac{\mathrm{d}P}{\mathrm{d}t} &= -\frac{\partial V_{\text{sc}}}{\partial R} = -f_2(x, R, t) & \frac{\mathrm{d}R}{\mathrm{d}t} &= \frac{P}{\mu_{\text{p}}} = g_2(P) \end{aligned} \tag{6}$$

the initial conditions $(x(0), p(0), R(0), P_R(0))$ we used in this paper can be chosen at random which will be stated in the following section. Then we can solve numerically the initial value problem of equation (6) and obtain the evolution of electronic coordinate $x(t)$ and internuclear distance $R(t)$ with time and the total-energy [8].

$$E_c(t) = V_{\text{p}} + \frac{1}{2\mu_{\text{e}}}\left(\mu_{\text{e}}\dot{x}(t) - \sigma\int_0^t E\left(t'\right)\mathrm{d}t'\right)^2, \tag{7}$$

where $V_{\text{p}} = V_{\text{sc}}(x, R) - 1/R$ is the Coulomb potential experienced by an electron. During the course of system evolution, the electron is ionized when the total-energy $E_c(t) > 0$ and two nuclei are dissociate when the distance between two protons $R(t) > R_D = 10.0$ a.u. [7] (R_D is the biggest internuclear distance). According to above two criteria, four process or channels may be occur at any time interval during the interaction of H_2^+ with the laser pulses:

$$
\begin{aligned}
&H_2^+ + [I] \to H_2^+ \, (E_c(t) \leqslant 0, R(t) \leqslant R_D),\\
&H_2^+ + [I] \to H + H^+ \, (E_c(t) \leqslant 0, R(t) > R_D),\\
&H_2^+ + [I] \to H_2^{2+} + e \, (E_c(t) > 0, R(t) \leqslant R_D),\\
&H_2^+ + [I] \to 2H^+ + e \, (E_c(t) > 0, R(t) > R_D),
\end{aligned} \tag{8}
$$

where $[I]$ stands for the interaction of laser pulse. We defined above dynamic process as survival, dissociation, ionization, and Coulomb explosion of H_2^+, respectively.

3. Numerical recipe for classical dynamics of H_2^+ in the intense laser pulse

3.1. Initial conditions

An initial condition of H_2^+ system decides a classical trajectory. We can select the initial condition by using a single trajectory in the field-free case at random in time intervals [7,9]. The justification is based on the ergodicity of the system. First we give the initial energy E_0 and the internuclear separation R^0, which are equal to those of the ground states of the corresponding quantum system and assume $P(0) = P^0 = 0$. And then we choose a set of (N) initial coordinates of electron $x_i(0) = x_i^0 (i = 1, \ldots, N)$ at random and obtain a set of (N) initial momentum $p_i(0) = p_i^0$ by mean of Hamiltonian (1). Next we solve numerically the initial value problem of the canonical equation of H_2^+system in the free-field for every initial condition $\{x_i^0, p_i^0, R_i^0 = R^0, P_i^0 = P^0\}$ and obtain the curves $S_i : (x_i(t), p_i(t), R_i(t), P_i(t))$ in phase space, In such way, we can obtain a set of (N) curves corresponding to the N initial conditions. We select M points on every curve at random as interactive M initial conditions of H_2^+system and obtain the interactive $NM = N \times M$ initial conditions. These initial conditions can guarantee the total energy is equal. Finally, we solve numerically NM initial value problem of canonical equation (6) of H_2^+system with laser fields and obtain NM classical trajectories of H_2^+in the laser pulse.

3.2. Symplectic method of classical dynamics

The classical dynamic of H_2^+ system in laser pulse is described by Hamiltonian canonical equation (6). The corresponding Hamiltonian function (1) can be written the form $H(P, p; x, R, t) = H_1(P, p) + H_2(x, R, t)$, which is the separated Hamiltonian form including explicitly time. As we all know that the symplectic method is the difference method that preserves the symplectic structure, and is a better method in the calculation of long-time many-step and preserving the structure of system [10,11]. We can construct directly the symplectic scheme tailored to the time-dependent Hamiltonian function from the known symplectic scheme for not including explicitly time [12,13]. For example, the four-stage fourth-order explicit symplectic scheme reads

$$
\begin{aligned}
&u_1^1 = p^n - hc_1 f_1(x^n, R^n, t_n) && v_1^1 = x^n + \tau d_1 g_1(u_1^1),\\
&u_2^1 = P^n - hc_1 f_2(x^n, R^n, t_n) && v_2^1 = R^n + \tau d_1 g_2(u_2^1),\\
& && t^1 = t_n + \tau d_1,\\
&u_1^2 = u_1^1 - hc_2 f_1(v_1^1, v_2^1, t^1) && v_1^2 = v_1^1 + \tau d_2 g_1(u_1^2),\\
&u_2^2 = u_2^1 - hc_2 f_2(v_1^1, v_2^1, t^1) && v_2^2 = v_2^1 + \tau d_2 g_2(u_2^2),\\
& && t^2 = t^1 + \tau d_2,\\
&u_1^3 = u_1^2 - hc_3 f_1(v_1^2, v_2^2, t^2) && v_1^3 = v_1^2 + \tau d_3 g_1(u_1^3),\\
&u_2^3 = u_2^2 - hc_3 f_1(v_1^2, v_2^2, t^2) && v_2^3 = v_2^2 + \tau d_3 g_2(u_2^3),\\
& && t^3 = t^2 + \tau d_3,\\
&p^{n+1} = u_1^3 - hc_4 f_1(v_1^3, v_2^3, t^3) && x^{n+1} = v_1^3 + \tau d_4 g_1(p^{n+1}),\\
&P^{n+1} = u_2^3 - hc_4 f_2(v_1^3, v_2^3, t^3) && R^{n+1} = v_2^3 + \tau d_4 g_2(P^{n+1}),\\
& && t_{n+1} = t^3 + \tau d_4 = t_n + \tau,
\end{aligned}
\tag{9}
$$

where $c_1 = 0$, $c_2 = c_4 = \alpha$, $c_3 = \beta$; $d_1 = d_4 = \alpha/2$, $d_2 = d_3 = (\alpha+\beta)/2$; $\alpha = \left(2 - 2^{1/3}\right)^{-1}$, $\beta = 1 - 2\alpha$, and u_i^j, v_i^j, $i = 1, 2$, $j = 1, 2, 3$ are intermediate stages. We can also use the partitioned Runge–Kutta (PRK) method for separated Hamiltonian function including explicitly time [11-12].

3.3. Probabilities of survival, dissociation, ionization, and Coulomb explosion

Under the action of the intense laser field, the electron of the H_2^+ may leave the two nuclei; this process is defined as ionization, or the two nuclei of the H_2^+ may separate from each other with positive velocity; this process is defined as dissociation or Coulomb explosion. We can distinguish the four dynamic processes (survival, dissociation, ionizations, and Coulomb explosion) according to the criteria (8). We can obtain NM classical trajectories of H_2^+ system in laser pulse under the NM initial conditions by solving numerically the Hamiltonian equation (6). For every time t_k, suppose S_{sur}, S_{dis}, S_{ion}, S_{exp} are the number of the classical trajectories of survival, dissociation, ionization, and Coulomb explosion, respectively, then we obtain the probabilities of survival, dissociation, ionization, and Coulomb explosion which are

$$
\begin{aligned}
P_{\text{s}} &= S_{\text{sur}}/NM,\\
P_{\text{i}} &= S_{\text{dis}}/NM,\\
P_{\text{d}} &= S_{\text{ion}}/NM,\\
P_{\text{ex}} &= S_{\text{exp}}/NM.
\end{aligned}
\tag{10}
$$

Thus the evolution of probabilities of survival, dissociation, ionization, and Coulomb explosion can be also determined.

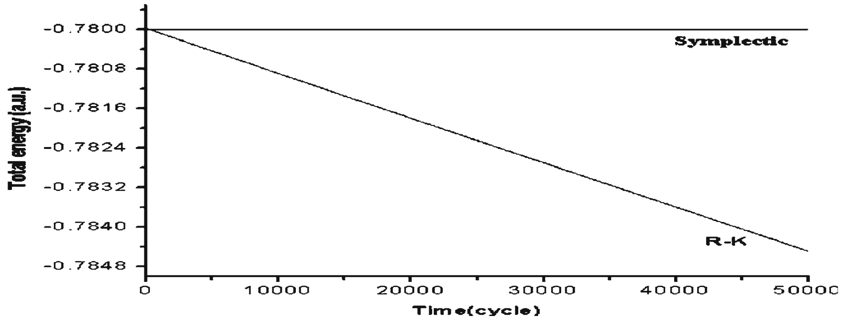

Figure 1. The evolution of the total energy in free-field by using symplectic method and Runge–Kutta method.

4. Results and discussion

We give an initial energy $E_0 = -0.78$ a. u. and compute the evolution of the total energy in free-field by using symplectic method and Runge–Kutta method. Figure 1 indicates that the evolution of the total energy in free-field by using symplectic method can be preserved for long-time computation, but the evolution of the total energy in free-field by using Runge–Kutta method decreases rapidly for long-time computation. We show the evolution of the electronic position and the internuclear distance in free-field by using symplectic method with time in figure 2. The electron and nuclear oscillate periodically near balanced position which illustrate that the system keeps stable by using symplectic method. It is shown that the initial conditions stated in section 3, by means of symplectic method are reasonable and effective.

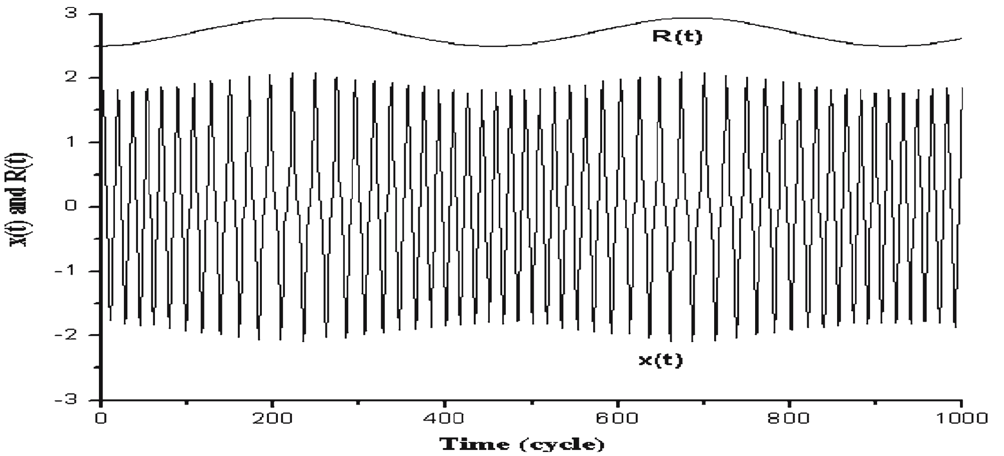

Figure 2. The evolution of the electronic position and the internuclear distance in free-field by using symplectic method.

In order to illustrate the evolution of probabilities of survival, dissociation, ionization and Coulomb explosion in intense laser field, we use 2000 trajectories ($N = 4$, $M = 500$) to generate these four processes. We choose different intensity of laser pulse ($I = 3.0 \times 10^{14}$ W/cm^2, $I = 4.0 \times 10^{14}$ W/cm^2, and $I = 7.0 \times 10^{14}$ W/cm^2) and take the wavelength λ as 532 nm and the laser pulse length as $T_D = 20\,T$, where T is the cycle of laser pulse. In the simulation, the envelope form of the laser pulse we used is

$$f(t) = \begin{cases} \sin^2 \dfrac{\pi t}{20T}, & 0 < t < T_D \\ 0, & \text{otherwise} \end{cases} . \tag{11}$$

In figure 3, we show the time-evolution of survival, dissociation, ionization, and Coulomb explosion of H_2^+ for different intensity of laser fields with wavelength $\lambda = 532$ nm. From figure 3, we can observe that the survival channel is turned off earlier with the increase of intense laser field, simultaneously

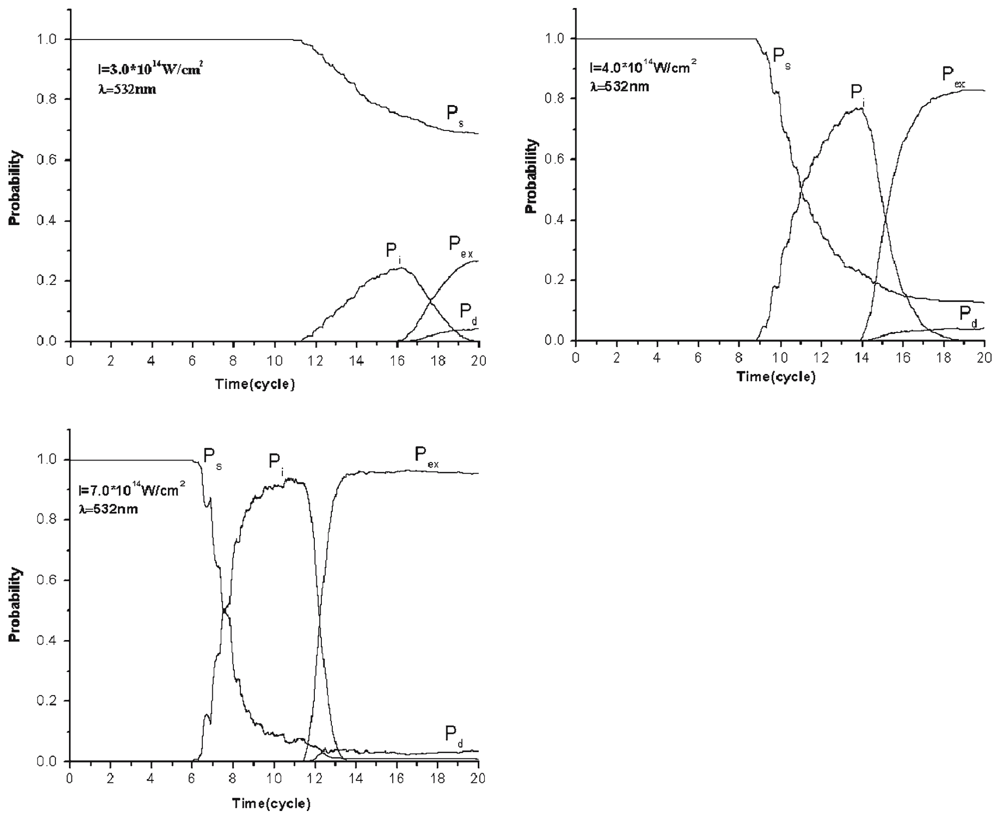

Figure 3. Variation of probability of survival P_s, ionization P_i, dissociation P_d, and Coulomb explosion P_{ex} for different intensity of laser pulse.

the others are turned on earlier. We can also observe that the ionization channel is turned on earliest and the dissociation channel and the Coulomb explosion channel are turned on at the same time. It is exhibited as shown in figure 3 that the curve of the probability of survival declines quickly, the curve of the probability of ionization and Coulomb explosion go up quickly, and the curve of the probability of dissociation do not vary almost with the increase of intense laser field. There is a very interesting phenomenon in figure 3 that the probability of Coulomb explosion does not appear until the probability of ionization reaches the peak value, and then the probability of ionization reduces rapidly and goes to zero. Finally, the probability of Coulomb explosion goes up rapidly and reaches its peak value which is the same as the peak value of ionization, then keeps unchanged. These results are in agreement with ones obtained by numerically solving the time-dependent Schrödinger equation (1D model) in the same conditions [14].

We can give our explanation of above dynamic process as follows:

(1) It is well known that the mass of electron is lighter than the mass of proton, the lighter electron near the nuclei gets the energy from the laser pulse rapidly until it is ionized, the heavier nuclei are not separated each other at that time. Thus the ionization channel is turned on first, the H_2^{2+} can be obtained, and the probability of ionization goes up with time.

(2) Two nuclei of H_2^{2+} are separated rapidly because of the Coulomb force of each other and the Coulomb explosion phenomenon appears. And then the probability of ionization declines rapidly and the probability of Coulomb explosion goes up rapidly. The probability of Coulomb explosion reaches its peak value which is the same as the peak value of the ionization. Finally ions of H_2^{2+} disappear and this peak value keeps unchanged.

(3) The variation of the probability of dissociation is not evident in the intense of laser fields, which is because that the electron is ionized rapidly in ultrashort intense laser, and it is difficult for the nuclei with big mass to obtain the momentum before the pulse ends. Thus it is almost impossible that the two nuclei separated and the electron still bounded around the nuclei in the intense ultrashort pulse.

(4) The probability of dissociation and Coulomb explosion appear almost at the same time, which is attributed to the following complex regime: the electron and two nuclei move on a beeline, the two nuclei continue to be separated after the Coulomb explosive channel is turned on. During the course of separation, there is a nuclear close to the electron continually, which is likely that the nuclear (H^+) closes to the electron continually and H atom is generated. This process will lead the increase

of the probability of dissociation. It is not the same as the regime of the fact that the H_2^+ is dissociated to $H+H^+$ in weakly long-wavelength laser pulse.

As stated above, the dynamic process of survival, dissociation, ionizations, and Coulomb explosion appears successively for H_2+ in the ultrashort intense laser pulse, but the arisen time is not the same. First the ionization channel is turned on, and then the channels of Coulomb explosion and dissociation are turned on nearly at the same time after the probability of ionization goes up its peak value. With the increase of intense of laser field, every channel is turned on ahead and the peak value of probabilities of ionization and Coulomb explosion is increased except for dissociation. Thus we can obtain the H_2^{2+}, H, and H^+ by adjusting the laser intensity and controlling the action time of H_2^+ in ultrashort intense laser pulse. For example, we take $I = 7.0 \times 10^{14}$W/cm^2 and 11 optics cycles for action time, then we can obtain a lot of H_2^{2+}. If we take 14 optics cycles, we can obtain many of H^+.

In conclusion, we adopt classic theory to discuss the dynamic process of 1D H_2^+ in intense field by using the symplectic method. The initial conditions are chosen at random in the field-free case, and then the Hamiltonian canonical equations of H_2^+ system in the intense laser field are solved numerically by mean of the symplectic method under these initial conditions. The time-evolution of survival, dissociation, ionization, and Coulomb explosion of H_2^+ for different intensity of laser fields is illustrated. The results obtained in this paper are in agreement with ones obtained by mean of quantum theory.

Acknowledgments

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