

Computation of quasiclassical trajectories by symplectic algorithm for the $\text{N}(^4\text{S}) + \text{O}_2(\text{X}^3\Sigma_g^-) \rightarrow \text{NO}(\text{X}^2\Pi) + \text{O}(^3\text{P})$ reaction system

Jianfeng He,* Wei Hua, Xueshen Liu, and Peizhu Ding

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

E-mail: hjf1919@yahoo.com.cn

Received 14 September 2004; revised 20 September 2004

Computation of quasiclassical trajectories for the $\text{N}(^4\text{S}) + \text{O}_2(\text{X}^3\Sigma_g^-) \rightarrow \text{NO}(\text{X}^2\Pi) + \text{O}(^3\text{P})$ atmospheric reaction system, based on a new ground potential energy surface reported by R.Sayós et al., has been performed in this work by means of both the fourth-order explicit symplectic algorithm (S4) and the fourth-order Runge–Kutta scheme (RK4), and then computed results of two schemes are compared. It is shown that RK4 cannot preserve energy conservation and symplectic structure of the reaction system, which results in the bad veracity of the trajectory calculation. RK4 cannot rightly reflect both the colliding mode and the reaction mode of the trajectories. Moreover, the amplitudes of vibration of the reactant molecule and the product molecule become gradually small with the time increasing, and their rotation–vibrational levels in fact vary during the integration. For these reasons, RK4 cannot assure the accuracy of the quasiclassical trajectory (QCT) study of the atmospheric reaction. However, S4 maintains these characteristics and can actually describe the circumstance of the reaction system. S4 is better than RK4 is prospective in the QCT study of the chemical reaction.

KEY WORDS: symplectic algorithm, quasiclassical trajectory, chemical reaction

1. Introduction

The quasiclassical trajectory (QCT) method has gradually developed and turned into an effectively academic method of the dynamics study in the chemical reaction [1]. In the QCT study, motion of atomic nuclei on the electronic potential energy surface (PES) has been described by the canonical equations of Hamilton system and the integral method frequently used is Runge–Kutta or Gear scheme [2–3]. The improvement of calculated results depends greatly on

*Corresponding author.

the PES accuracy of the reaction system, and the integral method that can preserve some constancies of the reaction system is rarely noticed. The Hamilton system has the symplectic structure. In the early 1980s, Ruth [4] and Feng Kang [5] advanced respectively the symplectic algorithm that is a difference method preserving the symplectic structure of Hamilton system, and then Feng Kang, Qin Mengzhao and Yoshida et al. carried out a systemic study on the symplectic algorithm [6–9]. To this day, the symplectic algorithm has been widely applied to astronomy [10], plasma physics [11], quantum mechanics [12–13] and other fields.

The elementary atmospheric reaction, $\text{N}(^4\text{S}) + \text{O}_2(\text{X}^3\Sigma_g^-) \rightarrow \text{NO}(\text{X}^2\Pi) + \text{O}(^3\text{P})$, and its reverse reaction play an important role in the earth's atmospheric chemistry. This reaction is a source of infrared chemiluminescence in the thermosphere [14]. High temperature studies of the kinetics and dynamics of the atmospheric reaction and its reverse one are also significant to interpret the chemical and physical phenomena taking place during the re-entry of spacecrafts into the Earth's atmosphere [15]. Some *ab initio* studies have been presented about the ground ($^2A'$) potential energy surface involved in this atmospheric reaction [16–18]. Using on a new analytical fit of *ab initio* electronic structure calculation for the ground PES reported by R.Sayós et al. [18] in this work, we present a calculation of quasiclassical trajectories with the fourth-order explicit symplectic algorithm [19] (S4) for the atmospheric reaction, and then the result is compared to that computed by the fourth-order Runge–Kutta scheme (RK4). It indicates that RK4 cannot preserve the energy constant and symplectic structure of Hamilton system, and computed trajectories actually do not describe the motion of the reaction system. However, S4 keeps these constancies of the reaction system, its results are markedly better than that of RK4. The organization of this paper is as follows: section 2 introduces the canonical equations of the atom–molecule reaction system and its fourth-order explicit symplectic algorithm (S4). In section 3, the results of the calculation and some discussions are given. Finally we have drawn some conclusions in section 4.

2. The computational method

In the atom–molecule ($A + BC$) reaction system, the mass of atom A, B, C, respectively denotes m_A , m_B , m_C . In the present case, A is taken to be the nitrogen atom (N), B is the first oxygen atom (O) and C is the second oxygen atom (O). Because the reaction system has no outfield action, the momentum of the reaction system is constant. Separating out the center-of-mass motion, we write the internal Hamiltonian in the form

$$H = \frac{1}{2\mu_{B,C}} \sum_{j=1}^3 P_j^2 + \frac{1}{2\mu_{A,BC}} \sum_{j=4}^6 P_j^2 + V(Q_1, Q_2, \dots, Q_6), \quad (1)$$

where Q_j ($j=1, 2, \dots, 6$) represents the generalized Cartesian coordinate, P_j ($j=1, 2, \dots, 6$) is the momentum conjugate to the Q_j , $V(Q_1, Q_2, \dots, Q_6)$ is the potential energy function, and the reduced masses are

$$\mu_{B,C} = \frac{m_B m_C}{m_B + m_C}, \quad \mu_{A,BC} = \frac{m_A(m_B + m_C)}{m_A + m_B + m_C}.$$

Canonical equations of the reaction system are

$$\dot{Q}_j = \frac{\partial H}{\partial P_j}, \quad \dot{P}_j = -\frac{\partial H}{\partial Q_j} = -\frac{\partial V}{\partial Q_j}. \quad (j = 1, 2, \dots, 6) \quad (2)$$

From (1), the Hamiltonian is separable and has the following fourth-order explicit symplectic algorithm [19]

$$\begin{aligned} P_j^1 &= P_j^n - C_1 \tau \left(\frac{\partial V}{\partial Q_j} \right)_{Q_j^n}, & Q_j^1 &= Q_j^n + d_1 \tau \left(\frac{\partial H}{\partial P_j} \right)_{P_j^1}, \\ P_j^2 &= P_j^1 - C_2 \tau \left(\frac{\partial V}{\partial Q_j} \right)_{Q_j^1}, & Q_j^2 &= Q_j^1 + d_2 \tau \left(\frac{\partial H}{\partial P_j} \right)_{P_j^2}, \\ P_j^3 &= P_j^2 - C_3 \tau \left(\frac{\partial V}{\partial Q_j} \right)_{Q_j^2}, & Q_j^3 &= Q_j^2 + d_3 \tau \left(\frac{\partial H}{\partial P_j} \right)_{P_j^3}, \\ P_j^{n+1} &= P_j^3 - C_4 \tau \left(\frac{\partial V}{\partial Q_j} \right)_{Q_j^3}, & Q_j^{n+1} &= Q_j^3 + d_4 \tau \left(\frac{\partial H}{\partial P_j} \right)_{P_j^{n+1}}, \end{aligned} \quad (j = 1, 2, \dots, 6) \quad (3)$$

where $C_1 = 0, C_2 = C_4 = \alpha, C_3 = \beta, d_1 = d_4 = \alpha/2, d_2 = d_3 = (\alpha + \beta)/2, \beta = 1 - 2\alpha, \alpha = (2 - 2^{1/3})^{-1}$.

3. Results and discussion

A lot of quasiclassical trajectories for the atmospheric reaction, based on a new analytical fit of *ab initio* electronic structure calculation for the ground PES reported by R. Sayós et al. [18], have been calculated by means of S4 and RK4. The following is computed results of two integral schemes and the comparison of them. (It should be noticed that RHO denotes the initial distance between the N atom and the O₂ molecule in a.u., E_t denotes the relative translational energy in eV, h is the time step size in second, ν and J represent respectively, the vibrational and rotational level of O₂ molecule, R is the separate distance of nuclei and the energy unit is taken to be kcal/mol.)

3.1. The deviation of total energy

Figure 1 depicts the comparison of total energies evolving with the time computed respectively by S4 and RK4. From figure 1a, when RK4 is used in the calculation, the total energy descends with the time increasing. This reveals that the

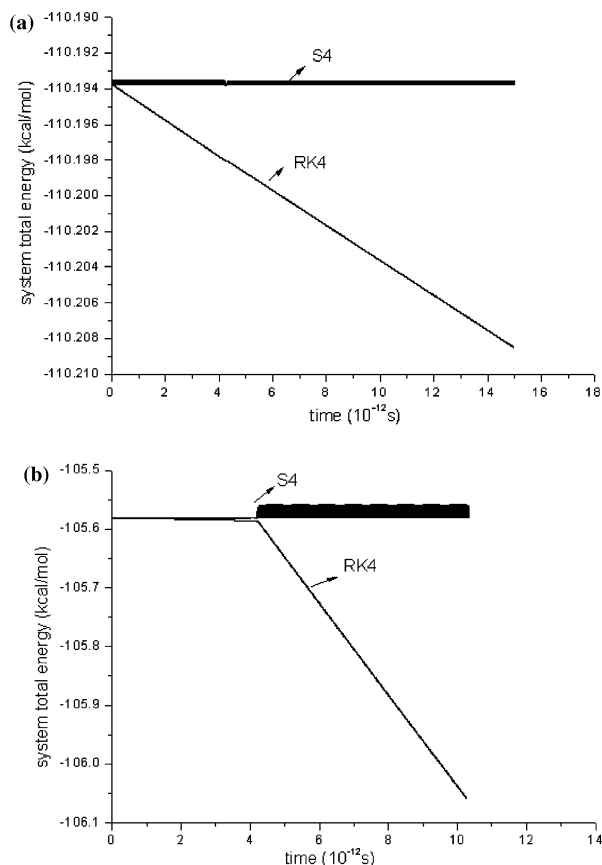


Figure 1. Comparison of total energies evolving with the time computed respectively by RK4 and S4: (a) $E_t = 0.3$ eV, $v = 0$, $J = 8$, $h = 5.0 \times 10^{-16}$ s (non-reaction), (b) $E_t = 0.5$ eV, $v = 0$, $J = 8$, $h = 5.0 \times 10^{-16}$ s (reaction).

deviation of total energy for the reaction system will become larger if the time is longer. We believe that the computed error contains the round error and the truncation error. The phenomenon in figure 1a is accounted for that the deviation of the total energy adds in value with the time since the truncation error continuously accumulates during the integration. However, since the truncation error does not accumulate with the integration using S4, no total energy loss occurs. Except that the total energy computed by S4 shakes slightly near the exact value, it is almost a constant in figure 1a. Since a reaction takes place in figure 1b (no reaction yet takes place in figure 1a), the phenomenon in figure 1b is a little different from that in figure 1a. The curve of the total energy evolving with the time computed by RK4 in the product part from figure 1b has a larger slope than in the reactant part, and meanwhile the vibrating amplitude of the total energy computed by S4 in the product part is clearly larger than that in the reactant part. When no reaction happens (in figure 1a), the deviation of the total energy evolving with the time is mainly connected with

the potential energy curve of O_2 molecule. However, the deviation is determined by the potential energy curve of O_2 molecule before the reaction takes place, and it is relative to that of NO molecule after the reaction if there is a reaction occurring (in figure 1b). Figure 1b characterizes the effect of NO molecule on the energy error is greater than that of O_2 molecule.

The deviation of total energy with respect to the exact value respectively computed by S4 and RK4 with different time step sizes at $RHO = 300$ a.u. and $E_t = 0.4$ eV is displayed in table 1. The results computed by RK4 in table 1a indicate that the loss of total energy increases with the time step size rising at the given initial condition of O_2 molecule. When the vibrational level of O_2 molecule (at $J = 8$) enlarges, the deviation of total energy increases in quantity at the fixed time step size. The rotational level of O_2 molecule (at $v = 0$) has almost the same influence on the deviation of total energy except for $J = 4$ and $J = 16$. Table 1b shows that the deviation of total energy computed by S4 exhibits either positive or negative value because the computed value vibrates near the exact energy value. The deviation of total energy computed by S4 is much less than that computed by RK4 at the same condition suggests that S4 can better preserve the total energy of the reaction system than RK4.

To research the affect of the initial distance on the deviation of total energy, we have computed these deviations by RK4 and S4, which are represented in table 2, with different initial distances at $E_t = 0.4$ eV and $h = 6.0 \times 10^{-16}$ s. From table 2a, the initial distance RHO becomes longer will result in that the loss of total energy computed by RK4 at the given initial condition is enhanced. The affect of the rotation–vibrational level on the deviation is similar to that in table 1a. Furthermore, the variable law of the deviation of total energy computed by S4 in table 2b is still according with table 1b. Now, we note that the deviation does not always grow up with the initial distance rising at $v = 0, 1, 2$ and $J = 8$ in table 2a. The reason is that the colliding case of trajectories (i.e., elastic collision, inelastic collision and reactive collision) shifts when the initial distance broadens and consequently the loss of total energy has a different trend.

3.2. The comparison of trajectories

Since RK4 cannot maintain energy conservation and symplectic structure of the reaction system, the trajectories computed by RK4 have some evident differences from those computed by S4 at the same condition. Figure 2 is the comparison of some typical trajectories. First, the trajectories computed by RK4 at $E_t = 0.9$ eV, $v = 0, J = 16$, $RHO = 110$ a.u and $h = 4.0 \times 10^{-16}$ s (in figure 2a) clarify that no reaction occurs although the collision go through a transition state. Moreover, after the O_2 molecule collides with the N atom, the period and amplitude of vibration of O_2 molecule become large. From figure 2b, however, a reaction that produces the NO molecule (the second oxygen atom) takes place.

Table 1
The deviation of total energy with respect to the exact value computed respectively by RK4 and S4 with different time step sizes at $RHO = 300$ a.u. and $E_t = 0.4$ eV.

	$h = 1.0 \times 10^{-16}$ s	2.0×10^{-16} s	4.0×10^{-16} s	6.0×10^{-16} s	8.0×10^{-16} s	10.0×10^{-16} s
<i>a</i>						
$v = 0, J = 0$	0.587×10^{-5}	0.188×10^{-3}	0.600×10^{-2}	0.451×10^{-1}	0.185	0.533
$v = 0, J = 4$	0.428×10^{-5}	0.137×10^{-3}	0.437×10^{-2}	0.330×10^{-1}	0.137	0.406
$v = 0, J = 8$	0.609×10^{-5}	0.195×10^{-3}	0.622×10^{-2}	0.466×10^{-1}	0.187	0.508
$v = 0, J = 12$	0.795×10^{-4}	0.260×10^{-2}	0.140	0.444	$0.191 \times 10^{+1}$	$0.168 \times 10^{+2}$
$v = 0, J = 16$	0.102×10^{-4}	0.325×10^{-3}	0.103×10^{-1}	0.760×10^{-1}	0.285	0.666
$v = 1, J = 8$	0.132×10^{-4}	0.421×10^{-3}	0.133×10^{-1}	0.925×10^{-1}	0.516	$0.121 \times 10^{+1}$
$v = 2, J = 8$	0.552×10^{-4}	0.179×10^{-2}	0.257×10^{-1}	0.717	$0.222 \times 10^{+1}$	$0.680 \times 10^{+1}$
<i>b</i>						
$v = 0, J = 0$	-0.915×10^{-6}	-0.441×10^{-6}	0.260×10^{-5}	-0.214×10^{-4}	-0.133×10^{-2}	0.110×10^{-3}
$v = 0, J = 4$	-0.210×10^{-5}	-0.439×10^{-5}	0.131×10^{-4}	0.780×10^{-4}	0.269×10^{-3}	0.681×10^{-3}
$v = 0, J = 8$	-0.627×10^{-6}	-0.743×10^{-6}	0.959×10^{-6}	-0.397×10^{-3}	0.670×10^{-4}	0.638×10^{-4}
$v = 0, J = 12$	-0.314×10^{-5}	-0.315×10^{-4}	-0.883×10^{-3}	0.103×10^{-3}	-0.575×10^{-2}	-0.818×10^{-2}
$v = 0, J = 16$	0.311×10^{-5}	0.330×10^{-5}	-0.157×10^{-4}	-0.103×10^{-4}	-0.4045×10^{-2}	-0.224×10^{-3}
$v = 1, J = 8$	-0.225×10^{-5}	-0.602×10^{-6}	-0.210×10^{-3}	-0.841×10^{-4}	-0.117×10^{-3}	0.268×10^{-3}
$v = 2, J = 8$	-0.233×10^{-5}	-0.769×10^{-5}	-0.216×10^{-3}	-0.231×10^{-3}	0.170×10^{-3}	-0.417×10^{-1}

(a) The results computed by RK4,

(b) The results computed by S4.

Table 2
 The deviation of total energy with respect to the exact value computed respectively by RK4 and S4 with different initial distances at $E_t = 0.4\text{eV}$ and $h = 6.0 \times 10^{-16}\text{s}$.

	RHO=20	40	100	200	300	500
<i>a</i>						
$v = 0, J = 0$	0.225×10^{-2}	0.398×10^{-2}	0.130×10^{-1}	0.165×10^{-1}	0.451×10^{-1}	0.387×10^{-1}
$v = 0, J = 4$	0.223×10^{-2}	0.344×10^{-2}	0.168×10^{-1}	0.418×10^{-1}	0.330×10^{-1}	0.677×10^{-1}
$v = 0, J = 8$	0.263×10^{-2}	0.147	0.124×10^{-1}	0.441×10^{-1}	0.466×10^{-1}	0.128
$v = 0, J = 12$	0.180×10^{-2}	0.476×10^{-2}	0.179	0.552	0.317	0.712
$v = 0, J = 16$	0.524×10^{-1}	0.367×10^{-1}	0.183×10^{-1}	0.65×10^{-1}	0.76×10^{-1}	0.917×10^{-1}
$v = 1, J = 8$	0.739×10^{-2}	0.166	0.326×10^{-1}	0.881×10^{-1}	0.925×10^{-1}	0.323
$v = 2, J = 8$	0.161×10^{-1}	0.146	0.514×10^{-1}	0.162	0.717	0.653
<i>b</i>						
$v = 0, J = 0$	-0.187×10^{-4}	0.493×10^{-4}	-0.101×10^{-4}	-0.800×10^{-4}	-0.214×10^{-4}	-0.731×10^{-4}
$v = 0, J = 4$	-0.166×10^{-3}	0.836×10^{-4}	0.265×10^{-4}	0.449×10^{-5}	0.781×10^{-4}	-0.204×10^{-5}
$v = 0, J = 8$	-0.306×10^{-5}	-0.139×10^{-2}	0.776×10^{-4}	-0.651×10^{-3}	-0.397×10^{-3}	0.667×10^{-5}
$v = 0, J = 12$	0.102×10^{-3}	0.339×10^{-4}	-0.593×10^{-3}	-0.932×10^{-3}	-0.12×10^{-2}	-0.187×10^{-4}
$v = 0, J = 16$	-0.293×10^{-4}	-0.26×10^{-2}	0.543×10^{-4}	-0.195×10^{-4}	-0.104×10^{-4}	-0.371×10^{-3}
$v = 1, J = 8$	0.964×10^{-5}	-0.532×10^{-3}	0.205×10^{-4}	0.251×10^{-4}	-0.839×10^{-4}	-0.736×10^{-5}
$v = 2, J = 8$	-0.113×10^{-3}	-0.428×10^{-3}	-0.185×10^{-2}	-0.866×10^{-4}	-0.485×10^{-3}	-0.461×10^{-2}

(a) The results computed by RK4,
 (b) The results computed by S4.

It is concluded that the loss of total energy may influence the colliding made of the trajectories. Second, two differences exist in figure 2c and figure 2d that respectively display the trajectories computed by RK4 and S4 at $E_t = 0.9$ eV, $v = 0$, $J = 0$, $RHO = 220.0$ a.u. and $h = 7.5 \times 10^{-16}$ s. One is the reaction mode, that is, figure 2c is a direct reaction and figure 2d is an indirect reaction. Another is that the product in figure 2c is the NO molecule (the first oxygen atom) and there is a different NO molecule (the second oxygen atom) in figure 2d. The third is that the amplitude of vibration of O_2 molecule computed by RK4 becomes gradually small with the time increasing, however the value computed by S4 is always consistent, as described in figure 2e (the comparison of trajectories in the reactant part at $E_t = 0.9$ eV, $v = 0$, $J = 8$, $h = 6.0 \times 10^{-16}$ s). From figure 2e, the amplitude computed by RK4 is much less than that computed by S4 between 2.0×10^{-11} s and 2.03×10^{-11} s. The reduction of the amplitude because of the loss of total energy corresponds in effect to the variation of the rotation–vibrational level of O_2 molecule before the collision. Thereby, the initial condition of the reaction system cannot be preserved during the integration when RK4 is used. Finally, the comparison of the trajectories in the product molecule part exhibits that the period and the amplitude of vibration of the product NO molecule computed by RK4 are less than those computed by S4. In the same way, the period and amplitude of vibration are relative to the rotation–vibrational level of NO molecule, and from this the accuracy of the QCT study of the rotation–vibrational level distribution of the product molecule cannot keep by RK4.

3.3. *Typical trajectories and reaction mode analysis*

We calculate a large number of trajectories by S4 for the atmospheric reaction, and some typical trajectories are sought out in figure 3 at different relative translational energies and rotation–vibrational energy levels. Even though most of the reactive trajectories evolve through a direct mechanism, some of them take place in an indirect way, whose number is actually rare. Figure 3a and b show the typical trajectories proceeding through an indirect mechanism. The N atom approaches the O_2 molecule until both N–O bonds are formed. And they keep vibrating for about 3.0×10^{-12} s, eventually evolving towards product, giving rise to a reaction at either end of the O_2 molecule. Figure 3a display that the N atom links with the first oxygen atom to make the NO molecule, however the reaction product in figure 3b is consisted of the N atom and the second oxygen atom. The typical trajectories in a direct mechanism are manifested in figure 3c. The N atom approaches continuously to the O_2 molecule, in such a way that the vibration of O_2 molecule does not influence by the incoming N atom until the NO bond distance is almost reached. When the NO molecule is formed, the O–O distance grows fast. Figure 3d in which no reaction occurs displays a

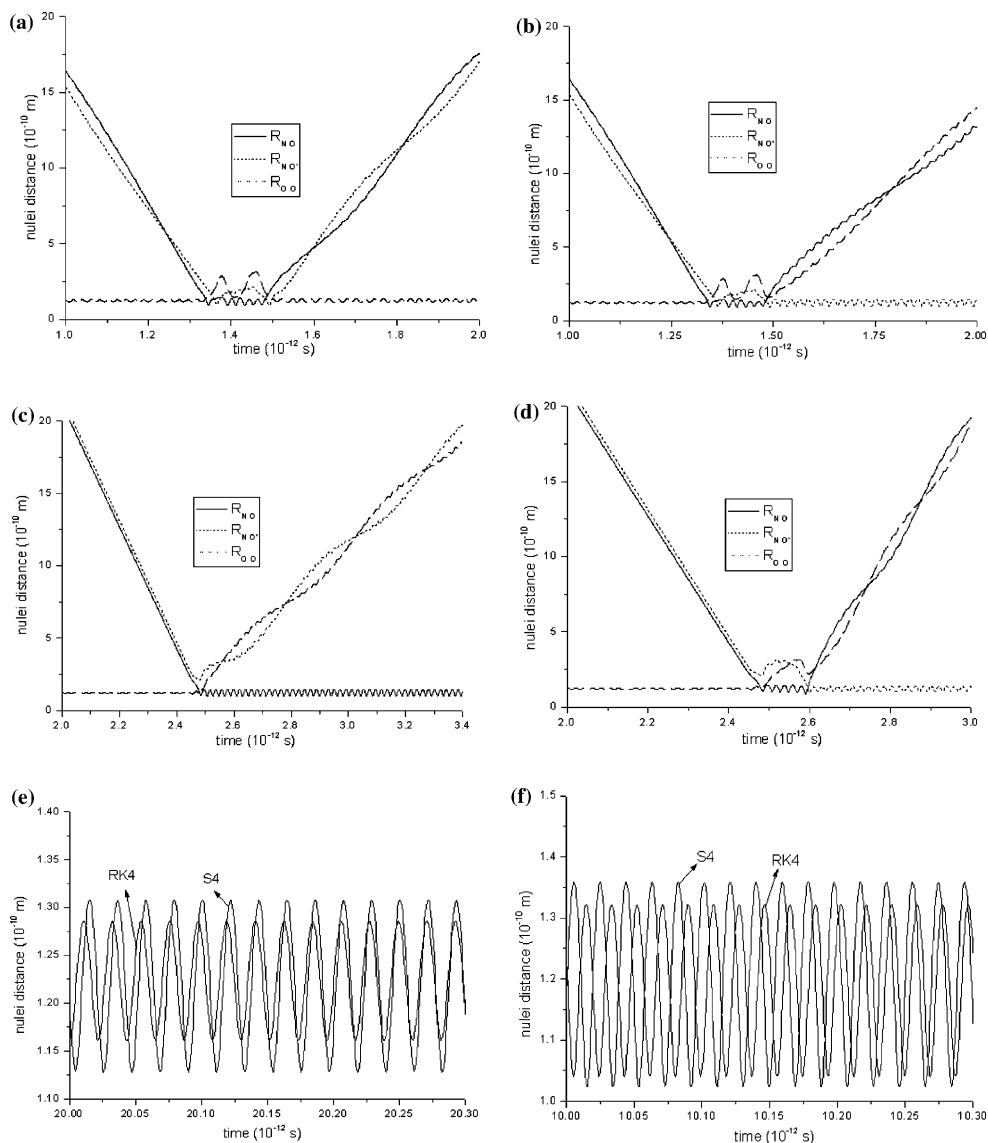


Figure 2. Comparison of trajectories evolving with time computed respectively by RK4 and S4. (a) $E_t = 0.9$ eV, $v = 0$, $J = 16$, $RHO = 110.0$ a.u., $h = 4.0 \times 10^{-16}$ s (by RK4). (b) $E_t = 0.9$ eV, $v = 0$, $J = 16$, $RHO = 110.0$ a.u., $h = 4.0 \times 10^{-16}$ s (by S4). (c) $E_t = 0.9$ eV, $v = 0$, $J = 0$, $RHO = 220.0$ a.u., $h = 7.5 \times 10^{-16}$ s (by RK4). (d) $E_t = 0.9$ eV, $v = 0$, $J = 0$, $RHO = 220.0$ a.u., $h = 7.5 \times 10^{-16}$ s (by S4). (e) $E_t = 0.9$ eV, $v = 0$, $J = 8$, $h = 6.0 \times 10^{-16}$ s (O₂ molecule). (f) $E_t = 0.6$ eV, $v = 0$, $J = 8$, $h = 5.0 \times 10^{-16}$ s (NO molecule).

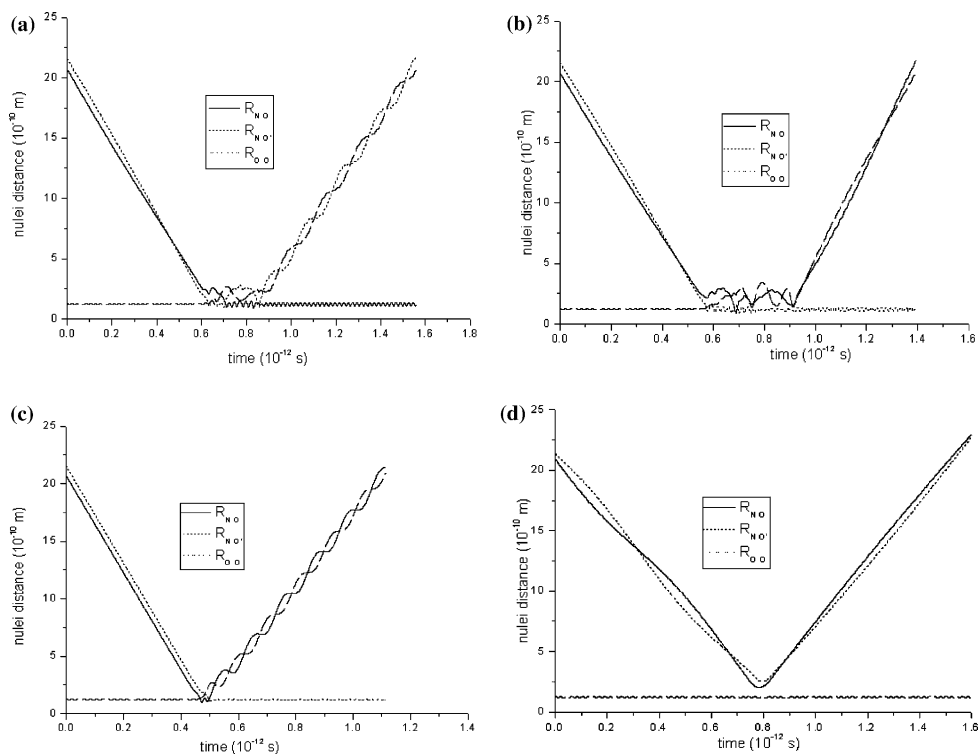


Figure 3. Typical trajectories and reactive mode analysis at $h = 1.0 \times 10^{-16}$ s and $RHO = 40.0$ a.u. (a) $E_t = 0.5$ eV, $v = 0$, $J = 8$ (b) $E_t = 0.6$ eV, $v = 0$, $J = 8$ (c) $E_t = 0.9$ eV, $v = 0$, $J = 0$ (d) $E_t = 0.3$ eV, $v = 0$, $J = 16$.

typically elastic collision, where the period and amplitude of vibration of O_2 molecule have no variation after the N atom collides with O_2 molecule. The inelastic collision that changes the internal energy of O_2 molecule also exists, and we do not exhibit for simplicity.

4. Conclusions

Based on a new analytical fit of *ab initio* electronic structure calculation for the ground PES reported by R. Sayós et al., we have presented the computation of quasiclassical trajectories for the $N(^4S) + O_2(X^3\Sigma_g^-) \rightarrow NO(X^2\Pi) + O(^3P)$ atmospheric reaction system by means of both S4 and RK4, and then the computed results of two schemes are compared. It is known that RK4 cannot preserve energy conservation and symplectic structure of the reaction system, which result in the bad veracity of the trajectory calculation. Because of the loss of total energy, RK4 cannot rightly reflect both the colliding mode and the reaction mode of the trajectories. The amplitude of vibration of the reactant O_2

molecule becomes gradually small with the time increasing, and the initial condition of O₂ molecule is correspondingly transformed before the reaction. Since RK4 also reduce the amplitude of the product NO molecule, it cannot guarantee the accuracy of the study of the rotation–vibrational level distribution of the product molecule. However, S4 maintains energy conservation and symplectic structure of the reaction system and can actually describe the colliding trajectories of the reaction system. Moreover, since S4 can choose larger time step size, it may markedly save the computed time of the QCT study. It is concluded that S4 is better than RK4 in the QCT study of the chemical reaction. If the S4 takes the place of the usual integral method (It is RK4 here), the validity and the reliability of the QCT study may be improved.

Acknowledgments

This work was supported by National Natural Science Foundation of China (10171039, 10074019) and Special Funds for Major State Basic Research Projects (G1999032804). The authors are grateful to “State Key Laboratory of Scientific and Engineering Computing, Chinese Academy of Sciences” for providing a part of computer time on the NO. 1 computer cluster.

References

- [1] L.M. Raff and D.L. Thompson, *Theory of Chemical Reaction Dynamics*, Vol. III, ed. M. Bear, (Florida: CRC Press, Inc. Boca Raton, FL 1985), 1. pp.
- [2] L.M. Raff and D.L. Thompson, *Theory of Chemical Reaction Dynamics*, Vol. III, ed. M. Bear (Florida: CRC Press, Inc. Boca Raton, 1985), 8. pp.
- [3] P. Brumer and M. Karplus, *Faraday Disc. Chem. Soc.* 55 (1973) 80.
- [4] R.D. Ruth, *IEEE Trans. Nuc. Sci.* 30 (1983) 2669.
- [5] K. Feng, in: *Proceedings of the 1984 Beijing Symposium on Differential Geometry and Differential Equations Computation of Partial Differential Equations*, ed. K. Feng (Science Press, Beijing, 1985), 42. pp.
- [6] K. Feng, *J. Comp. Math.* 4 (1986) 279.
- [7] K. Feng and M.Z. Qin, *Prog. Nat. Sci.* 1 (1991) 105.
- [8] K. Feng, in: *Proceedings of the 1st China–Japan Conference on Numerical Mathematics* (World Scientific, Beijing, 1992; Singapore, 1993).
- [9] H. Yoshida, *Phys. Lett. A.* 150 (1990) 262.
- [10] L. Liu, X.H. Liao, *Celest. Mech. Astron.* 59 (1994) 221.
- [11] B. Gladman, M. Duncan and J. Candy, *Celest. Mech. Dynam. Astron.* 52 (1991) 221.
- [12] X.S. Liu, X.Y. Liu, Z.Y. Zhou, P.Z. Ding and S.F. Pan, *Int. J. Quantum Chem.* 79 (2000) 343.
- [13] X.S. Liu, L.W. Su, X.Y. Liu and P.Z. Ding, *Int. J. Quantum Chem.* 83 (2001) 303.
- [14] P. Warneck, *Chemistry of the Natural Atmosphere*, chap. 3 (Academic, San Diego, 1998).
- [15] N. Balakrishnam, E. Sergueeva, V. Kharchenko and A. Dalgarno, *J. Geo-phys. Res.* 105 (2000) 18549.
- [16] M. González, I. Miquel and R. Sayós. *J. Chem. Phys.* 115 (2001) 8838.
- [17] M. González, I. Miquel and R. Sayós. *Chem. Phys. Lett* 360 (2002) 521.
- [18] R. Sayós, C. Oliva and M. González, *J. Chem. Phys.* 117 (2002) 670.

- [19] M.Z. Qin, D.L. Wang and M.Q. Zhang. *J. Comp. Math.* 9 (1991) 211.
- [20] M. Karplus, R.N. Porter and R.D. Sharma. *J. Chem. Phys.* 43 (1965) 3259.