

The comparative of a family of high order Predictor-Corrector algorithms for First Principle Chemical Dynamics Simulation

Xuchong Liu^{1,2}, Dafang Zhang¹, Heng Gong³, Heng Wu⁴

¹Post station of computer science and technology, Hunan University, Changsha, China

²Department of information technology, Hunan Police Academy, Changsha, China

³Department of computer science, Civil Aviation Flight University of China, Sichuan, China

⁴Department of computer science, Texas Tech University, Lubbock, USA

ABSTRACT

This article describes the comparative of a family of prediction-correction integration algorithms with a high-order predictor for first principle chemical dynamics simulations. The previous paper shows the prediction-correction integration algorithm with high-order predictor is better than Verlet by comparing. However, parts of the results are worse than Verlet since the high-order predictor uses two positions to predict indirect increases in the step size. Moreover, the external interpolation is also worse than the internal interpolation in some cases.

Keywords: High order; predictor corrector; Integrate; dynamics

1. INTRODUCTION

Classical trajectory chemical dynamics simulations [1,2,3,4,5] have been widely used to study reaction dynamics since the 1960s. Also, some scholars focus on high performance computing [6,7,8,9,10,11,12]. Different from the variational transition state theory (VTST) and reaction path Hamiltonian methods [13], they provide a much greater insight into the dynamics of reactions, for the classical equations of motion of the atoms are numerically integrated on a potential energy surface (PES). In contrast, the traditional approaches adopt an analytic function obtained by fitting ab initio and/or experimental data [13,14,15] to construct the surface. Regardless of a small number of atoms or a high degree of symmetry [16,17,18,19,20,21,22,23], it is practical. Recently, some researchers show additional approaches and algorithms for representing PESs. Wang and Karplus first demonstrated that the trajectories may be integrated “on the fly” when the potential energy and gradient are available at each point of the numerical integration according to an electronic structure theory calculation. During the numerical integration, the method directly calculates the local potential and gradient under an electronic structure theory in a “direct dynamics” simulation.

However, regarding a high-level electronic structure theory, the computation of direct dynamics simulations become quite expensive. Thus, it is important to use the largest numerical integration step size when maintaining the accuracy of the trajectory. Helgaker et al. adopt the second derivative of the potential (Hessian). Using a second order Taylor to expand the Hessian, a local approximation PES can be constructed and the trajectories can be approximately calculated. For local quadratic potential is only valid in a small region (named a “trust radius”), the equations of motion are only integrated within the trust radius. Millam et al. used a fifth-order polynomial or a rational function to fit the potential between the starting and the ending of each integration step. It provides a more accurate trajectory in the trust region and calculates a larger integration steps. That involves a predictor step, the integration on the approximate quadratic model potential. The following step, fitting on the fifth order PES between the start point and the end point in the trust radius, is also called the “corrector step.” It is named the Hessian based predictor-corrector integration scheme.

In the study reported here, we present the comparative of a family of Hessian based predictor-corrector integration schemes. Those schemes adopt parts of the Position, Velocity, Gradient and Hessian of the previous and full of them of current time step position of atom to predict the next time step position of atom. The corrector step employs a fifth-order polynomial fitted to the Energy, Gradient and Hessian at the beginning and end points of each step. No additional ab initio calculations are required beyond those needed for the second-order scheme in new schemes, since the energy, gradient, and Hessian calculated at the end of the current step are used for the local quadratic surface in the predictor phase of the next step.

The paper is organized as follows. Section 2 presents a family of high order time-polynomial predictor which is derived as solutions for the second-order equation. Section 3 describes numerical studies of the new scheme as compared to some existing schemes through three chemical reaction dynamics simulations. Section 4 draws the conclusions.

2. METHODOLOGY

Firstly, we present the new family of integration method for direct dynamics simulations developed from a family of algorithms [SchHesInt, SchHesUpd1999, HessInt2007, ZhuangHessUpdt] employing a prediction-correction approach[24,25]. As illustrated in Fig. 1, in each time step of the integration method, the prediction is used to identify the direction the trajectory, ab initio potential energy, ab initio gradient, and ab initio or Hessian are computed at the end point $X_{i,p}$ of predicted trajectory. The potential information calculated at the end of predicted trajectory is used with the potential energy information at point $X_{i-1,p}$ near the trajectory starting point X_{i-1} of this time step, which is the end point of corrected trajectory of the previous time step, to interpolate a highly accurate local PES. This highly accurate PES is used in the correction phase of the time step to re-compute a more accurate trajectory.



Fig.1. The Prediction-correction approach during the i-th step

In each time step, to obtain an accurate predicted trajectory, the prediction utilizes the Hessian in addition to the potential energy and its gradient. Assuming the current time step is the i^{th} time step, the potential energy information needed during the prediction to integrate the trajectory is obtained by the quadratic expansion

$$E(X_i) = E(X_{i-1,p}) + G(X_{i-1,p})(X_i - X_{i-1,p}) + (X_{i-1} - X_{i-1,p})^T H(X_{i-1,p})(X_{i-1} - X_{i-1,p})$$

$$i > 2, p \in N \tag{1}$$

about the point $X_{i-1,p}$, the end point of the predicted trajectory of the $(i-1)^{th}$ time step at which ab initio potential energy $E(X_{i-1,p})$, ab initio gradient $G(X_{i-1,p})$, and ab initio or updated Hessian $H(X_{i-1,p})$ have been computed on a region within a trust radius from $X_{i-1,p}$.

Here, we propose a family of methods for calculating predicted trajectory based on the previous and current positions. Let the predicted trajectory be of the form of a polynomial in time, the new methods has the form

$$X_p(t) = C_0 + C_1t + \dots + C_nt^n \tag{2}$$

The coefficient vectors C_1, \dots, C_n will be determined by the known information. Assuming there are N atoms, each of these coefficient vectors C_i has $3*N$ entries. The time t is the difference between the current time and the time of next step. It is very small to guarantee the next position in the trust radius of the current position. The next position will be obtained from the calculated result based on them.

Consider the family of methods:

$$\text{Case I: } X_p(t) = C_0 + C_1t + C_2t^2 + C_3t^3 + C_4t^4 \tag{3}$$

$$\text{Case II: } X_p(t) = C_0 + C_1t + C_2t^2 + C_3t^3 + C_4t^4 + C_5t^5 \tag{4}$$

$$\text{Case III: } X_p(t) = C_0 + C_1t + C_2t^2 + C_3t^3 + C_4t^4 + C_5t^5 + C_6t^6 \tag{5}$$

$$\text{Case IV: } X_p(t) = C_0 + C_1t + C_2t^2 + C_3t^3 + C_4t^4 + C_5t^5 + C_6t^6 + C_7t^7 \tag{6}$$

where, we use one of the position, the velocity, the gradation and the Hession of the previous time step position and all of the current time step positions to predict the next time step trajectory in case I; similarly, adopt two of the four

information of the previous time step position and all of the current time step positions to calculate the next time step trajectory in case II and three of them in case III. According to different options, there are four methods in case I, called Position (P), Velocity (V), Gradient (G), Hessian (H) method respectively. Likewise, there are PV, PG, PH, VG, VH and GH in case II and PVG, PGH, PVH and VHG in case III.

In here, we use case IV as an example of how to determine the coefficient vectors of methods. Suppose there is an ensemble of N atoms, each of the coefficient C_i vectors has $3*N$ entries. For the position, velocity, and gradient of previous time step position are known, the position, velocity, gradient and Hessian of current time step position are known also, according to Eq.(6) the initial equations is as follows.

$$\begin{aligned} X_p(0) &= X_{i-2} & X_p(\Delta t) &= X_{i-1} \\ X_p'(0) &= V_{i-2} & X_p'(\Delta t) &= V_{i-1} \\ X_p''(0) &= -M^{-1}G(X_{i-2}) & X_p''(\Delta t) &= -M^{-1}G(X_{i-1}) \\ X_p'''(0) &= -M^{-1}H(X_{i-2})V_{i-2} & X_p'''(\Delta t) &= -M^{-1}H(X_{i-1})V_{i-1} \end{aligned}$$

Where $\Delta t = t_{i-1} - t_{i-2}$, and the last two equations are the result of taking the derivative with respect to time on both sides of the Newton's equation $X_p'' = -M^{-1}G(X_{i-1})$ and $X_p''' = -M^{-1}H(X_{i-1})V_{i-1}(t)$ and then applying chain rule. Plugging Eq(1) and Eq(2) into the eight equations above, we obtain the following.

$$\begin{aligned} C_0 &= X_p(0) = X_{i-2} \\ C_1 &= X_p'(0) = V_{i-2} \\ 2C_2 &= X_p''(0) = -M^{-1}G(X_{i-2}) \\ 6C_3 &= X_p'''(0) = -M^{-1}H(X_{i-2})V_{i-2} \\ \sum_{k=0}^7 C_k (\Delta t)^k &= X_p(\Delta t) = X_{i-1} \\ \sum_{k=0}^6 k C_k (\Delta t)^k &= X_p'(\Delta t) = V_{i-1} \\ \sum_{k=0}^5 k(k-1) C_k (\Delta t)^k &= X_p''(\Delta t) = -M^{-1}G(X_{i-1}) \\ \sum_{k=0}^4 k(k-1)(k-2) C_k (\Delta t)^k &= X_p'''(\Delta t) = -M^{-1}H(X_{i-1})V_{i-1} \end{aligned}$$

From these equation equations, we obtain that

$$\begin{aligned} C_0 &= X_{i-2} \\ C_1 &= V_{i-2} \\ C_2 &= -M^{-1}G(X_{i-2}) / 2 \\ C_3 &= -M^{-1}H(X_{i-2})V_{i-2} / 6 \\ C_4 &= 35r_1 - 15r_2 + 5r_3 / 2 - r_4 / 6 \\ C_5 &= -84r_1 + 39r_2 - 7r_3 + r_4 / 2 \\ C_6 &= 70r_1 - 34r_2 + 13r_3 / 2 - r_4 / 2 \\ C_7 &= -20r_1 + 10r_2 - 2r_3 + r_4 / 6 \\ r_1 &= (X_{i-1} - C_3(\Delta t)^3 - C_2(\Delta t)^2 - C_1(\Delta t) - C_0) / (\Delta t)^4 \\ r_2 &= (V_{i-1} - 3C_3(\Delta t)^2 - 2C_2(\Delta t) - C_1) / (\Delta t)^3 \\ r_3 &= (-M^{-1}G(X_{i-1}) - 6C_3(\Delta t) - 2C_2) / (\Delta t)^2 \\ r_4 &= (-M^{-1}H(X_{i-1})V_{i-1} - 6C_3) / (\Delta t) \end{aligned}$$

After computing the coefficients C_k for the predicted trajectory $X_p(t)$ in the form of equation 1, the end point of the predicted trajectory $X_{i,p}$ for the i -th time step can be obtained by set $t = t_i - t_{i-1}$ in Eq(1), that is, $X_{i,p} = X_p(t_i - t_{i-1})$. Similarly, We obtain the other schemes.

For 4P,

$$\begin{aligned}
 C_0 &= X_{i-2} & X_{i-1}(\Delta t) - C_0 &= r_1 \\
 C_1 &= -r_4/6 + r_3 - 3r_2 + 4r_1 & X_{i-1}(\Delta t) &= r_2 \\
 C_2 &= r_4/2 - 5r_3/2 + 6r_2 - 6r_1 & X'_{i-1}(\Delta t)^2 &= r_3 \\
 C_3 &= (-r_4 + 4r_3 - 8r_2 + 8r_1)/2 & X''_{i-1}(\Delta t)^3 &= r_4 \\
 C_4 &= (r_4 - 3r_3 + 6r_2 - 6r_1)/6
 \end{aligned}$$

For 4V,

$$\begin{aligned}
 C_0 &= -r_4/24 + r_3/4 - 3r_2/4 + r_1 & X_{i-1}(\Delta t) - C_1(\Delta t) &= r_1 \\
 C_1 &= X'_{i-2} & X'_{i-1}(\Delta t) - C_1(\Delta t) &= r_2 \\
 C_2 &= r_4/4 - r_3 + 3r_2/2 & X''_{i-1}(\Delta t)^2 &= r_3 \\
 C_3 &= (-r_4 + 3r_3 - 3r_2)/3 & X'''_{i-1}(\Delta t)^3 &= r_4 \\
 C_4 &= (r_4 - 2r_3 + 2r_2)/8
 \end{aligned}$$

For 4G,

$$\begin{aligned}
 C_0 &= -r_4/12 + 5r_3/12 - r_2 + r_1 & X_{i-1}(\Delta t) - C_2(\Delta t)^2 &= r_1 \\
 C_1 &= r_4/6 - 2r_3/3 + r_2 & X'_{i-1}(\Delta t) - 2C_2(\Delta t)^2 &= r_2 \\
 C_2 &= X''_{i-2} & X''_{i-1}(\Delta t)^2 - 2C_2(\Delta t)^2 &= r_3 \\
 C_3 &= (-r_4 + 2r_3)/6 & X'''_{i-1}(\Delta t)^3 &= r_4 \\
 C_4 &= (r_4 - r_3)/12
 \end{aligned}$$

For 4H,

$$\begin{aligned}
 C_0 &= -r_4/8 + r_3/2 - r_2 + r_1 & X_{i-1}(\Delta t) - C_3(\Delta t)^3 &= r_1 \\
 C_1 &= r_4/3 - r_3 + r_2 & X'_{i-1}(\Delta t) - 3C_3(\Delta t)^3 &= r_2 \\
 C_2 &= (-r_4/2 + r_3)/2 & X''_{i-1}(\Delta t)^2 - 6C_3(\Delta t)^3 &= r_3 \\
 C_3 &= X''_{i-2} & X'''_{i-1}(\Delta t)^3 - 6C_3(\Delta t)^3 &= r_4 \\
 C_4 &= r_4/24
 \end{aligned}$$

For 5PV,

$$\begin{aligned}
 C_0 &= X_{i-2} & X_{i-1}(\Delta t) - C_0 - C_1(\Delta t) &= r_1 \\
 C_1 &= X'_{i-2} & X'_{i-1}(\Delta t) - C_1(\Delta t) &= r_2 \\
 C_2 &= -r_4/6 + 3r_3/2 - 6r_2 + 10r_1 & X''_{i-1}(\Delta t)^2 &= r_3 \\
 C_3 &= r_4/2 - 4r_3 + 14r_2 - 20r_1 & X'''_{i-1}(\Delta t)^3 &= r_4 \\
 C_4 &= -r_4/2 + 7r_3/2 - 11r_2 + 15r_1 \\
 C_5 &= r_4/6 - r_3 + 3r_2 - 4r_1
 \end{aligned}$$

For 5PG,

$$\begin{aligned}
 C_0 &= X_{i-2} & X_{i-1}(\Delta t) - C_0 - C_2(\Delta t)^2 &= r_1 \\
 C_1 &= -r_4/24 + 3r_3/8 - 3r_2/2 + 5r_1/2 & X'_{i-1}(\Delta t) - 2C_2(\Delta t)^2 &= r_2 \\
 C_2 &= X''_{i-2}/2 & X''_{i-1}(\Delta t)^2 - 2C_2(\Delta t)^2 &= r_3 \\
 C_3 &= r_4/4 - 7r_3/4 + 5r_2 - 5r_1 & X'''_{i-1}(\Delta t)^3 &= r_4 \\
 C_4 &= -r_4/3 + 2r_3 - 5r_2 + 5r_1 \\
 C_5 &= (r_4 - 5r_3 + 12r_2 - 12r_1)/8
 \end{aligned}$$

For 5PH,

$$\begin{aligned}
 C_0 &= X_{i-2} & X_{i-1}(\Delta t) - C_0 - C_3(\Delta t)^3 &= r_1 \\
 C_1 &= -r_4/12 + 4r_3/6 - 14r_2/6 + 20r_1/6 & X'_{i-1}(\Delta t) - 3C_3(\Delta t)^3 &= r_2 \\
 C_2 &= r_4/6 - 7r_3/6 + 10r_2/3 - 10r_1/3 & X''_{i-1}(\Delta t)^2 - 6C_3(\Delta t)^3 &= r_3 \\
 C_3 &= X'''_{i-2}/6 & X'''_{i-1}(\Delta t)^3 - 6C_3(\Delta t)^3 &= r_4 \\
 C_4 &= (-r_4 + 5r_3 - 10r_2 + 10r_1)/6 \\
 C_5 &= (r_4 - 4r_3 + 8r_2 - 8r_1)/12
 \end{aligned}$$

For 5VG,

$$\begin{aligned}
 C_0 &= -r_4/60 + 3r_3/20 - 3r_2/5 + r_1 & X_{i-1}(\Delta t) - C_1(\Delta t) - C_2(\Delta t)^2 &= r_1 \\
 C_1 &= X_{i-2} & X'_{i-1}(\Delta t) - C_1(\Delta t) - 2C_2(\Delta t)^2 &= r_2 \\
 C_2 &= X'_{i-2}/2 & X''_{i-1}(\Delta t)^2 - 2C_2(\Delta t)^2 &= r_3 \\
 C_3 &= (r_4/2 - 3r_3 + 6r_2)/3 & X'''_{i-1}(\Delta t)^3 &= r_4 \\
 C_4 &= (-r_4 + 5r_3 - 8r_2)/4 \\
 C_5 &= (r_4 - 4r_3 + 6r_2)/10
 \end{aligned}$$

For 5VH,

$$\begin{aligned}
 C_0 &= -r_4/40 + r_3/5 - 7r_2/10 + r_1 & X_{i-1}(\Delta t) - C_1(\Delta t) - C_3(\Delta t)^3 &= r_1 \\
 C_1 &= X_{i-2} & X'_{i-1}(\Delta t) - C_1(\Delta t) - 3C_3(\Delta t)^3 &= r_2 \\
 C_2 &= (r_4/6 - r_3 + 2r_2)/2 & X''_{i-1}(\Delta t)^2 - 6C_3(\Delta t)^3 &= r_3 \\
 C_3 &= X'''_{i-2}/6 & X'''_{i-1}(\Delta t)^3 - 6C_3(\Delta t)^3 &= r_4 \\
 C_4 &= (-r_4 + 4r_3 - 4r_2)/8 \\
 C_5 &= (r_4 - 3r_3 + 3r_2)/15
 \end{aligned}$$

For 5GH,

$$\begin{aligned}
 C_0 &= -r_4/20 + 7r_3/20 - r_2 + r_1 & X_{i-1}(\Delta t) - C_2(\Delta t)^2 - C_3(\Delta t)^3 &= r_1 \\
 C_1 &= r_4/12 - r_3/2 + r_2 & X'_{i-1}(\Delta t) - 2C_2(\Delta t)^2 - 3C_3(\Delta t)^3 &= r_2 \\
 C_2 &= X''_{i-2}/2 & X''_{i-1}(\Delta t)^2 - 2C_2(\Delta t)^2 - 6C_3(\Delta t)^3 &= r_3 \\
 C_3 &= X'''_{i-2}/6 & X'''_{i-1}(\Delta t)^3 - 6C_3(\Delta t)^3 &= r_4 \\
 C_4 &= (-r_4 + 3r_3)/12 \\
 C_5 &= (r_4 - 2r_3)/20
 \end{aligned}$$

For 6VGH

$$\begin{aligned}
 C_0 &= -r_4/120 + r_3/10 - r_2/2 + r_1 & X_{i-1}(\Delta t) - C_1(\Delta t) - C_2(\Delta t)^2 - C_3(\Delta t)^3 &= r_1 \\
 C_1 &= X'_{i-2} & X'_{i-1}(\Delta t) - C_1(\Delta t) - 2C_2(\Delta t)^2 - 3C_3(\Delta t)^3 &= r_2 \\
 C_2 &= X''_{i-2}/2 & X''_{i-1}(\Delta t)^2 - 2C_2(\Delta t)^2 - 6C_3(\Delta t)^3 &= r_3 \\
 C_3 &= X'''_{i-2}/6 & X'''_{i-1}(\Delta t)^3 - 6C_3(\Delta t)^3 &= r_4 \\
 C_4 &= (r_4/2 - 4r_3 + 10r_2)/4 \\
 C_5 &= (-r_4 + 7r_3 - 15r_2)/5 \\
 C_6 &= (r_4 - 6r_3 + 12r_2)/12
 \end{aligned}$$

For 6PVH

$$\begin{aligned}
 C_0 &= X_{i-2} & X_{i-1}(\Delta t) - C_0 - C_1(\Delta t) - C_3(\Delta t)^3 &= r_1 \\
 C_1 &= X'_{i-2} & X'_{i-1}(\Delta t) - C_1(\Delta t) - 3C_3(\Delta t)^3 &= r_2 \\
 C_2 &= -r_4/24 + r_3/2 - 20r_2/8 + 5r_1 & X''_{i-1}(\Delta t)^2 - 6C_3(\Delta t)^3 &= r_3 \\
 C_3 &= X'''_{i-2}/6 & X'''_{i-1}(\Delta t)^3 - 6C_3(\Delta t)^3 &= r_4 \\
 C_4 &= r_4/4 - 5r_3/2 + 10r_2 - 15r_1 \\
 C_5 &= -r_4/3 + 3r_3 - 11r_2 + 16r_1 \\
 C_6 &= (r_4 - 8r_3 + 28r_2 - 40r_1)/8
 \end{aligned}$$

For 6PVG

$$\begin{aligned}
 C_0 &= X_{i-2} \\
 C_1 &= X'_{i-2} \\
 C_2 &= X''_{i-2} / 2 \\
 C_3 &= -r_4 / 6 + 2r_3 - 10r_2 + 20r_1 \\
 C_4 &= r_4 / 2 - 11r_3 / 2 + 25r_2 - 45r_1 \\
 C_5 &= -r_4 / 2 + 5r_3 - 21r_2 + 36r_1 \\
 C_6 &= (r_4 - 9r_3 + 36r_2 - 60r_1) / 6
 \end{aligned}
 \quad
 \begin{aligned}
 X_{i-1}(\Delta t) - C_0 - C_1(\Delta t) - C_2(\Delta t)^2 &= r_1 \\
 X'_{i-1}(\Delta t) - C_1(\Delta t) - 2C_2(\Delta t)^2 &= r_2 \\
 X''_{i-1}(\Delta t)^2 - 2C_3(\Delta t)^2 &= r_3 \\
 X'''_{i-1}(\Delta t)^3 &= r_4
 \end{aligned}$$

For 6PGH

$$\begin{aligned}
 C_0 &= X_{i-2} \\
 C_1 &= -r_4 / 60 + r_3 / 5 - r_2 + 2r_1 \\
 C_2 &= X''_{i-2} / 2 \\
 C_3 &= X'''_{i-2} / 6 \\
 C_4 &= (r_4 / 2 - 9r_3 / 2 + 15r_2 - 15r_1) / 3 \\
 C_5 &= (-r_4 + 8r_3 - 24r_2 + 24r_1) / 4 \\
 C_6 &= (r_4 - 7r_3 + 20r_2 - 20r_1) / 10
 \end{aligned}
 \quad
 \begin{aligned}
 X_{i-1}(\Delta t) - C_0 - C_2(\Delta t)^2 - C_3(\Delta t)^3 &= r_1 \\
 X'_{i-1}(\Delta t) - 2C_1(\Delta t)^2 - 3C_3(\Delta t)^3 &= r_2 \\
 X''_{i-1}(\Delta t)^2 - 2C_2(\Delta t)^2 - 6C_3(\Delta t)^3 &= r_3 \\
 X'''_{i-1}(\Delta t)^3 - 6C_3(\Delta t)^3 &= r_4
 \end{aligned}$$

According to the above formulas, we can get the high predictor of the family predictor integration scheme.

3. RESULTS AND ANALYSIS

A. The Comparative of Fourth Order, Fifth Order, Sixth Order Schemes

To compare all predictors of Hessian-based predictor-corrector integration schemes within a group (fourth-order, fifth-order and sixth-order methods), this session takes a chemical reaction $F^- + CH_3OOH$ [26] listed on the Chemical Dynamics Software and Simulation System (cdssim.chem.ttu.edu) website [22] as testing chemical reaction. We implemented the integration algorithm in the VENUS [22] dynamics simulation package interfaced with the electronic structure calculation NWChem [27,28]. The parameter files for the chemical reaction are gotten from the same website [22].

In the simulations, ab initio potential energy, ab initio gradient and ab initio Hessian were calculated using the electronic structure theory $B3LYP/6-311+G^{**}$ and ab initio Hessian is calculated once in every K steps. During the remaining $K-1$ steps, the Hessian update scheme is executed. The initial energy for chemical reaction sets $182484.8089 \text{ kcal/mol}$. For the difference appears beyond 100 fs in some tests, the time limit is not fixed to distinguish clearly the difference among the same order algorithms. Trad denotes the time step size and its unit is fs. In the following figures, x axis means the time and its unit is fs, y axis denotes the potential energy of PES for $F^- + CH_3OOH$. The change of potential energy directly shows the algorithm of reliability. Intuitively find energy deviation, there is a baseline using initial energy (the red line is the baseline on Fig. 2, Fig. 3 and Fig. 4) on each figure.

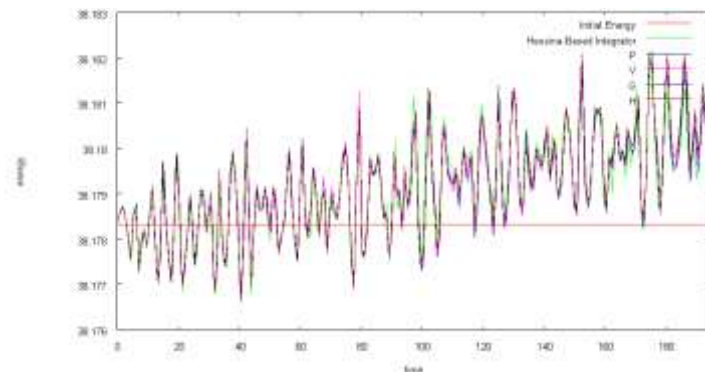


Fig.2. The figure of fourth order predictor schemes in dynamics simulation of chemical reaction $F^- + CH_3OOH$ when $K=12$ and $Trad=0.9\text{fs}$ with exact method

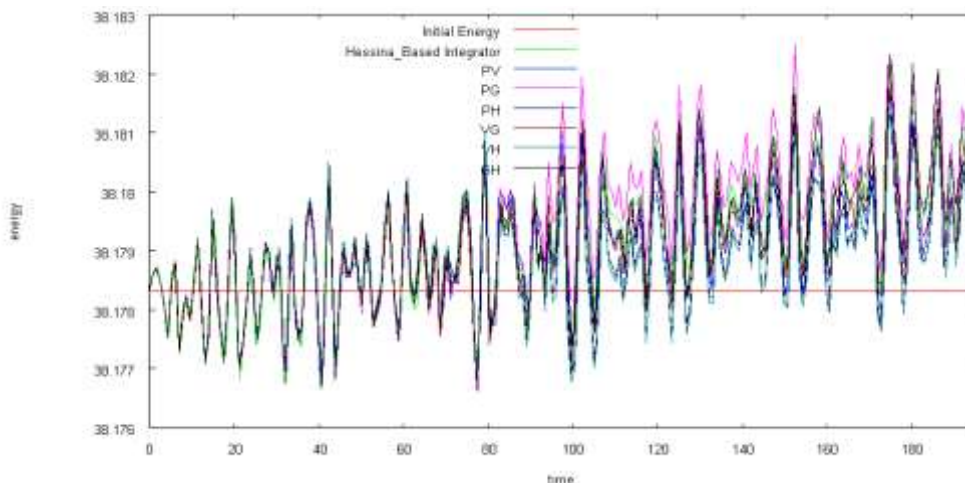


Fig.3. The figure of fifth order predictor schemes in dynamics simulation of chemical reaction $F^- + CH_3OOH$ when $K=12$ and $Trad=0.9fs$ with exact method.

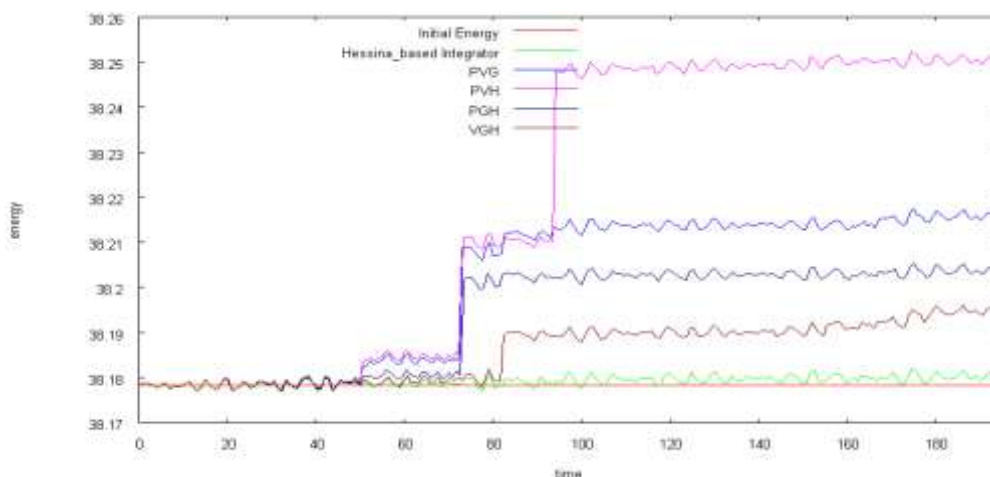


Fig.4. The figure of sixth order predictor schemes in dynamics simulation of chemical reaction $F^- + CH_3OOH$ when $K=12$ and $Trad=0.9fs$ with exact method

B. The Comparative of Fourth Order, Fifth Order, Sixth Order and Seventh Order Schemes
 Using the best one of fourth order, fifth order and sixth order schemes (4H,5GH,6VGH) , to compare with seventh order scheme on $F^- + CH_3OOH$ (see Fig. 5, Fig. 6 and Fig.6).

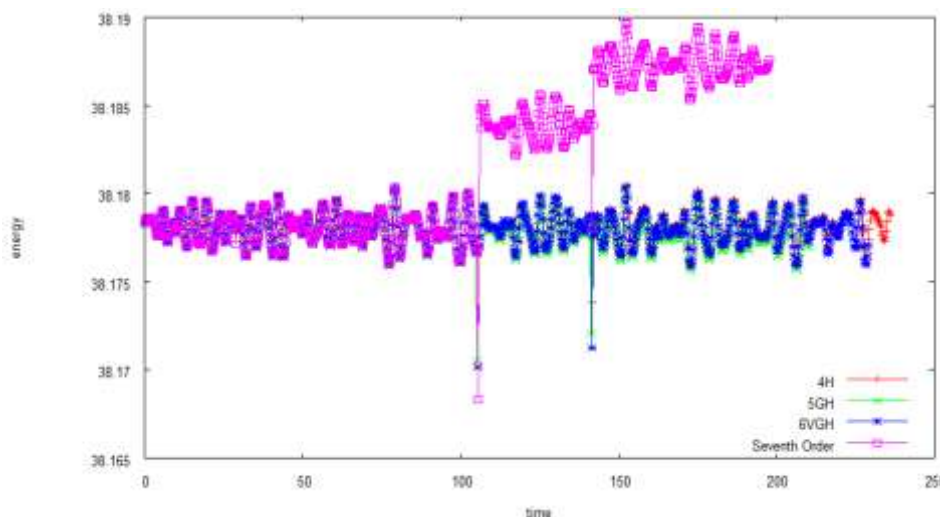


Fig.5. The figure of fourth order, fifth order, sixth order and seventh order predictor schemes in dynamics simulation of chemical reaction $F^- + CH_3OOH$ when $K=4$ and $Trad=0.3fs$ with exact method

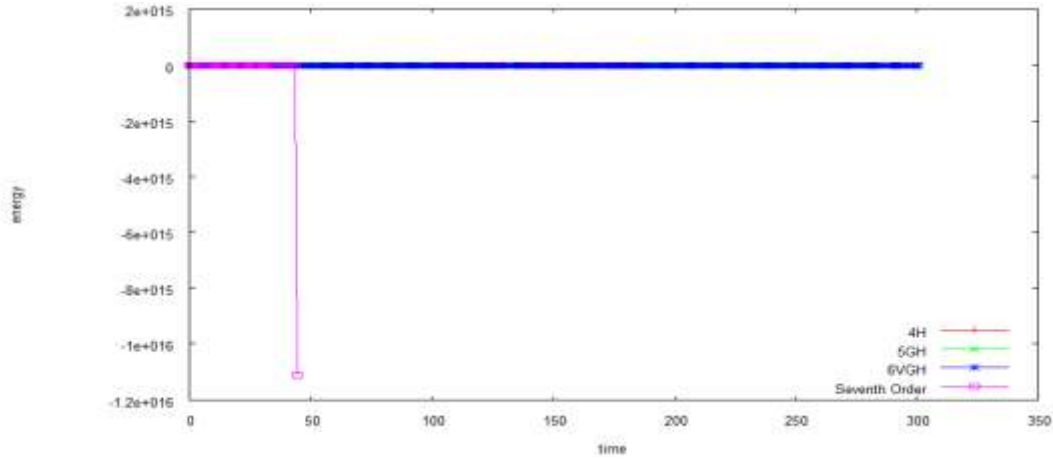


Fig.6. The figure of fourth order, fifth order, sixth order and seventh order predictor schemes in dynamics simulation of chemical reaction $F + CH_3OOH$ when $K=12$ and $Trad=0.9fs$ with exact method

C. The Comparative of Fourth Order, Fifth Order, Sixth Order and Seventh Order Schemes on CO_2
 For more comparison to the new family predictor schemes, we test them on large inertia molecular like CO_2

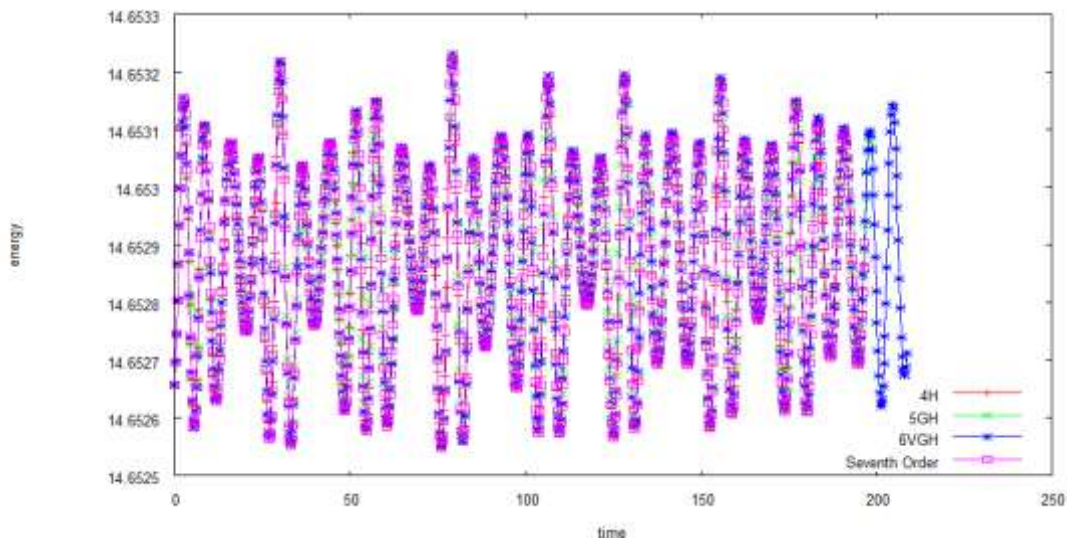


Fig.7. The figure of fourth order, fifth order, sixth order and seventh order predictor schemes in dynamics simulation of chemical reaction CO_2 when $K=4$ and $Trad=0.3fs$ with exact method.

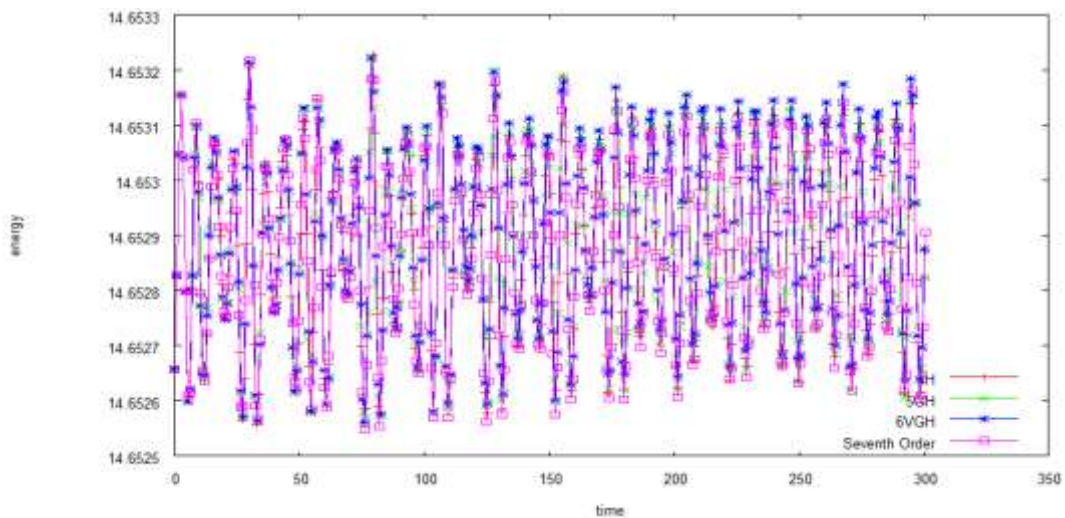


Fig.8. The figure of fourth order, fifth order, sixth order and seventh order predictor schemes in dynamics simulation of chemical reaction CO_2 when $K=12$ and $Trad=0.9fs$ with exact method

D. The Comparative of Fourth Order, Fifth Order, Sixth Order and Seventh Order Schemes on H_2O

For more comparative to the new family predictor schemes, we test them on small inertia molecular like H_2O

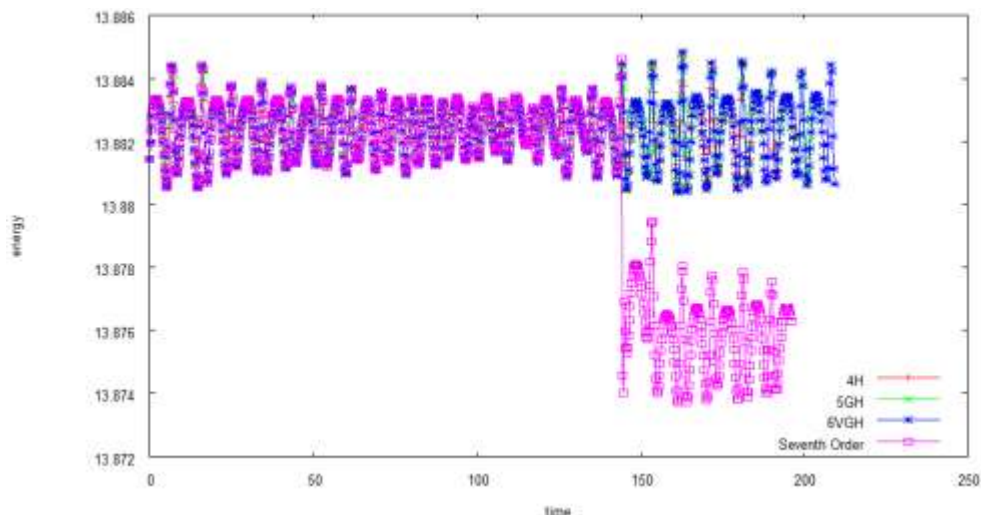


Fig.9. The figure of fourth order, fifth order, sixth order and seventh order predictor schemes in dynamics simulation of chemical reaction H_2O when $K=4$ and $Trad=0.3fs$ with exact method

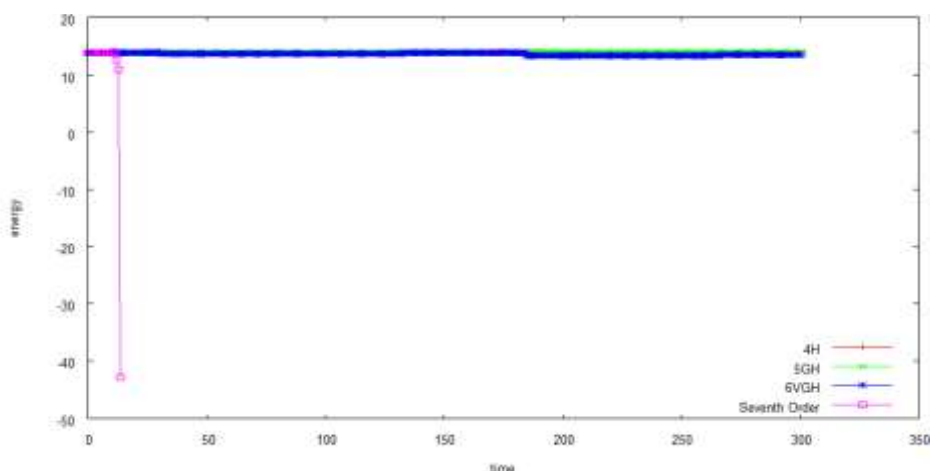


Fig.10. The figure of fourth order, fifth order, sixth order and seventh order predictor schemes in dynamics simulation of chemical reaction H_2O when $K=12$ and $Trad=0.9fs$ with exact method

E. Analysis

From above dynamics simulation of the chemical reaction $F^- + CH_3OOH$, all methods of the fourth-order group, P,V,G,H, are almost overlapping (see Fig. 2). In the fifth-order group, there are subtle differences in them (see Fig. 3). When $K=12$ and $Trad=0.9fs$, only PV has a little distinction beyond 140 fs (see Fig. 3), the best one of them is 4GH. In the sixth-order group, VGH is the best one of them. Using 4H, 5GH, 6VGH to compare with seventh order scheme, it approves the worst one is seventh order scheme (See Fig. 5 and 6). In dynamics simulation of large inertia molecular, all of them are similar, even $K=12$ and $Trad=0.9 fs$ (See Fig. 7 and 8). While to small inertia molecular, the higher order schemes are slightly worse (See Fig. 9 and 10).

4. CONCLUDING

This paper proposes the comparative of a family of high order predictor of Prediction-Correction integration schemes for First Principle Chemical Dynamics Simulation. They use some of the location information of previous time step and the location information of current time step to predict the location of next time step. All location information includes Position, Velocity, Gradient and Hessian. Therefore, the fourth order schemes are 4P, 4V, 4G and 4H, the fifth order schemes have 5PV, 5PG, 5PH, 5VG, 5VH and GH, the sixth order ones are 6PVH, 6PGH, 6VGH, 6PVG, while there is only one to the seventh order scheme. According to the above discussion, we can draw the following conclusions: (1) the higher order predictor schemes are worse than others' predictor method; (2) The higher order schemes reveal almost the same performance as the others for molecules without hydrogen atoms, but becomes less performance for molecules

with hydrogen atoms;(3) The effect of the information of previous time step is negative in the process of predicting the next position using current and previous time step;(4) using extrapolation, more location information of the previous time step, enhances the time step indirectly;(5) the higher order one shows the same performance as the others' for large inertia molecular, while it shows worse for small inertia molecular.

5. ACKNOWLEDGEMENT

This work is supported in part by the National Science Foundation under Grant Nos. CHE-10xxxx, OISE-0730114, and the Robert A. Welch Foundation under Grant No.D-0005. The authors thank the High Performance Computing Center at Texas Tech University for their support. Also appreciate Danielle Zaragoza(danielle.zaragoza@ttu.edu) for his aid.

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