Higher-accuracy schemes for approximating the Hessian from electronic structure calculations in chemical dynamics simulations

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In this paper, we present a family of generally applicable schemes for updating the Hessian from electronic structure calculations based on an equation derived with compact finite difference (CFD). The CFD-based equation is of higher accuracy than the quasi-Newton equation on which existing generally applicable Hessian update schemes are based. Direct tests of Hessian update schemes, as well as dynamics simulations using an integrator incorporating Hessian update schemes, have shown four of the new schemes produce reliably higher accuracy than existing Hessian update schemes. © 2010 American Institute of Physics. [doi:10.1063/1.3407922]

I. INTRODUCTION

Hessian updating is a technique frequently used to replace electronic structure calculations of the Hessian in optimization and dynamics simulations. Existing generally applicable Hessian update schemes, e.g., the symmetric rank one (SR1) scheme also see descriptions in Refs. 7 and 18, Powell’s symmetrization of Broyden’s (PSB) method (also see descriptions in Refs. 5–7), the scheme of Bofill, the Broyden–Fletcher–Goldfarb–Shanno (BFGS) scheme (see descriptions in Refs. 5–8), the scheme of Farkas and Schlegel, and other Hessian update schemes, are based on the equation

\[ H(X_{k+1})(X_{k+1} - X_k) = G(X_{k+1}) - G(X_k), \]

(1.1)

where \( G(X) \) and \( H(X) \), respectively, denote the gradient and Hessian of the potential energy at point \( X \). Bofill calls Eq. (1.1) the “quasi-Newton method.” It is verifiable from a Taylor expansion that Eq. (1.1) is of first-order accuracy with an error term of \( O(|\Delta X|^3) \), and all existing generally applicable Hessian update schemes known to the authors are solutions of Eq. (1.1). The general applicability of these Hessian update schemes is due to the fact that Eq. (1.1), is valid up to an \( O(|\Delta X|^2) \) error in all cases as long as the potential energy is adequately smooth.

In this paper, we present a family of generally applicable Hessian update schemes that are based on an equation of higher accuracy than Eq. (1.1). Starting from the derivation of an equation which is of second-order accuracy, we first borrow Bofill’s technique to develop a set of update schemes that are solutions of this second-order equation. We also utilize the relationship between our second-order equation and Eq. (1.1) to derive another formula for generating new Hessian update schemes. This formula generalizes the second-order Hessian update scheme developed by Schlegel for the gradient extremal following algorithm of Jørgensen, Jensen, and Helgaker. The second-order accuracy of Schlegel’s update scheme results from utilizing numerical properties of this gradient extremal following algorithm. Hence, before the work presented here, it was not known if Schlegel’s update scheme was applicable to problems other than the algorithm of Jørgensen, Jensen, and Helgaker. It is worth noting that Bofill’s first-order update scheme was used to develop a Hessian-based integration algorithm instead of Schlegel’s second-order Hessian update scheme.

The Hessian update schemes presented in this paper are based on a second-order equation derived using compact finite difference (CFD). This second-order equation is valid in all cases up to an \( O(|\Delta X|^3) \) error as long as the potential energy is adequately smooth, leading to the general applicability of our Hessian update schemes. Besides the theoretical work of utilizing CFD for the derivation of higher accuracy Hessian update schemes, this paper also reports comparative numerical tests of different Hessian update schemes. Improved accuracy for chemical dynamics simulations is found when the second-order Hessian updating schemes are implemented in a Hessian-based integration algorithm.

The remainder of this paper is organized as follows. Section II presents the CFD, its application to the derivation of a second-order equation for the Hessian, and new Hessian update schemes derived as solutions for the second-order equation. Section III contains a comparative study with similar existing work. Section IV describes numerical studies of the new Hessian update schemes as compared to existing Hessian update schemes including the application of the Hessian update schemes to a Hessian-based integrator. Section V gives the conclusion.
II. HESSIAN UPDATE SCHEMES

A. Underlying theory

An important goal in a numerical approximation is to improve the approximation accuracy without using a larger stencil (i.e., more sampling points). CFDs\textsuperscript{21\textendash}25 are high-order methods for approximating differentiation of functions without incurring a larger stencil. The higher accuracy is attained by including differentiated terms at more locations within the stencil.

Our new Hessian update scheme is developed from a CFD, which is presented below. Let $F: \mathbb{R}^n \rightarrow \mathbb{R}^m$ be a vector-valued continuously differentiable function defined on $\mathbb{R}^n$. Represent $F(X)$ in column-vector form by $F(X) = (f_1(X), f_2(X), \ldots, f_m(X))^T$, and the vector variable $X$ also in column-vector form by $X = (x_1, x_2, \ldots, x_n)^T$. Let $DF(X)$ denote the first-order differentiation matrix

\[
DF(X) = \begin{bmatrix}
\frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \cdots & \frac{\partial f_1}{\partial x_n} \\
\frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} & \cdots & \frac{\partial f_2}{\partial x_n} \\
\vdots & \vdots & \ddots & \vdots \\
\frac{\partial f_m}{\partial x_1} & \frac{\partial f_m}{\partial x_2} & \cdots & \frac{\partial f_m}{\partial x_n}
\end{bmatrix}.
\]

Using a Taylor expansion, it can be verified that the CFD scheme

\[
\frac{1}{2}[DF(X_{k+1}) + DF(X_k)](X_{k+1} - X_k) = F(X_{k+1}) - F(X_k)
\]

(2.1)

has a second-order accuracy with an error of $O(|\Delta X|^3)$ as long as $F(X)$ is three times continuously differentiable. Compared to the first-order finite difference

\[
[DF(X_{k+1})](X_{k+1} - X_k) = F(X_{k+1}) - F(X_k) + O(|\Delta X|^2),
\]

(2.2)

a multidimensional counterpart to the one-dimensional finite difference $f'(x_k)\approx[f(x_{k+1}) - f(x_k)]/(x_{k+1} - x_k)$, Eq. (2.1) has the same stencil (i.e., the same set of sampling points in variable $X$), but uses one more differentiated term.

B. Application of CFD to Hessian update

To apply CFD to Hessian update, we plug $G(X_k)$ and $G(X_{k+1})$, the gradient of the potential energy at $X_k$ and $X_{k+1}$, into Eq. (2.1) to replace $F(X_k)$ and $F(X_{k+1})$, respectively, yielding

\[
\frac{1}{2}[H(X_{k+1}) + H(X_k)](X_{k+1} - X_k) = G(X_{k+1}) - G(X_k),
\]

(2.3)

where $H(X)$ denotes the Hessian of the potential energy. A Hessian update scheme approximates the Hessian $H(X_{k+1})$ given $G(X_k)$, $G(X_{k+1})$, and $H(X_k)$. To approximate $H(X_{k+1})$ using the information provided by Eq. (2.3), we rewrite Eq. (2.3) as

\[
\Delta H_{k+1} \Delta X_{k+1} = 2 \Delta G_{k+1} - 2H(X_k)\Delta X_{k+1},
\]

(2.4)

with $\Delta X_{k+1} = X_{k+1} - X_k$, $\Delta G_{k+1} = G(X_{k+1}) - G(X_k)$, and $\Delta H_{k+1} = H(X_{k+1}) - H(X_k)$. Using the notation $R_{k+1}$ for $2\Delta G_{k+1} - 2H(X_k)$, Eq. (2.4) becomes

\[
\Delta H_{k+1} \Delta X_{k+1} = R_{k+1}.
\]

(2.5)

Equation (2.5) has infinitely many solutions since there are more unknowns (the unknowns are the entries of $H_{k+1}$) than the number of equations (the same as the number of entries in $\Delta X_{k+1}$). If we impose symmetry on $\Delta H_{k+1}$, then Eq. (2.5) has $m(m+1)/2$ unknowns but only $m$ equations, where $m$ is the number of entries of $X_k$’s or $G_k$’s. Then, linear algebra\textsuperscript{27} tells us that all solutions of Eq. (2.5) form a $[m(m+1)/2-\text{m}]$-dimensional space.

Since the goal of Hessian update is to obtain an approximation of $H(X_{k+1})$, we need to find a solution $\Delta H_{k+1}$ for Eq. (2.5). To find a symmetric matrix $H_{k+1}$ as a solution for Eq. (2.5), we follow Bofill’s technique\textsuperscript{1} in restricting the solution space to a low dimensional subspace. Here, we consider solutions of Eq. (2.5) only in the following two-dimensional subspace:

\[
\Delta H_{k+1} = C_1 \Delta X_{k+1} \Delta X_{k+1}^T + C_2 R_{k+1} R_{k+1}^T + C_3 (\Delta X_{k+1} R_{k+1}^T + R_{k+1} \Delta X_{k+1}^T).
\]

(2.6)

We choose the above subspace since this subspace is constructed from the two vectors $\Delta X_{k+1}$ and $R_{k+1}$ in Eq. (2.5). To determine the coefficients $C_1$, $C_2$, and $C_3$, we multiply both sides of Eq. (2.6) by $\Delta X_{k+1}$ and obtain

\[
\Delta H_{k+1} \Delta X_{k+1} = (C_1 \Delta X_{k+1}^T \Delta X_{k+1} + C_2 R_{k+1}^T \Delta X_{k+1}) \Delta X_{k+1} + (C_3 R_{k+1}^T \Delta X_{k+1} + C_3 \Delta X_{k+1}^T \Delta X_{k+1}) R_{k+1}.
\]

Comparing the equation above with Eq. (2.5) for coefficients of the same terms, we obtain

\[
C_1 \Delta X_{k+1}^T \Delta X_{k+1} + C_3 \Delta X_{k+1}^T \Delta X_{k+1} = 0,
\]

\[
C_2 R_{k+1}^T \Delta X_{k+1} + C_2 \Delta X_{k+1}^T \Delta X_{k+1} = 1,
\]

which lead to $C_1 = C_2 (\Delta X_{k+1}^T \Delta X_{k+1} - 2 R_{k+1}^T \Delta X_{k+1})$ and $C_2 = (1 - C_3 \Delta X_{k+1}^T \Delta X_{k+1})^{-1}$. Plugging $C_1$ and $C_2$ into Eq. (2.6), we have

\[
\Delta H_{k+1} = (1 - C_3 \Delta X_{k+1}^T \Delta X_{k+1}) R_{k+1} R_{k+1}^T / (R_{k+1}^T \Delta X_{k+1}) + C_3 [(\Delta X_{k+1}^T R_{k+1} + R_{k+1}^T \Delta X_{k+1})^T - |\Delta X_{k+1}| R_{k+1}^T \Delta X_{k+1} \Delta X_{k+1}^T].
\]

(2.7)

For comparison analysis to be given later, let $\lambda = C_3 \Delta X_{k+1}^T \Delta X_{k+1}$ and the formula above becomes

\[
\Delta H_{k+1} = (1 - \lambda) R_{k+1} R_{k+1}^T + \lambda \frac{\Delta X_{k+1}^T R_{k+1} + R_{k+1}^T \Delta X_{k+1}}{|\Delta X_{k+1}|^2} \frac{\Delta X_{k+1} \Delta X_{k+1}^T}{|\Delta X_{k+1}|^4}.
\]

With the parameter $\lambda$ allowed to vary, scheme (2.7) defines a family of Hessian update schemes.

To the best of our knowledge, all existing generally applicable Hessian update schemes are solutions of the first-
order equation (1.1), which is the result of putting the potential gradient G into Eq. (2.2) to replace the function F. Subtracting both sides of Eq. (1.1) by $H(X_k)(X_{k+1} - X_k)$, we obtain

$$
\Delta H_{k+1}\Delta X_{k+1} = \Delta G_{k+1} - H(X_k)\Delta X_{k+1}.
$$

(2.8)

It is verifiable that the existing Hessian update schemes including the BFGS update scheme $\Delta H_{\text{BFGS}}$ and the SR1 update scheme $\Delta H_{\text{SR1}}$ are solutions of Eq. (2.8). Thus, the existence of such update schemes is verified. The solution $\Delta H_{\text{BFGS}}$ is also a generalization of the Broyden update scheme $\Delta H_{\text{Broyden}}$. The solution $\Delta H_{\text{SR1}}$ is the origin of Eq. (2.10). Our motivation to minimize the norm of the vector $\Delta H_{k+1}V_j$ is explained in Sec. IV A with the help of testing data.

### III. COMPARISON WITH SIMILAR WORK

Update scheme (2.9) is actually a generalization of the scheme developed by Schlegel for the gradient extremal following algorithm of Jørgensen, Jensen, and Helgaker.

Schlegel derived the update scheme based on the observation that several existing updating formulas “all have the property: $\Delta \delta_i = \Sigma H^0_{ij} \partial x_j + \Sigma \lambda_{ij}^0 \lambda_{ij} \partial x_j$.” Since this is the result of the updating procedure of Schlegel’s update formula $H^1 = H^0 + \Delta H$, with $\Delta H$ by an existing Hessian update formula such as DFP, BFGS, OC, etc.

When setting all $C_{ij}$ in Eq. (2.9) to zero, update scheme (2.9) has the exact form as Schlegel’s, but they differ in the following. The derivation of Schlegel’s Hessian update is based on properties of the Jørgensen–Jensen–Helgaker algorithm and properties of some of the existing updating formulas discussed in Schlegel’s paper, and hence Schlegel’s update scheme $H^1 = H^0 + \Delta H$ was proven to be valid only for that gradient extremal following algorithm. By comparison, our Hessian update schemes generalize Schlegel’s scheme in that they only require the potential energy function to be adequately smooth. Hence, our schemes are applicable in any case as long as the potential energy function has some order of differentiability (or derivatives). Thus, the higher accuracy of schemes (2.7) and (2.9), and their general applicability are the main contributions of our Hessian update schemes.

Update schemes (2.7) and (2.9) are developed from the second-order equation (2.3), which can be viewed as an improvement over the “quasi-Newton equation” (1.1). Since Eq. (1.1) is similar to and also has the same order of accuracy as the Newton–Raphson method $H(X_k)(X_{k+1} - X_k) = G(X_{k+1}) - G(X_k)$ with $G(X_{k+1})$ set to zero, it is reasonable to ask if Eq. (2.3) can be modified to produce an optimization method that is convergent faster than the Newton iterative procedure, probably the fastest convergent method known today.

Optimization methods including the Newton–Raphson method find an approximate solution of $G(X) = 0$ iteratively in the manner of $X_{k+1} = f(X_k)$, starting from a point $X_0$ near the solution $X_\infty$. To obtain $X_{k+1}$ from Eq. (2.3) and move
toward the solution $X_{k+1}$, we first set $G(X_{k+1})=0$ in Eq. (2.3) exactly as what the Newton–Raphson method does to equation $H(X_k)(X_{k+1} - X_k) = G(X_{k+1}) - G(X_k)$, which is the first-order Taylor expansion of $G(X_{k+1})$ about point $X_k$. Now Eq. (2.3) becomes

$$\frac{1}{2}[H(X_{k+1}) + H(X_k)](X_{k+1} - X_k) = - G(X_k).$$

However, this equation is not useful for obtaining $X_{k+1}$ since it is a nonlinear equation in $X_{k+1}$ due to the existence of the unknown term $H(X_{k+1})$. However, replacing $H(X_{k+1})$ by $H(X_k)$ in the equation above, an attempt out of observing and utilizing the difference between Eq. (1.1) and the Newton–Raphson method, does not work since it leads back to the Newton–Raphson procedure. After such an examination, we believe the Newton–Raphson method remains the fastest convergent procedure in terms of the number of iterations.

IV. NUMERICAL STUDIES

A. Direct tests of the Hessian update schemes

To test the new Hessian update schemes, we chose the chemical reaction $F^- + CH_2OOH$ listed on the Chemical Dynamics Software and Simulation System (cdsssim.chem.tu-etu.edu) website. In the tests, we calculated the potential energy, its gradient, and Hessian at 200 configurations with the B3LYP/6-311+G** electronic structure theory using the VENUS package interfaced with NWChem. We picked four configurations, $X_1, X_2, X_3, and X_4$, from the 200 configuration points, with $X_1$ and $X_2$ close to each other and $X_3$ and $X_4$ close to each other. The Euclidean distances between these points are

$$\|X_1 - X_2\| = 0.103 657 71 \text{ Å} ,$$

$$\|X_3 - X_4\| = 0.151 259 13 \text{ Å} ,$$

$$\|X_1 - X_3\| = 1.302 803 92 \text{ Å} .$$

The following nine Hessian update schemes were used to calculate the approximate Hessian $H_2$ at $X_2$ using the $ab$ initio data $G(X_1)$, $H(X_1)$, and $G(X_2)$, and the approximate Hessian $H_3$ at $X_3$ using the $ab$ initio data $G(X_2)$, $H(X_2)$, and $G(X_3)$. For the calculations of the approximate Hessians, we used nine Hessian update schemes:

1. the CFD-SR1 scheme, i.e., the SR1 formula originally for the quasi-Newton equation applied to the CFD-based equation (2.4);
2. the CFD-PSB scheme;
3. the CFD-Bofill scheme with $\lambda = 1 - (R_{k+1}^T \Delta X_{k+1})^2|R_{k+1}|^{-2}|\Delta X_{k+1}|^{-2}$;
4. the pCFD-SR1 scheme, the CFD-SR1 scheme perturbed with $\sum_{i,j} C_{i,j} (V_i V_j^T + V_j V_i^T)$ according to Eq. (2.9);
5. the pCFD-PSB scheme, the CFD-PSB scheme perturbed with $\sum_{i,j} C_{i,j} (V_i V_j^T + V_j V_i^T)$;
6. the CFD-Bofill scheme, the CFD-Bofill scheme perturbed with $\sum_{i,j} C_{i,j} (V_i V_j^T + V_j V_i^T)$;
7. the qN-SR1 scheme, i.e., the original SR1 scheme. Here we call it qN-SR1 since it is the SR1 solution-generating formula applied to the qN equation in order to distinguish it from the CFD-SR1 scheme as applied to the CFD-based equation;
8. the qN-PSB scheme; and
9. the qN-Bofill scheme [with $\lambda = 1 - (B_{k+1}^T \Delta X_{k+1})^2|B_{k+1}|^{-2}|\Delta X_{k+1}|^{-2}$].

The Hessians calculated with the above nine schemes are used in the second-order Taylor expansion

$$V(X_{test}) = V(X_0) + G(X_0)(X_{test} - X_0)$$

$$+ \frac{1}{2}(X_{test} - X_0)^T H(X_0)(X_{test} - X_0)$$

(4.1)

to approximate the potential energy at point $X_{test}$ near point $X_0$ at which the approximate Hessian $H(X_0)$ was calculated using an update scheme. In our tests, $X_0$ is $X_2$ or $X_4$. Near point $X_2$, we choose five points $X_{2,1}, X_{2,2}, X_{2,3}, X_{2,4},$ and $X_{2,5}$ as the testing point $X_{test}$, and near point $X_4$, we also chose five points $X_{4,1}, X_{4,2}, X_{4,3}, X_{4,4},$ and $X_{4,5}$ as $X_{test}$. The five points $X_{2,j}$ ($j=1,2,\ldots,5$) have different distances from $X_2$ and the vectors $(X_{2,j} - X_2)$ form different angles with vector $X_2 - X_2$. The points $X_{4,j}$ ($j=1,2,\ldots,5$) have different distances from $X_4$ and the vectors $(X_{4,j} - X_4)$ form different angles with vector $X_3 - X_4$. These distances and angles are listed in Table I.

To study the accuracy of the Hessian update schemes, reference potential energies $V_{2,i}$ and $V_{4,i}$ were calculated at testing points $X_{2,i}$ and $X_{4,i}$ ($i=1,2,\ldots,5$) using the second-order Taylor expansion (4.1) with the $ab$ initio Hessians at $X_2$ and $X_4$. The potential energies calculated with updated Hessians were then compared against $V_{2,i}$ and $V_{4,i}$. The magnitude of the difference between the potential energy calculated from Eq. (4.1) using the $ab$ initio Hessian and updated Hessian is listed in Tables II and III for the ten testing points. This difference is computed for the nine Hessian update schemes.
The potential energy differences listed in Tables II and III show that the new update schemes have much better accuracy than the three existing schemes at all points except $X_{2,3}$ and $X_{4,3}$. In addition, all six CFD-based new schemes have the same errors at $X_{2,1}$, $X_{2,5}$, $X_{4,1}$, $X_{4,5}$, and all three existing schemes also have the same errors at these four points. These errors are the same because all six new schemes are exact solutions of Eq. (2.5), that is, $\Delta^{2}H_{k+1}$ evaluated at $X_{k+1}$ is the same for all six schemes. In addition, the subspace spanned by the vectors $X_{2,1} - X_{2}$ and $X_{1}$ is the same as the subspace spanned by the vectors $X_{2,5} - X_{2}$ and $X_{1}$ in the tests. The subspaces satisfy the quadratic expansion (4.1).

Equations (2.5) and (2.8), of which the new and existing schemes are solutions, respectively, define constraints that an updated Hessian $\Delta H$ must satisfy on the subspace spanned by $X_{k+1}$. Thus, the new schemes may or may not produce higher accuracy on any subspace perpendicular to $X_{k+1}$. This uncertainty in accuracy can be seen from the data for $X_{2,3}$ and $X_{4,3}$, which are on a line parallel to $X_{k+1}$ (see the angles in Table I). Such uncertainty in the error on subspaces perpendicular to $X_{k+1}$ is the reason why we chose coefficients $C_{i,j}$’s in scheme (2.9) according to Eq. (2.10) to minimize $\Delta H_{k+1} V_j$ on the subspace spanned by the vector $V_j$ perpendicular to $X_{k+1}$. With this minimization, $H_{k+1} = H_k + \Delta H_{k+1}$ remains as close as possible to $H_k$ on all parallel subspaces.

For points which have both parallel and perpendicular components such as $X_{2,2}$ and $X_{4,4}$ in Table II and $X_{2,2}$ and $X_{4,4}$ in Table III, the new schemes produce better approximations for the parallel components but have unknown performance for the perpendicular components. The test data for the four points of this type show higher accuracy for five of the six new schemes, CFD-PSB, CFD-Bofill, pCFD-SR1, pCFD-PSB, and pCFD-Bofill. Update scheme CFD-SR1 shows mixed results when compared with the existing qN-SR1 scheme.

The test data in Tables II and III show that there is no consistent improvement in the accuracy when an update scheme is perturbed by minimizing the component of the Hessian perpendicular to $X_{k+1}$. However, perturbed CFD-based schemes perform better than all three existing schemes.

### B. Application to a Hessian-utilizing integrator

We applied the nine Hessian update schemes to a modification of the numerical integrator[26] that uses the Hessian of the potential energy to calculate classical trajectories. Our modified integrator used trust radius in time instead of the trust radius originally in the Cartesian coordinate space, and all other algorithmic features remain the same. In the

| Table II. Magnitude of the differences between the potential energies at testing points $X_{2j}$ ($j=1,2,\ldots,5$) using the quadratic expansion (4.1), with the correct $ab\!\!$ initio and updated approximate Hessians at $X_{2}$ (The energy unit is kcal/mol.) |
|-------------------------------|-----------------|-----------------|-----------------|-----------------|
|                              | $X_{2,1}$       | $X_{2,2}$       | $X_{2,3}$       | $X_{2,4}$       | $X_{2,5}$       |
| Existing schemes             | $qN$-SR1: $2.844 \times 10^{-5}$ | $1.456 \times 10^{-5}$ | $6.075 \times 10^{-6}$ | $4.464 \times 10^{-6}$ | $1.683 \times 10^{-6}$ |
|                              | $qN$-PSB: $2.844 \times 10^{-5}$ | $1.471 \times 10^{-5}$ | $5.163 \times 10^{-6}$ | $4.497 \times 10^{-6}$ | $1.683 \times 10^{-6}$ |
|                              | $qN$-Bofill: $2.844 \times 10^{-5}$ | $1.469 \times 10^{-5}$ | $5.288 \times 10^{-6}$ | $4.492 \times 10^{-6}$ | $1.683 \times 10^{-6}$ |
| CFD-based schemes             | CFD-SR1: $1.789 \times 10^{-5}$ | $5.407 \times 10^{-6}$ | $6.988 \times 10^{-6}$ | $1.104 \times 10^{-6}$ | $1.058 \times 10^{-6}$ |
|                              | CFD-PSB: $1.789 \times 10^{-5}$ | $8.327 \times 10^{-6}$ | $5.163 \times 10^{-6}$ | $4.472 \times 10^{-6}$ | $1.058 \times 10^{-6}$ |
|                              | CFD-Bofill: $1.789 \times 10^{-5}$ | $7.928 \times 10^{-6}$ | $5.412 \times 10^{-6}$ | $5.369 \times 10^{-6}$ | $1.058 \times 10^{-6}$ |
| Perturbed CFD-based schemes   | pCFD-SR1: $1.789 \times 10^{-5}$ | $1.007 \times 10^{-5}$ | $4.072 \times 10^{-6}$ | $5.459 \times 10^{-6}$ | $1.058 \times 10^{-6}$ |
|                              | pCFD-PSB: $1.789 \times 10^{-5}$ | $8.327 \times 10^{-6}$ | $5.163 \times 10^{-6}$ | $4.472 \times 10^{-6}$ | $1.058 \times 10^{-6}$ |
|                              | pCFD-Bofill: $1.789 \times 10^{-5}$ | $8.565 \times 10^{-6}$ | $5.014 \times 10^{-6}$ | $3.936 \times 10^{-6}$ | $1.058 \times 10^{-6}$ |

| Table III. Magnitude of the differences between the potential energies at testing points $X_{4j}$ ($j=1,2,\ldots,5$) using the quadratic expansion (4.1), with the correct $ab\!\!$ initio and updated approximate Hessians at $X_{4}$ (The energy unit is kcal/mol.) |
|-------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                              | $X_{4,1}$       | $X_{4,2}$       | $X_{4,3}$       | $X_{4,4}$       | $X_{4,5}$       |
| Existing schemes             | $qN$-SR1: $3.625 \times 10^{-5}$ | $5.177 \times 10^{-5}$ | $4.135 \times 10^{-5}$ | $4.201 \times 10^{-5}$ | $2.145 \times 10^{-5}$ |
|                              | $qN$-PSB: $3.625 \times 10^{-5}$ | $6.379 \times 10^{-5}$ | $3.381 \times 10^{-5}$ | $1.495 \times 10^{-5}$ | $2.145 \times 10^{-5}$ |
|                              | $qN$-Bofill: $3.625 \times 10^{-5}$ | $6.355 \times 10^{-5}$ | $3.233 \times 10^{-5}$ | $1.548 \times 10^{-5}$ | $2.145 \times 10^{-5}$ |
| CFD-based schemes             | CFD-SR1: $9.994 \times 10^{-6}$ | $2.751 \times 10^{-6}$ | $1.165 \times 10^{-6}$ | $5.073 \times 10^{-6}$ | $5.914 \times 10^{-6}$ |
|                              | CFD-PSB: $9.994 \times 10^{-6}$ | $3.461 \times 10^{-6}$ | $3.381 \times 10^{-6}$ | $3.386 \times 10^{-6}$ | $5.914 \times 10^{-6}$ |
|                              | CFD-Bofill: $9.994 \times 10^{-6}$ | $3.932 \times 10^{-6}$ | $3.086 \times 10^{-6}$ | $2.325 \times 10^{-6}$ | $5.914 \times 10^{-6}$ |
| Perturbed CFD-based schemes   | pCFD-SR1: $9.994 \times 10^{-6}$ | $4.294 \times 10^{-6}$ | $2.859 \times 10^{-6}$ | $1.510 \times 10^{-6}$ | $5.914 \times 10^{-6}$ |
|                              | pCFD-PSB: $9.994 \times 10^{-6}$ | $3.461 \times 10^{-6}$ | $3.381 \times 10^{-6}$ | $3.386 \times 10^{-6}$ | $5.914 \times 10^{-6}$ |
|                              | pCFD-Bofill: $9.994 \times 10^{-6}$ | $3.477 \times 10^{-6}$ | $3.370 \times 10^{-6}$ | $3.349 \times 10^{-6}$ | $5.914 \times 10^{-6}$ |
existing version of the integrator, the \textit{ab initio} Hessian is calculated once in every \(K\) steps, with \(K\) ranging from 5 to 10. During the remaining \((K-1)\) steps, Bofill’s update scheme is used to produce approximate Hessians.

1. Dynamics simulation test on the \(\text{F}^- + \text{CH}_3\text{OOH}\) reaction

In this study, we used this modified integrator, with \(K=10\), to test the nine update schemes listed in Sec. IV A. Nine trajectories were calculated for the \(\text{F}^- + \text{CH}_3\text{OOH}\) chemical reaction system described in Sec. IV A. Each trajectory has the same initial condition and 60 integration time steps with a fixed step size of 0.7 fs. Two of the nine trajectories, one calculated with qN-SR1 and the other with CFD-SR1, failed to complete the simulation due to a large error in the energy. We examined the numerical data of the integration and found that the value of the denominator for each of these two SR1 schemes became fairly small several times, causing an increase in the error of the energy each time. Such accumulated errors in the energy finally led to inadequate energy conservation, triggering the premature termination of the simulations. However, the perturbed CFD-SR1 completed the simulation without overwhelming energy deviation, a sign that the perturbation might be able to suppress large numerical errors and improve the SR1 scheme.

We also calculated the trajectory with the integrator using only the \textit{ab initio} Hessian, and the trajectories calculated using the remaining seven update schemes were compared against the trajectory using only the \textit{ab initio} Hessian. The Euclidean distances of the Cartesian coordinates of the atom positions of each of the seven trajectories from this \textit{ab initio} Hessian trajectory are plotted in Fig. 1. In the figure, the
curves for the CFD-PSB, pCFD-PSB, and pCFD-Bofill schemes overlap, given the resolution of the plots. The differences in the distances for the CFD-PSB and the pCFD-PSB schemes are quite small and first occur in the eighth digit after the most significant digit. The distances for the pCFD-Bofill scheme differ from these two after the fourth digit. The curves in Fig. 1 show that the four new schemes CFD-PSB, CFD-Bofill, pCFD-PSB, and pCFD-Bofill produce better accuracy than the existing qN-PSB and qN-Bofill schemes. The pCFD-SR1 scheme is not as good as the other CFD-based schemes but shows comparable results when compared with the qN-PSB and qN-Bofill schemes.

2. Dynamics simulation test on the Cl$^- +$CH$_3$I reaction

To see the performance of the CFD-based update schemes for different molecules, we also tested the integrator described at the beginning of Sec. IV B on the Cl$^- +$CH$_3$I chemical reaction$^{33}$ listed on the cdssim.chem.ttu.edu website. Using this integrator, we calculated a total of 12 trajectories, each with the same initial condition, with the 6 Hessian update schemes: qN-Bofill, qN-PSB, CFD-Bofill, CFD-PSB, pCFD-Bofill, and pCFD-PSB. Each of these schemes was used to calculate two trajectories, one with a time step being 0.7 fs and the update parameter $K=10$, and the other with time step of 1.0 fs and $K=12$, for a total of 12 trajectories. The potential energy information needed in the integration was calculated with the MP2(fc)/ECP/d electronic structure theory$^{33}$ using a development version of the VENUS package interfaced with NWChem. Each trajectory was calculated for 140 fs, and the total energy was computed at each time step. The total energies of the 12 trajectories are plotted in Figs. 2–5, where Figs. 2 and 3 plot the energies for time steps of 0.7 fs and 1.0 fs, respectively.

![Fig. 3](image_url)  
**FIG. 3.** Total energies of the Cl$^- +$CH$_3$I chemical reaction system for simulations of 140 fs. Time step=0.7 fs and $K=10$. The units for the horizontal and vertical axes, respectively, are femtosecond and kcal/mol.

![Fig. 4](image_url)  
**FIG. 4.** Total energies of the Cl$^- +$CH$_3$I chemical reaction system for simulations of 140 fs. Time step=1.0 fs and $K=12$. The units for the horizontal and vertical axes, respectively, are femtosecond and kcal/mol.
step=0.7 and K=10, and Figs. 4 and 5 plot the energies for time step=1.0 and K=12. In the figures, the CFD-based schemes show better energy conservation than the existing quasi-Newton equation-based schemes, especially during later simulation times. The differences in energy conservation between CFD-Bofill and pCFD-Bofill is very small but visible in Figs. 2 and 4, while the differences between CFD-PSB and pCFD-PSB is not visible from Figs. 3 and 5. An examination of the simulation data reveals that their differences are after the eighth decimal point. These four figures comparatively show that when used in a dynamics simulation, the CFD-based Hessian update schemes have better energy conservation than their corresponding qN-based update schemes. Another observation is that the energy curves for the CFD schemes and the curves for the qN schemes are closer for time step=0.7 fs and K=10 in Figs. 2 and 3 than they are for time step=1.0 fs and K=12 in Figs. 4 and 5.

Two Cl−+CH3I trajectories were also calculated, for the above initial condition, using the ab initio Hessian at each time step, one with a time step of 0.7 fs and the other with a...
time step of 1.0 fs. The Euclidean distances between each of the two \textit{ab initio} Hessian trajectories (different in time step sizes) and the 6 corresponding trajectories calculated using update Hessians are plotted versus time in Figs. 6 and 7. In the figures, the curves for the CFD-PSB and pCFD-PSB schemes overlap, given the resolution of the plots. The differences in the distances for the CFD-PSB and the pCFD-PSB schemes start at the eighth most significant digit. The curves in Figs. 6 and 7 show that, when the testing parameters time step=0.7 fs and K=10 in Fig. 6 increase to time step=1.0 fs and K=12 in Fig. 7, the distances between the updated and the \textit{ab initio} Hessian trajectories have approximately doubled for both the CFD-based schemes and the existing schemes. This is most clearly visible during the 100-140 fs time interval. However, in both figures the new schemes produce better accuracy than the qN-PSB and qN-Bofill schemes.

V. CONCLUSION

Using CFD, we derive in this article a fundamental equation relating the gradient and Hessian of the potential energy for two configuration points. This equation gives one order of magnitude higher accuracy than does the quasi-Newton equation for generally applicable Hessian update schemes. New Hessian update schemes are derived as solutions of this CFD-based equation. Four CFD-based schemes exhibit substantially higher accuracy than do existing Hessian update schemes in direct tests as well as in chemical dynamics simulations.

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