

***Ab initio* classical trajectories on the Born–Oppenheimer surface: Updating methods for Hessian-based integrators**

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For the integration of the classical equations of motion in the Born–Oppenheimer approach, each time the energy and gradient of the potential energy surface are needed, a properly converged wave function is calculated. If Hessians (second derivatives) can be calculated, significantly larger steps can be taken in the numerical integration of the equations of motion without loss of accuracy. Even larger steps can be taken with a Hessian-based predictor–corrector algorithm. Since updated Hessians are used successfully in quasi-Newton methods for geometry optimization, it should be possible to improve the performance of trajectory calculations using updated Hessians. The Murtagh–Sargent (MS) update, the Powell-symmetric–Broyden (PSB) update and Bofill’s update (a weighted combination of MS and PSB) were tested, and Bofill’s update was found to be the best. Slightly smaller step sizes were needed with Hessian updating to maintain good conservation of the energy, but this was more than compensated by the reduction in total computational cost. An overall factor of 3 in speed-up was obtained for trajectories of systems containing 4 to 6 heavy atoms computed at the HF/3-21G level. © 1999 American Institute of Physics. [S0021-9606(99)30443-8]

INTRODUCTION

Simulation of dynamics provides a much more detailed picture than can be obtained from transition states, reaction paths and statistical treatments of reaction rates.¹ However, until recently, the only reactions that could be studied by molecular dynamics simulations were those for which analytical surfaces had been carefully crafted. The advent of *ab initio* classical trajectory calculations has changed the picture dramatically.² Because of advances in computer speed and improvements in molecular orbital software, it is now possible to compute classical trajectories directly from electronic structure calculations without first fitting a global potential energy surface. There are two basic approaches: the Car–Parrinello (CP) method,³ in which both the electronic wavefunction and the atoms are propagated, and the Born–Oppenheimer (BO) approach,² in which the electronic structure calculations are converged and the atoms move on a well defined surface. In the integration of classical trajectories on the Born–Oppenheimer surface, electronic structure calculations are performed each time there is a need for information about the potential energy surface or its derivatives. Standard numerical methods for integrating the classical equations of motion require only the first derivatives or gradients of the potential energy surface.⁴ However, relatively small step sizes are needed so that energy and angular momentum are conserved with sufficient accuracy. If analytical second derivatives (i.e., Hessians) can be computed, the equations of motion can be calculated on a local quadratic approximation to the potential energy surface. The extra cost of computing the second derivatives is offset by the larger

step sizes that can be taken with Hessian-based trajectory integration schemes. Helgaker and co-workers⁵ have used this second order Hessian-based trajectory integration method to study a number of reactions.

In recent work, we have outlined a more accurate Hessian-based integration scheme for classical trajectory calculations.⁶ This scheme uses a second order predictor step on a local quadratic surface, followed by a corrector step on a more accurate local surface fitted to the energies, gradients and Hessians computed at the beginning and end points of each step along the trajectory. The electronic structure work per step is the same as for the second order Hessian based integrator, since the energy, gradient and Hessian for the corrector step used to construct the local quadratic surface for the next predictor step. A fifth order polynomial fit to the potential energy surface performs slightly better than a rational function fit, and the step size can be increased by an order of magnitude over the simple second order method without loss of accuracy.

METHODOLOGY

To study larger and more interesting systems, the efficiency of *ab initio* classical trajectory calculations must be improved further. For geometry optimization, very good performance is obtained with quasi-Newton methods, which use gradients to update an approximate Hessian.⁷ This suggests that for trajectories, rather than computing the Hessian at each step, considerable CPU time can be saved by updating the Hessian for several steps before re-computing it.

Updating the Hessian. For minimizations, the BFGS Hessian updating scheme is preferred because it maintains the positive definite character of the Hessian.⁸ However, for many regions of the potential energy surface explored by trajectory calculations, such as near transition states, the Hes-

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sian is not positive definite. Hence, Hessian updating schemes that have been used for transition structure optimization are more appropriate. The Murtagh–Sargent update (MS), also known as the symmetric rank one formula (SR1), does not force a positive definite update and thus is suitable for updating the Hessian along a trajectory calculation:

$$\Delta H_{\text{MS}} = H^{\text{new}} - H^{\text{old}} = \frac{(\Delta g - H^{\text{old}} \Delta x)(\Delta g - H^{\text{old}} \Delta x)^t}{(\Delta g - H^{\text{old}} \Delta x)^t \Delta x}. \quad (1)$$

For optimization on a quadratic function, MS converges to the correct Hessian without exact line searches.⁸ However, care must be taken to avoid the update if the denominator becomes too small. An alternate updating formula that does not have this problem is the Powell-symmetric–Broyden (PSB) update:

$$\Delta H_{\text{PSB}} = \frac{(\Delta g - H^{\text{old}} \Delta x) \Delta x^t + \Delta x (\Delta g - H^{\text{old}} \Delta x)^t}{\Delta x^t \Delta x} - \frac{\Delta x^t (\Delta g - H^{\text{old}} \Delta x) \Delta x \Delta x^t}{(\Delta x^t \Delta x)^2}. \quad (2)$$

Bofill⁹ has proposed an updating formula for transition state optimizations that is a combination of the PSB and MS updates:

$$\Delta H_{\text{Bofill}} = \phi \Delta H_{\text{MS}} + (1 - \phi) \Delta H_{\text{PSB}}; \quad \phi = \frac{(\Delta x^t (\Delta g - H^{\text{old}} \Delta x))^2}{\Delta x^2 (\Delta g - H^{\text{old}} \Delta x)^2}. \quad (3)$$

Implementation. The integration of a trajectory starts with an analytic calculation of the energy, gradient and Hessian. Then, for a given number of steps, only the energy and gradient are calculated analytically, and the Hessian is obtained by updating. Each step uses the Hessian based predictor-corrector algorithm described earlier.⁶ After the desired number of steps with the updated Hessian, the full Hessian is calculated again analytically. A better estimate of the previous Hessian can be obtained by updating using the current analytic Hessian and the previous gradient. The previous step can then be re-integrated with the better data. However, the improvement using this scheme is very modest.

The number of times that the Hessian may be updated can vary with the region of the potential energy surface explored by the trajectory. However, as will be shown below, most of the savings in CPU cost are already obtained with four or five updates. Thus, not much is to be gained by dynamically adjusting the number of updates. The optimal step size may also vary with the region of the potential energy surface. A Taylor expansion employing the energy, gradient and Hessian from the previous step can be used to predict the energy and gradient at the current point. The difference between the predicted quantities and the calculated energy or gradient could be a useful diagnostic for adjusting the step size while maintaining the desired accuracy in the integration. Unfortunately, there appears to be very little correlation between the errors in the predicted energy or gradient and the error in the energy conservation for a step ($R^2 \sim 0.3$). Until a better diagnostic can be developed, we will use a fixed step size.

As discussed in Refs. 5 and 6, the equations of motion for Hessian-based methods are most easily integrated in mass-weighted instantaneous normal mode coordinates. Because the quadratic approximation of the potential energy surface is valid only for a given trust radius, it is more convenient to choose an integration step size in terms of a displacement rather than in terms of time. The displacement step in mass-weighted coordinates, σ , is related to the time step, Δt , through the integrated path length defined by

$$\sigma = \int_{t'}^{t'+\Delta t} \sqrt{\sum_i w_i(t)^2} dt \approx \bar{w} \Delta t, \quad (4)$$

where $w_i(t)$ are the components of the mass-weighted velocity. This equation does not have an analytical solution for Δt , and the time step has to be determined iteratively. For a fixed displacement step, the time steps are larger when the molecule is moving slowly and smaller when it is moving rapidly.

NUMERICAL TESTS

The performance of different Hessian updating formulas.

The decomposition of H_2CO is a well studied reaction and thus was used to test whether Hessian updating is feasible and which formula is most suitable for trajectory calculations. The Murtagh–Sargent (MS), the Powell–symmetric–Broyden (PSB) and the Bofill updates have been examined, and the trajectories were run with 0, 3, 6, and 9 updates between analytic Hessian calculations. The conservation of energy is used to evaluate the quality of the trajectory integrations, and is calculated as the absolute value of the difference of the total energy at the start and the end of the trajectory.

As in our previous papers,⁶ the trajectories for $\text{H}_2\text{CO} \rightarrow \text{H}_2 + \text{CO}$ were started from the optimized transition structure with 5.145 kcal/mol of energy in the transition mode. Step sizes of 0.250 and 0.350 amu^{1/2} bohr were used (on average corresponding to 0.5 and 0.7 fs), as well as rotational temperatures of 0 K and 298 K. The four trajectories with the different combinations of step sizes and temperatures were calculated for each type (MS, PSB, Bofill) and number of Hessian updates ($n=0,3,6,9$). For each case, the error in the conservation of energy was computed as the average of the four trajectories. The calculations were carried out with the current development version of the Gaussian series of programs¹⁰ using the RHF/3-21G level of theory.

Generally it is desirable to conserve the energy over the length of a trajectory in the micro-Hartree range (i.e., errors of less than 1.0×10^{-5} Hartree), corresponding to approximately 0.01–0.02 kJ/mol (0.005 kcal/mol). Figure 1 shows the average energy conservations for 0, 3, 6, and 9 updates between analytic calculations of the full Hessian. In addition to the MS, PSB, and Bofill updating formulas, results are also shown for trajectories where the Hessian is kept fixed between each recalculation of the Hessian. The results for $n=0$ are obviously all the same, since no updates are done between Hessian calculations. It is clear from Fig. 1 that updating the Hessian is dramatically better than using a fixed Hessian. Furthermore, of the three formulas examined, the

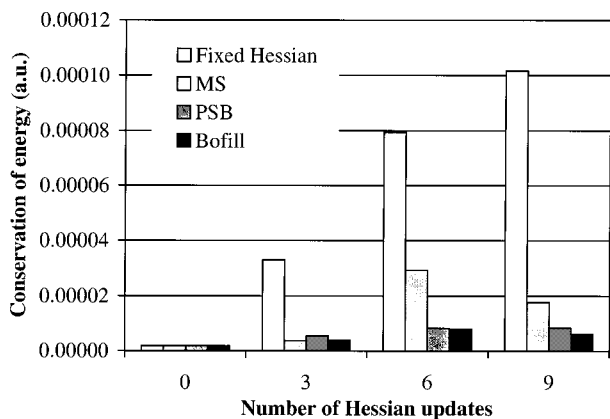


FIG. 1. Conservation of energy as a function of the number of Hessian updates between each time the Hessian is calculated analytically. With zero updates the Hessian is calculated at each step; a fixed Hessian means no updating is done between the analytical calculations. The results are averages based on four different trajectories (step size 0.250 and 0.350 $\text{amu}^{1/2}$ bohr temperatures of 0 K and 298 K).

Murtagh–Sargent update is distinctly inferior to the others. The MS update is actually worse than indicated in the figure, since the formula breaks down completely for certain combinations of updates, step size and temperature. Errors as large as 0.1 Hartree were observed in the conservation of energy, and can probably be attributed to the denominator in Eq. (1) becoming too small.

Both the Powell-symmetric–Broyden and Bofill updates perform well, and conservation of energy is satisfactory even with nine updates. The fact that Bofill's update is somewhat better agrees with the literature for transition state optimization.^{7,9} Bofill's update includes the Murtagh–Sargent update, but the switching function, ϕ , is very effective in controlling the problems arising from the denominator in the Murtagh-Sargent formula. Based on these results, Bofill's update is chosen as the default updating method for our Hessian-based integrators.

H₂CO trajectories with updated Hessians. Good energy conservation is an obvious requirement, but it is also necessary to show that essentially the same trajectories are traced out both with and without updates. Once more formaldehyde decomposition is used as a simple test case. Trajectories were run in the same manner as outlined above, this time with step sizes of 0.100, 0.200, and 0.300 $\text{amu}^{1/2}$ bohr and temperatures of 0 K and 298 K.

Both the carbon-oxygen and the hydrogen-hydrogen bond lengths were plotted as functions of time. Figure 2 shows the H–H bond for trajectories with different number of updates, all with a rotational temperature of 298 K and step size of 0.300 $\text{amu}^{1/2}$ bohr. The solid line shows the “exact” trajectory, generated with a small step size (0.100 $\text{amu}^{1/2}$ bohr) and with Hessians calculated at every step. Very small differences for the various trajectories ($n=3, 6,$ and 9) can be discerned in the figure, but these were the largest deviations seen for this test case. For the C–O bond, the trajectories were essentially superimposable, and the agreement was even better for trajectories using shorter steps and/or lower rotational temperatures. This indicates that at 298 K, 0.300 $\text{amu}^{1/2}$ bohr is near the limit of the step size that

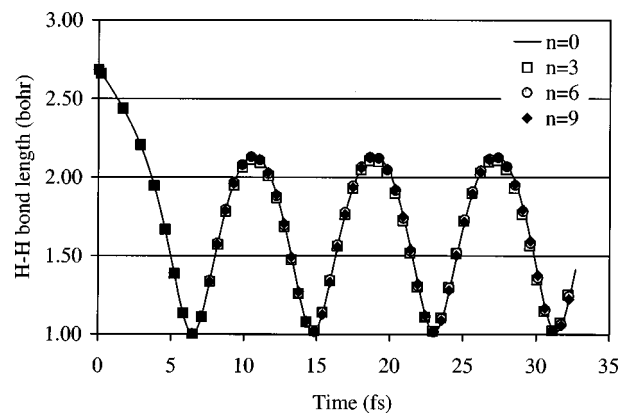


FIG. 2. The hydrogen–hydrogen bond length in an H₂CO dissociation trajectory as a function of time for different number of updates, n . The trajectories were run with a step size of 0.300 $\text{amu}^{1/2}$ bohr, and the solid line corresponds to a step size of 0.100 $\text{amu}^{1/2}$ bohr with analytical Hessians computed at each step.

can be used with updated Hessians for this particular system.

The bounds on acceptable step sizes are even clearer in Fig. 3. For a step size of 0.300 $\text{amu}^{1/2}$ bohr, the trajectories with $n=6$ and $n=9$ have a final energy conservation that is slightly worse than the desired accuracy; for step sizes of 0.200 and 0.100 $\text{amu}^{1/2}$ bohr, the conservation of energy is excellent for all values of n . The decrease in the error in going from 6 to 9 updates is due to a fortuitous cancellation in the particular trajectories examined. Averaging over a large number of trajectories would yield smoother trends. The marked improvement in the energy conservation indicates that it may be beneficial to shorten the steps slightly in order to increase the number of updates between each Hessian calculation. As will be discussed later, the cost of a small increase in the number of steps is readily offset by a reduction in the total CPU cost since fewer Hessian calculations are needed. When the rotational temperature is reduced from 298 K to 0 K, the error in the energy conservation is typically two orders of magnitude lower (10^{-7} – 10^{-8} Hartree), and larger step sizes and a high number of updates can be used.

In addition to the energy, it is also important that the total angular momentum of the system is well preserved.

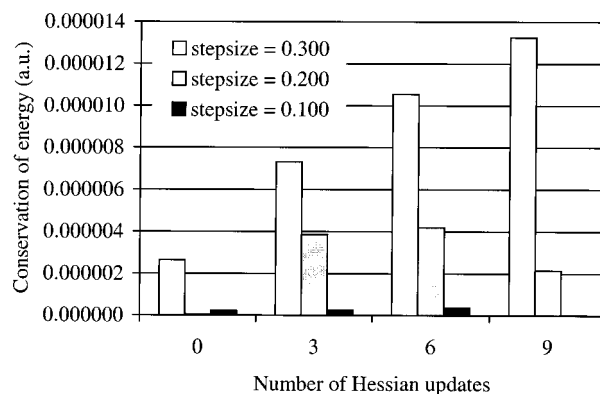


FIG. 3. Conservation of energy for H₂CO dissociation as a function of the number of Hessian updates using different step sizes. All step sizes are in units $\text{amu}^{1/2}$ bohr.

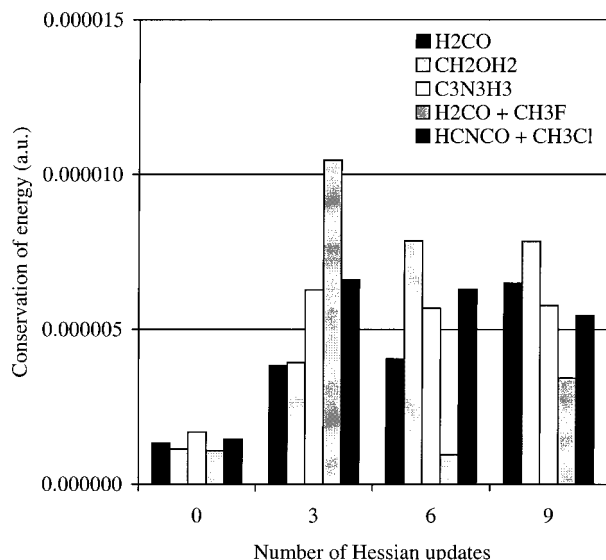


FIG. 4. Conservation of energy for five different systems as the number of updates are varied. Different step sizes were used for the different systems to give approximately the same energy conservation for $n=0$, but all the trajectories were run for 50 steps (corresponding to 25–35 fs).

Even at a rotational temperature of 298 K and $0.300 \text{ amu}^{1/2} \text{ bohr}$ step size, the error in the conservation of angular momentum is only of the order $10^{-8} \hbar$. The error does not appear to increase with the number of updates, although the conservation does become even better with smaller step sizes.

Performance and CPU cost using updated Hessians.

Having explored the performance and limits of updated Hessians on the simple formaldehyde case, we now turn to a few other systems. The H_2CO decomposition is, of course, a very small system and there is little to be gained by using updating, since the Hessians are relatively inexpensive (at least at the HF/3-21G level). Our method needs to be validated for a somewhat broader selection of systems.

We have chosen a small test suite containing five different systems, ranging in size from two to six heavy atoms (up to ten atoms total). All of the systems were run with a rotational temperature of 298 K. Three of the systems, H_2CO , $\text{H}_2\text{CO}^- + \text{CH}_3\text{F}$, and $\text{HCNCO}^- + \text{CH}_3\text{Cl}$, were started from optimized transition states. The initial conditions for formaldehyde dissociation were described above; for the other two reactions, the energy of the transition mode was sampled from a thermal distribution at 298 K. The last two systems CH_2OH_2^+ and *s*-triazine ($\text{C}_3\text{N}_3\text{H}_3$) were started from minimized structures. For all five systems, the energies of the vibrational modes were sampled from a thermal distribution at 298 K. The step sizes were adjusted for each system so that the conservation of energy without Hessian updating was in the micro-Hartree range. For formaldehyde $0.250 \text{ amu}^{1/2} \text{ bohr}$ was chosen, whereas for CH_2OH_2^+ it was necessary to reduce the step size to $0.100 \text{ amu}^{1/2} \text{ bohr}$. The other reactions were run with $0.200 \text{ amu}^{1/2} \text{ bohr}$. To keep the testing manageable, all trajectories were run for exactly 50 steps, giving total integration times in the range 25–35 fs (the exception again being CH_2OH_2^+ where the trajectories only covered 21 fs).

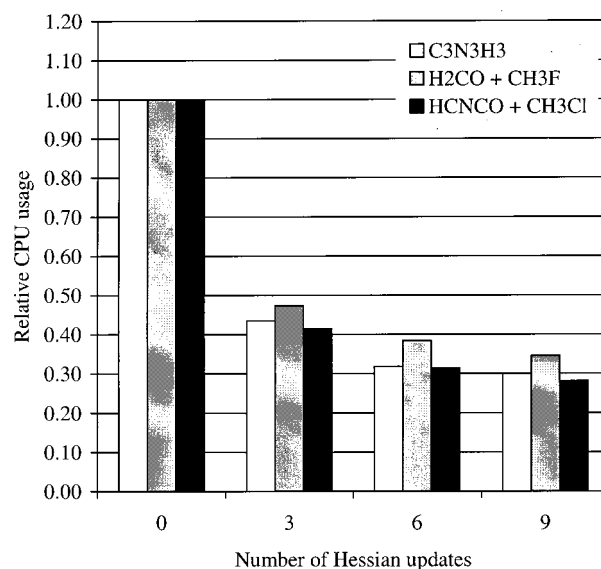


FIG. 5. Relative CPU cost as a function of the number of Hessian updates. All numbers are relative to the CPU cost of the trajectories with no updating (i.e., Hessian calculated at each step), and all trajectories were run for 50 steps.

The conservation of energy for these systems is shown in Fig. 4, and with the exception of one trajectory ($n=3$ for $\text{H}_2\text{CO}^- + \text{CH}_3\text{F}$), all results meet or exceed our criterion for energy conservation. It is clear that the error in energy conservation is slightly worse using updated Hessians, but the increase is not dramatic. Furthermore, there does not seem to be a large change in the conservation of energy as the number of Hessian updates is increased. It is very satisfying to see how well the energy and angular momentum is conserved, even with as many as nine updates between each analytical Hessian calculation.

Given the excellent energy conservation, we can examine the reduction in CPU cost that can be obtained with Hessian updating. The relative CPU cost as a function of the number of Hessian updates, n , has been calculated for each the system as a ratio of the actual CPU time for the trajectory with $n \neq 0$ and the trajectory with $n=0$. In Fig. 5 the results are shown for the three largest systems. For $n=3$, the cost is already less than half that with no updating, and for $n=6$ the cost is approximately one third. From there it starts to flatten out and there is not too much to be gained by increasing the number of updates even further. The limit is the ratio of the cost of the gradient to the cost of the Hessian.

CONCLUSIONS

Based on the results discussed above, it seems best to use five or six updates between Hessian calculation. Most of the reduction in CPU time can be achieved and, at the same time, good conservation of energy and angular momentum can be maintained even if fairly large step sizes are used. It is further clear that any slight reduction in the step size that may be needed to utilize the Hessian updating is more than compensated by the reduction in total CPU cost. From the present work, it seems apparent that for typical small systems suitable for *ab initio* direct dynamics, a factor of three

increase in speed can easily be obtained using Hessian updating methods. This is a significant improvement in performance, and the gain should be even more substantial for systems larger than the ones considered here.

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