384d Efficient Methods for Finding Transition States in Chemical Reactions: Comparison of Improved Dimer Method and Partitioned Rational Function Optimization Method

Andreas Heyden, Alexis T. Bell, and Frerich J. Keil

The harmonic approximation to transition state theory is often used to predict the rates of chemical reactions. Such calculations require knowledge of the electronic energy, the geometry and the real vibrational frequencies at the first-order saddle point (transition state) and at the reactant minimum. While locating potential energy minima can routinely be done, finding saddle points on potential energy surfaces (PES) determined from quantum chemical calculations can be extremely difficult, and remains one of the major challenges in chemical kinetics for medium to large systems.

A combination of interpolation methods and local saddle point search algorithms is probably the most efficient way of finding transition states in chemical reactions. Interpolation methods such as the growing string method[1] and the nudged elastic band are able to find an approximation to the minimum energy pathway (MEP) and thereby provide a good initial guess for a transition state and imaginary mode connecting both reactant and product states. Since interpolation methods employ usually just a small number of configurations and converge slowly close to the minimum energy pathway, local methods such as partitioned rational function optimization (P-RFO) methods using either exact or approximate Hessians or minimum mode following methods like the dimer or the Lanczos method have to be used to converge to the transition state. A modification to the original dimer method proposed by Henkelman and Jónnson is presented[2], reducing the number of gradient calculations per cycle from eight to four gradients or three gradients and one energy, and improve the overall performance of the algorithm on quantum chemical potential energy surfaces (PES). A comparison is made between the dimer methods and the well-established partitioned rational function optimization methods for finding transition states after the use of interpolation methods. Results for 24 different small to medium sized chemical reactions covering a wide range of structural types demonstrate that the improved dimer method is an efficient and reliable alternative saddle point search algorithm on medium sized to large systems and is often even able to find transition states when partitioned rational function optimization methods fail to converge.

Depending how tight the convergence criterion is chosen the improved dimer method requires about 1.10 to 1.45 more cycles to converge to a saddle point than a P-RFO algorithm using a Hessian updating scheme. As a result of the better scaling with system size, the improved dimer method is recommended relative to the P-RFO method for systems with more than 1.5 × X atoms (1.2 × X atoms for a loose convergence criterion), where the Hessian matrix is calculated in the P-RFO method every X cycle. A mode-following algorithm based on the P-RFO can fail to find the right transition state if the reaction coordinate does not correspond to the eigenvector with the lowest eigenvalue. Under similar circumstances, the improved dimer method converges to the correct transition state, provided a good initial guess for the path tangent is available.

[1] Peters, B., Heyden, A., Bell, A. T., Chakraborty, A., J. Chem. Phys., 120, 7877 (2004).

[2] Heyden, A., Bell, A. T., Keil, F. J., J. Chem. Phys., submitted.