Efficient transition state searches

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The localization of transition state (TS) structures is one of the most challenging tasks for any computational chemist: given that the energy at the TS determines the reaction barrier and hence the reaction rate, the localization of the TS structures is often the most critical task within a (bio)chemical study. Moreover, one should always verify that any TS-candidate has one imaginary frequency, which should correspond to the reaction under study. For this, one needs to compute the Hessian matrix with second derivatives of the energy with respect to atomic displacements, which can be a time-consuming exercise.

One of us has in the past[1,2] proposed the use of a model Hessian for the initial guess of the curvature, which has proven to be very successful in recent studies.[3-10] As a result, one can avoid the calculation of the Hessian matrix initially, but one still needs to do so at the end, to verify the correctness of the curvature at the TS (*i.e. the number of imaginary frequencies*). Here we report a further enhancement,[11] through which we avoid the calculation of the Hessian matrix altogether, but nevertheless still obtain the information needed for the characterization of the TS being indeed a TS.

The new methodology is checked both for the Baker-Chan set with 25 transition states,[12] for a number of Diels-Alder reactions of different size,[11] and some other typical examples.

References

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