Finding Minima, Transition States, and Conical Intersections: the Development of a Geometry Optimiser for Atomistic Simulation Codes

Geometry optimisation is a major task in atomistic simulations of materials, chemical systems, and biological matter. Several types of optimisation are possible depending on the feature of the energy surface that needs to be located. Minima of the energy surface refer to structures the system is most likely to adopt. A transition state (first-order saddle point on the energy surface) is the average crossing point in a transition from one minimum to another, which occurs for example during a chemical reaction. A conical intersection is a geometrical region where two electronic states are degenerate (that is, they have the same energy). The lowest energy point of conical intersection is the most likely geometry for a radiationless transition to occur between the two states.

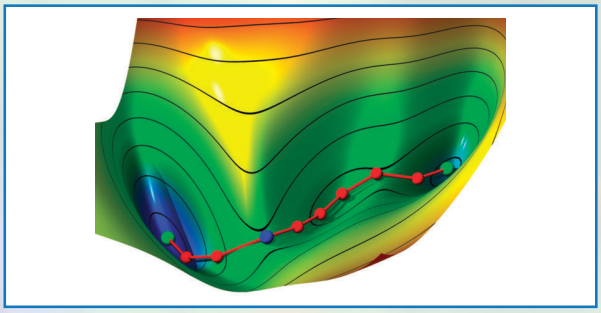

Figure 1: Converged nudged-elastic band path on an example surface (Müller-Brown potential). The green spheres indicate minima, the blue sphere the climbing image which converged to the transition state.

We have designed and implemented a novel geometry optimiser, DL-FIND, which provides several algorithms for finding minima and conical intersections. Its main strength, however, are the transition state optimisation routines. Besides the standard P-RFO method, the nudged-elastic band and the dimer method are implemented. The modular design of DL-FIND separates the handling of the coordinate system and the optimisation algorithm. This facilitates new combinations of optimisation techniques, such as using the dimer method with second-order optimisers (see below).

The code is included in the CSED software packages ChemShell and GAMESS-UK. It is designed to present a well-defined minimal interface to the calling code, which should facilitate its inclusion into other codes as well.

Coordinate Systems

DL-FIND geometry optimisations can be carried out in Cartesian coordinates, mass-weighted Cartesian coordinates, redundant internal coordinates, and hybrid delocalised internal coordinates (HDLC). HDLC coordinates are less coupled than Cartesians but still scale linearly with system size. Internal constraints (bond lengths, angles, and dihedrals) can also be applied in internal coordinates.

The coordinate transformation can be extended to a combination of multiple images of the system, which is required for transition state optimisations using the nudged-elastic band and dimer methods.

Nudged-Elastic Band Method

NEB connects two energy minima with a chain of images of the system connected by springs. The spring forces are modified so that when converged, the images are aligned along the minimum-energy path between the minima. One image can be defined as the climbing image: it does not experience spring forces, but its energy is maximised along the NEB path while minimised in all other directions. Thus, it converges to a transition state. NEB with a climbing image is implemented in DL-FIND. It can be combined with any of the optimisation algorithms mentioned below. Particularly promising is the combination with the L-BFGS algorithm, which leads to super-linear convergence.

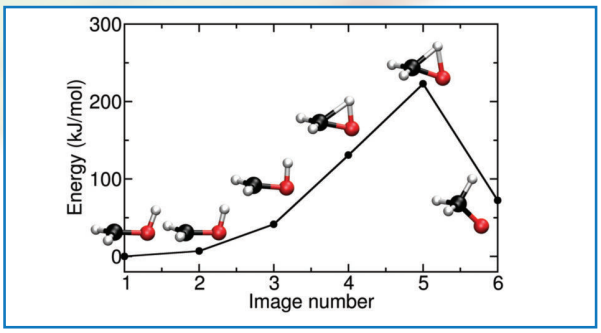

Figure 2: Energy and geometries of a nudged-elastic band path of a simple chemical system.

Dimer Method

The dimer method can be used to find transition states without calculating the Hessian (the second derivatives of the energy). It considers two images of the system separated by a constant distance in configuration space (i.e. by a constant root mean square distance). The problem of finding a transition state is converted into two minimisation problems.

First, the dimer rotation is optimised: the dimer is rotated around its midpoint until (1) the sum of the energies of the dimer endpoints is minimised, or (2) the curvature of the energy surface along the dimer axis is minimised, or (3) the dimer is aligned along the eigenvector of the Hessian with the lowest eigenvalue (the softest vibrational mode), or (4) the rotational force – the projection of the forces on the dimer endpoints onto the dimer normal – vanishes. All four criteria are equivalent. In practice, the rotational force is minimised.

With the dimer aligned along the softest mode, the transition state can be found by minimising the energy perpendicular to the dimer axis and maximising the energy along the dimer axis, similar to the climbing image in NEB. Dimer rotation and translation are optimised iteratively. However, in practice only a few rotational iterations are necessary after the initial optimisation of the dimer direction.

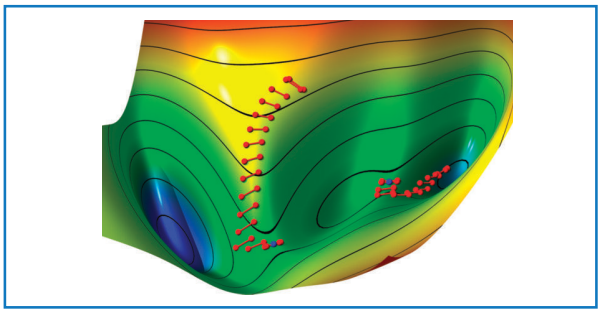

Figure 3: Trajectories of two transition-state searches using the dimer method. The dimer midpoint converges to the transition state (blue sphere).

Optimisation Algorithms

Once the coordinate transformation is defined (including the definition of the NEB and dimer systems if applicable), the optimiser can be used with any type of system. Atoms, internal degrees of freedom, or simply 2-dimensional functions (as in Figures 1 and 3) can all be optimised. The standard minimisation algorithms implemented in DL-FIND include steepest descent, conjugate gradient, Newton-Raphson, Broyden-Fletcher-Goldfarb-Shanno (BFGS), and the limited-memory version of BFGS (L-BFGS). The L-BFGS method is particularly useful for minimisation problems, as it is a second-order optimiser but scales linearly in terms of CPU time and memory requirement.

To search for a transition state by traditional algorithms (i.e. other than the NEB or dimer methods), we have implemented the partitioned-rational function optimisation (P-RFO) algorithm. It turned out to be superior to the dimer method for the most part only in cases where an initial analytic Hessian is available.

Conical intersections may be located and minimised by a penalty function method, a gradient-projection method, and a Lagrange-Newton method.

DL-FIND is currently included in GAMESS-UK and ChemShell. To encourage external contributions, the source code is available under an open source license at http://ccpforge.cse.rl.ac.uk/projects/dl-find.

Outlook

DL-FIND was designed and written with the philosophy that efficient optimisations can best be achieved by a flexible code that makes the implementation of new algorithms easy. A highly specialised code may run faster, but at the cost of making it more difficult to include new functionality. DL-FIND will enable us to locate minima, transition states and conical intersections more efficiently and thus in larger systems than previously envisaged.

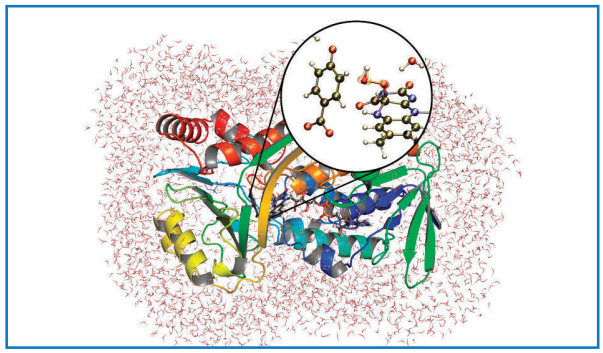

Figure 4: The dimer method applied to a biological system (the enzyme PHBH) in HDLC coordinates. The resulting transition mode is indicated by the transparent spheres in the insert.

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