

Improved Multi-Objective Particle Swarm Optimisation for Molecular Transition State Search

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Abstract

1. Extended Abstract

A significant challenge in computational chemistry is the efficient and accurate identification of molecular Transitions States (TS). Knowledge of the TS of a reaction is required to understand chemical reactivity, reaction rates, and mechanisms for catalysed reactions. This paper looks at TS in the context of isomerisation, the process of a chemical compound transitioning from one stable conformation, or isomer, to another with identical atoms but different physical and chemical properties. Every isomer corresponds to a local minimum of the Potential Energy Landscape (PEL). The process of isomerisation can then be described as a movement along the lowest energy path from a reactant local minimum via the transition state to a product local minimum. The distance between minima is commonly expressed by a scalar value aggregating the changes between the two isomers. A common definition is the root mean square deviation (RMSD), defined as

$$RMSD(\vec{x}, \vec{y}) = \sqrt{\frac{1}{N_{atoms}} \sum_{i=1}^N |\vec{x}_i - \vec{y}_i|^2} \quad (1)$$

for corresponding sets of atoms \vec{x} and \vec{y} of size N_{atoms} and assuming Cartesian coordinates.

A variety of deterministic TS finding methods exist but no general solution for this problem is available yet. Comprehensive overviews of existing methods can be found

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in Del Campo and Köster [1], Schlegel [2] and Fournier et al [3]. A non-deterministic approach using a group of “climbers” was developed by Fournier et al [3]. Recently, Hettenhausen et al [4] presented a new formulation of this problem as a multi-objective optimisation problem of the form:

$$a^2 + b^2 = c^2 \text{math error with the stylesheet, have to redo this equation.} \quad (2)$$

This is based on part-wise treatment of the reaction path as a Pareto-front for each section between a minimum and a TS. While in principal this allows for the use of any metaheuristic to solve the problem, in practice a number of difficulties have to be addressed for a solver to be efficient. In particular, using a scalar measure for distance and the unpredictable nature of the energy landscape for solutions not close to the minimum energy path pose significant challenges. However, knowledge of the reactant and the gradient for each conformation is available to the algorithm and can aid the search process.

An implementation of a MOPSO algorithm based on these principles was presented by Hettenhausen et al [4]. The proposed modifications include a Monte-Carlo style initialisation procedure around the known reactant, velocity clamping to limit the step size, and use of a simple corrective vector based on the gradient component to improve proximity to the Pareto-front. While demonstrating that the algorithm was reasonably successful at finding solutions close to the transition state, the prototype struggled with the convex part of the minimum energy pathway and identification of the best candidate for the transition state from the Pareto-optimal set.

Several extensions to this algorithm have improved its stability and effectiveness. Most significantly, an adaptive velocity component is presented that dynamically adjusts the corrective vector of the velocity using a tangential component, the gradient, and a forward corrective component to the gradient. These adaptations allow the swarm to more closely adhere to the Pareto-front, particularly while progressing along the convex sections, without losing forward momentum. This results in more accurate and stable progression towards the TS. In addition, improvements to the identification of candidate TS are discussed.

The performance is evaluated on a series of small molecules and comparison made with other TS search methods. The results show that the MOPSO-based approach is quickly becoming competitive with other methods.

References

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