Strong and Weak Coordinates within the Context of the Multi-Coordinate Driven Algorithm

Chin Hui Yu
Department of Chemistry, National Tsing Hua University, 30013 Taiwan

The multi-coordinate driven (MCD) algorithm [1] is the application of a simple gradient search algorithm to a reaction path problem. A central part of the MCD algorithm is the differentiation between driving and driven geometry coordinates. Driving coordinates are used to expand the energy of the system in a Taylor series at any given point of the reaction path. The MCD algorithm picks the next step into the direction of the slowest ascent or steepest decent based on the conditions. The driven coordinates, which are the majority, are optimized as usual within the molecular framework as defined by the driving ones. The MCD algorithm follows a minimum work path on the potential energy surface of the system. The choice of the reaction pathway to be explored is determined by the selection of the driving coordinates. Therefore, the MCD algorithm can be used to search for unknown products and transition states starting form a minimum energy structure while keeping the computationally expensive Hessian matrix at a minimum size.

Problems arise when weak and strong coordinates are mixed in the set of driving coordinates. Weak coordinates have small gradients and small force constants. The energy penalties for changes in weak coordinates are low during the energetic climb phase of the search. As the MCD search algorithm follows the path of the smallest energy increase, weak coordinates tend to dominate the energetic uphill search. For example, one of the driving coordinates can lead to a change of the molecular conformation away from the investigated reaction path and ultimately to unphysical jumps in the energetic profile of the system. Several methods, such as dynamic step size control, harmonic and anharmonic corrections to the energy prediction, external optimization steps, and on the fly path analysis are applied to resolve this problem. The application of the aforementioned methods to chemical reactions are investigated, too. It is discovered that the handling of three groups of coordinates instead of the driving and driven two originally defined in the MCD algorithm greatly simplifies the application of the MCD algorithm to chemical reactions.

[1] Berente; G. Náray-Szabó J. Chem. Phys. A 113 (2006) 772.