Zbl 0888.92042

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Theoretical implications involved in the DDRP method. (English)

J. Math. Chem. 17, No.4, 377-393 (1995).
http://dx.doi.org/10.1007/BF01165756
http://www.springerlink.com/openurl.asp?genre=journalissn=0259-9791

Summary: The aim of this paper is to prove that safe success in finding reaction paths (RPs) can only be expected from global path-determining methods. Some extensions of the mathematical arguments leading to the introduction of the DDRP (dynamically defined reaction path) method have been sketched. Four cases involving relaxation of analyticity, variability of the gradient field, minimum energy (reaction) paths (MEPs) and "golf pocket holes" on the potential energy surface (PES), and the rather strange consequences of the main theorem of the DDRP method giving a rigorous mathematical basis to chemical intuition in reaction kinetics have been discussed.
The discussions show that the DDRP method – when changing the conditions and parameters – may, in essence, involve all other global methods. It has been shown that the DDRP method works in a stable way even for non-analytic though smooth energy functions; moreover, the gradient field can be replaced by other vector fields resulting in better convergence to the reaction path. As a by-product, the question of the existence of MEPs can safely be handled and golf pocket holes are constructed on the PES in order to prove that local methods have chance to search faithfully the RPs in complicated systems only if the energy function can be restored from its arbitrarily small pieces.

Keywords : dynamically defined reaction paths; intrinsic reaction coordinate; minimum energy paths; golf pocket holes
Classification :
∗92E20 Chemical flows, reactions, etc.
92E99 Appl. of mathematics to chemistry