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BOOK OF ABSTRACTS

Reaction Paths Defined by Global Variational Principles

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Various time-independent reaction path (RP) concepts defined in terms of the Born-Oppenheimer approximation of the energy function have been discussed. Approximate RPs considered as stationary curves obeying to some global variational principles have been introduced and shown that they are more suited for numerical calculations than the classical concepts of Fukui's intrinsic reaction coordinate (IRC) or the minimum energy RP (MEP) defined by local differential properties. The theoretical backgrounds of the various RP concepts have been conferred critically. Though the RPs given by the Olender-Elber minimization[1] do not coincide with MEPs generally, they can provide a better approximation for the conformations of species in a reaction than the usual classical concepts, whenever tunnelling effects are to be considered. Therefore, a mathematically corrected version (given in this paper) of Olender-Elber's steepest descent concept can be a more faithful approximation for tunnelled RPs (e.g. that of H_3) than those based on the classical RP concepts. Our result can also be a starting point to investigations for revising the role and importance of the saddle point in the theory of RP concepts.

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1. R. Olender and R. Elber, J. Mol. Struct. (Theochem) 398-399 (1997) 63.

Key words: Reaction path, IRC, MEP, steepest descent path, Olender-Elber method

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