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REACTION PATHS IN LARGER CHEMICAL SYSTEMS BY THE DDRP-2 METHOD

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Fukui's IRC was originally defined as the union of the steepest descent paths from the transition state to the reactant and product minima. Even in systems of small molecules more than one chemical reactions can take place therefore also bifurcations and multiple branchings of reaction paths may occur. This may lead, on the potential energy hypersurface, to a complicated network of minima and saddle points the accurate exploration of which encounters great difficulties both for computational (e.g. convergence problems of mainly the quantum chemical program used) and for financial (extraordinarily high computational expenditures) reasons. This is why the local (direct) path- following methods to date have been advantages and preferences over the global (indirect) methods. The latter methods may still have enough grounds of using them because in exploring the network mentioned above and the connecting points and couplings of the branches of various ramifying reaction steps one cannot expect success from other than global methods. Another aspect is the stability of the actual path-following method. Even in this respect the global methods generally are superior to local ones. The global DDRP-2 method* fulfils these requirements, therefore, to show its effectiveness, it has been applied to a far-reaching investigation of the $CH_3 + O_2$ system being important from both in theoretical and practical views and giving rise to doubts when exploring it by a local method**. The oxidation mechanism of the CH_3 radical involves two competing reactions among others:

$$CH_3 + O_2 \longrightarrow CH_2O + OH \ ,$$
$$CH_3 + O_2 \longrightarrow CH_3O + O \ .$$

Both reaction branches have been studied and the variations in internal coordinates along the reaction paths clearly show the characteristic changes of the molecular systems between the stationary points. The investigations of further reaction branches of the same system have been in progress.

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* L. L. Stachó, Gy. Dömötör, M. I. Bán, Sz. Szakacsits, *Parallelization strategies and experiences with the path- following method DDRP-2* (Poster in this Congress); **DDRP-2:** a QCPE program, to be published in 1996.

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SCRUTINIES OF SIMPLE CHEMICAL REACTIONS BY THE PATH-FOLLOWING METHOD DDRP-2

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Standardized coordinates have been obtained by projecting the coordinates of atoms n the configuration space onto a submanyfold the members of which have already been n a locally one-to- one correspondence with the internal coordinates. Simple chemical systems and elementary steps of chemical reactions of molecules have been treated by a new version* of the Dynamically Defined Reaction Path method** and bifurcation-free reaction paths/intrinsic reaction coordinates (IRCs) between reactants and products have been nvestigated thoroughly using coordinates with and without standardization. As to our experiences, the calculations can highly be facilitated by help of standardized coordinates and it is expected that in this case less convergence problems will occur. An important difference is that by using standardized coordinates not the real IRC but a pseudo reaction path (PRP) can be obtained, nevertheless, the internal coordinates of both the IRC and the PRP of the same system will be the same. Comparisons of the evolutions of molecular geometries along the IRC and the PRP show exact analogies because of the translational and rotational invariances of the energy of the system. From the investigations it can be concluded that the variation of the geometry during the reaction is more important than the exact course of the reaction investigated.

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* L.L. Stachó, Gy. Dömötör, M. I. Bán, Sz. Szakacsits, *Parallelization strategies and experiences with the path-following method DDRP-2* (Poster in this Congress) and **DDRP-2**: a QCPE program, to be published in 1996.

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PARALLELIZATION STRATEGIES AND EXPERIENCES WITH THE PATH-FOLLOWING METHOD DDRP-2

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Fukui type reaction paths (IRCs) have been determined by a new version* of the global path-following Dynamically Defined Reaction Path method** by moving the points of an initial curve, given arbitrarily in the configuration space between reactants and products, along the negative gradient with respect to mass weighted coordinates, in the Born-Oppenheimer approximation. The shifted images of each point of the initial curve are calculated independently from the images of other initial points. The image curves are obtained from the constructed set of image points by a homogenization procedure. This method is preferably suitable in calculating the images of the points of the approximation curves representing the reaction path/IRC in an entirely parallel way. In practice, the available quantum chemical methods cannot calculate the energy function, from any initial data, in a conveniently short time. Therefore complete parallelization can only be carried out by vector computers with huge memories. We adopt the following techniques to treat this difficulty with smaller machines of limited parallelizability. First we determine suitable initial data at the endpoints and store the essential parameters (e.g. density matrices) to construct suitable initial data for calculating the energy at points lying near to them. The density matrix obtained by the initial curve represented by dense points is stored and the further approximate curves are calculated by the aid of this density matrix. This idea leads to various parallel storage and homogenization strategies modifying the original DDRP methods. We investigate them both theoretically and by computer experiments on the chemical reactions between small molecules. For this purpose we used a configuration of an eight node SP1 machine with three IBM RS/6000 RISCs under PVM. For the energy calculations we applied a version in C language of the MNDO program whose portability for the widely used UNIX machines seems to be superior to the classical FORTRAN realization. The used strategies will expectedly be applicable to other global methods approximating the IRC transversely.

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* L. L. Stachó, Gy. Dömötör, M. I. Bán, Sz. Szakacsits, **DDRP-2**: QCPE program, to be published in 1996.

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