

Momentum space investigation of C_{2v} dissociation of water

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MS received 25 November 1992; revised 22 January 1993

Abstract. The momentum space perspective of a typical dissociative reaction viz. that of H_2O along a C_{2v} constrained path is brought out. The tool for the investigation of such a reaction path is provided by the distinctive topography of molecular electron momentum densities (EMD's). The EMD as well as Laplacian of EMD at $\mathbf{p} = \mathbf{0}$ are seen to follow the reaction path. The most important outcome of this work is that the information around $\mathbf{p} = \mathbf{0}$ seems to be sufficient for the momentum space follow-up of a chemical reaction. Qualitative features of the EMD topography for this reaction seem to remain unaffected by the choice of basis-set beyond double-zeta quality. The inclusion of correlation has seemingly no major effects on the qualitative nature of molecular EMD topographies.

Keywords. Chemical reaction; momentum space; topography; critical points; electron momentum density.

1. Introduction

Theoretical analysis of a chemical reaction is made possible by a study of the corresponding potential energy surfaces. The reaction paths on this surface are formed by numerous molecular structures which could be utilized for monitoring the progress of the reaction under study. Apart from the conventional methods which employ the total electronic energy for such an investigation, yet another powerful way is offered by the topographical analysis of electron density along the reaction path as proposed by Bader and coworkers (Bader *et al* 1979; Bader 1990, 1991). In this catastrophe theory-based approach, critical points (CPs) of electron density are isolated and characterized for various molecular structures. The CPs of a three-dimensional scalar field f are defined as those points \mathbf{p} where $\nabla f|_{\mathbf{p}} = 0$. A CP is termed as non-degenerate one if all the eigenvalues of the Hessian,

$$\left. \frac{\partial^2 f}{\partial x_i \partial x_j} \right|_{\mathbf{p}}$$

at the CP are non-zero. The non-degenerate CPs in this case are: (3, + 3), a minimum; (3, - 3) a maximum and (3, - 1) as well as (3, + 1) saddles[†]. Bader *et al* (1979) reported an investigation along a C_{2v} dissociative path of the water molecule using electron density as a tool. Catastrophes (instabilities) of two kinds (viz. fold and conflict) were

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[†] The notation (R, σ) represents rank of the Hessian matrix, R and excess of positive eigenvalues over the negative ones of the Hessian matrix by σ .

observed by them. For instance, the coalescence of a bond CP (of type (3, - 1)) with a ring CP (of type (3, + 1)) gives rise to a fold-type catastrophe (Tal *et al* 1981). Catastrophe theory-based studies have been reported (Bader *et al* 1979; Tal *et al* 1981) for some isomerization- and dissociation-type reactions to establish a connection between the change of molecular structure and the observed catastrophe points. Yet another approach in terms of change in bond orders to monitor chemical reactions has been proposed and tested for isomerization as well as dissociation of H-N-O (Maity and Bhattacharya 1990). The inflection point on the plot of bond-order against the bond angle has been correlated to the transition state in the isomerization of H-N-O. This approach, in addition to probing the chemical reaction, gives a better view of bond reorganization along the reaction path. It may be pointed out, however, that the bond-order being a theoretically defined quantity, is not directly amenable to experimental investigations. The latter, on the other hand, are possible for the electron densities in the complementary spaces.

The electron density in the complementary space, viz., the electron momentum density (EMD) is defined as:

$$\gamma(\mathbf{p}) = N \int |\phi(\mathbf{p}, \mathbf{p}_2, \dots, \mathbf{p}_N)|^2 d^3 p_2 \cdots d^3 p_N \quad (1)$$

with $\phi(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)$ being a $3N$ -dimensional Fourier-Dirac transform of the position space N -electron wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$. The EMD can be measured experimentally via the X-ray/ γ -ray scattering, positron annihilation as well as ($e, 2e$) technique (Williams 1977; Moore *et al* 1982). The pioneering work by Coulson and coworkers (Coulson 1941; Coulson and Duncanson 1941) has been followed by several others (Epstein 1970, 1975; Thakkar *et al* 1984; Westgate *et al* 1985; Tanner 1988). However, detailed topographical analyses of molecular EMD's have been conspicuously absent in the literature. Gadre and coworkers have recently brought out the symmetry and topographical aspects of molecular EMD's (Gadre *et al* 1991; Kulkarni *et al* 1992).

The noteworthy aspects of the topographical studies (Kulkarni *et al* 1992) is that the origin in momentum space viz. $\mathbf{p} = \mathbf{0}$ is necessarily a critical point, independent of the choice of the molecule as well as the nuclear coordinates. Due to the reciprocity between the position and momentum space wavefunctions, the 'valence region' pertains to the information centred around $\mathbf{p} = \mathbf{0}$ (Epstein and Tanner 1977). Another novel feature brought out by these studies (Kulkarni *et al* 1992) is: a typical hierarchical structure in the EMD topography is governed solely by the criticality at $\mathbf{p} = \mathbf{0}$. The existence of a minimum at $\mathbf{p} = \mathbf{0}$ allows exclusively CPs of (3, + 1), (3, - 1) and (3, - 3)-types away from the origin. Similarly, if EMD topology exhibits a (3, + 1) saddle at the origin, then at most CPs of (3, - 1) and (3, - 3) could be found at $\mathbf{p} \neq \mathbf{0}$; whereas for a (3, - 1) at $\mathbf{p} = \mathbf{0}$, EMD topology may show (3, - 3) CPs elsewhere. A (3, - 3) CP at $\mathbf{p} = \mathbf{0}$ rules out the existence of any other CP in the EMD topology. Also, the type of criticality observed at $\mathbf{p} = \mathbf{0}$ never makes an appearance elsewhere in the EMD topology.

The purpose of the present work is to investigate the possibility of use of the distinctive topography of molecular EMD to probe chemical reactions. A C_{2v} dissociative path of water is taken up as a test case in the next section.

2. Momentum space picture of C_{2v} dissociation of H_2O

Bader and Gangi (1971) and Gangi and Bader (1971) studied a minimum energy C_{2v} dissociative path of H_2O separating it to $O(^1D)$ and $H_2(^1\Sigma_g^+)$. The electronic energy of this reaction path is monotone increasing (uphill), without encountering a transition state. This reaction path has also been studied by Bader *et al* (1979) using the topography of charge density. In the present study, we have investigated the EMD topography for this reaction using geometrical parameters reported by them (Bader *et al* 1979) and using $tz2p$ [(5s, 2p/3s, 2p) for H and (9s, 5p, 2d/5s, 3p, 2d) for O] and dzp basis-sets. The intermediate geometries are obtained by linear interpolation and the respective wavefunctions are generated using program INDMOL (Shirsat *et al* 1993). A FORTRAN program was developed using analytical expressions for EMD as well as its first and second derivatives at any point, \mathbf{p} . The geometrical as well as topographical parameters and the corresponding energies of this reaction presented in table 1 show that at the equilibrium geometry, EMD topology exhibits a minimum at $\mathbf{p} = \mathbf{0}$ (for both dzp and $tz2p$ bases). This typical feature of criticality is retained (we refer to the $tz2p$ basis in the following discussion and atomic units are used throughout) until the two hydrogens are brought close to each other and are separated from the oxygen i.e. for $R_H = 1.98$ and $R_{MO} = 2.525$. A first changeover in the critical structure of EMD (exhibiting (3, +1) CP at $\mathbf{p} = \mathbf{0}$) takes place in the region of $1.99 > R_H > 1.98$ and $2.525 > R_{MO} > 2.5125$. This criticality is retained over a small finite region of the reaction path. Yet another changeover in the nature of CP at $\mathbf{p} = \mathbf{0}$ is observed when $1.92 > R_H > 1.9$ and $2.625 > R_{MO} > 2.6$. The critical point smoothly changes over from

Table 1. Geometrical parameters^a on the C_{2v} dissociative path of water with eigenvalues and EMD value at $\mathbf{p} = \mathbf{0}$ using $tz2p$ and dzp basis-sets (all values in a.u.).

(R_H, R_{MO})	Basis	Energy	Eigenvalues at $\mathbf{p} = \mathbf{0}$			$\gamma(\mathbf{0})$
			λ_1	λ_2	λ_3	
(2.88, 1.11)	$tz2p$	-76.057	2.61	2.71	2.62	0.564
	dzp	-75.994	1.33	1.48	1.37	0.402
(2.16, 2.30)	$tz2p$	-75.872	0.72	4.25	2.04	0.856
	dzp	-75.821	-0.50	2.62	1.67	0.647
(2.10, 2.39)	$tz2p$	-75.859	0.42	4.14	1.44	0.904
	dzp	-75.809	-0.79	2.52	1.08	0.687
(2.00, 2.50)	$tz2p$	-75.848	0.07	3.84	0.69	0.960
	dzp	-75.800	-1.09	2.29	0.38	0.729
(1.98, 2.525)	$tz2p$	-75.846	-0.01	3.76	0.53	0.973
	dzp	-75.799	-1.16	2.23	0.22	0.739
(1.92, 2.60)	$tz2p$	-75.841	-0.25	3.49	0.07	1.010
	dzp	-75.795	-1.35	2.03	-0.22	0.766
(1.90, 2.625)	$tz2p$	-75.839	-0.32	3.34	-0.08	1.022
	dzp	-75.793	-1.41	1.95	-0.36	0.775
(1.80, 2.75)	$tz2p$	-75.834	-0.67	2.85	-0.72	1.078
	dzp	-75.790	-1.66	1.56	-0.95	0.813

^a R_H corresponds to the distance between two hydrogen atoms whereas R_{MO} is the distance from the midpoint of H-H bond to the oxygen nucleus.

(3, + 1) type to (3, - 1) in this region. Thereafter, the nature of topography of EMD is retained until the dissociation of water. However, it should be noted that the actual regions on the reaction path spanned by both the basis-sets viz. $tz2p$ and dzp for (3, + 3), (3, + 1) and (3, - 1) criticalities at the origin are different (cf. table 1).

The most remarkable feature exhibited by the EMD is that its value at origin, viz. $\gamma(\mathbf{0})$, is monotonic increasing and so is the total electronic energy of the structures on this reaction path. Also, as pointed out in the earlier studies (Kulkarni and Gadre 1993a), the Laplacian of EMD at the origin is an indicator of the quality of the wavefunction. The positive Laplacian implies that there exist more charge in the valence region of wavefunction (in accordance with Fourier transform relation) and such wavefunctions are known to be of better quality (Ohno and Ishida 1985; Brion 1986). In a similar spirit, one can say that a molecular structure is relatively stable if it has high positive Laplacian of EMD at $\mathbf{p} = \mathbf{0}$. In this study, we employ Laplacian of the EMD as yet another parameter which can follow the reaction path and which is indicative of the stability of structure. From table 1, it is clear that water in its equilibrium geometry has the highest positive Laplacian and thereafter it decreases monotonically, i.e. it also follows the reaction path. That our results are almost independent of the choice of basis-set is clearly brought out by table 1 in which results corresponding to the dzp basis-set are also incorporated.

Bawagan *et al* (1987) have discussed in detail the effect of inclusion of correlation on the spherically averaged EMD of valence orbitals for water molecule and have compared it to that obtained from ($e, 2e$) technique. They suggested the use of correlated wavefunction for comparison with the experiment. The effect of inclusion of correlation on the qualitative nature of CP at $\mathbf{p} = \mathbf{0}$ is observed for H_2O and HF molecules in their ground-states equilibrium geometry using natural orbitals for these molecules with 6-31G basis reported by Luque *et al* (1991). The eigenvalues of CP at $\mathbf{p} = \mathbf{0}$ for H_2O and HF molecules are (1.08, 2.62, 1.86) and (0.38, 0.38, 1.23) respectively using the natural orbitals; whereas they are (1.93, 2.55, 2.22) and (0.87, 0.87, 1.33) using dz basis (Snyder and Basch 1972) with SCF calculations. It is observed that there is no qualitative change in the overall EMD topography of the molecular system although its eigenvalues change to some extent. It may be premature to make a generalized statement, but the trends are suggestive enough. Such changes in eigenvalues with the change in the basis-set or by addition of correlation are in fact expected. Moreover, it is well known that the one-electron densities have little effect on their values due to inclusion of correlation (Bader 1975). From the feature of EMD at equilibrium geometry, it is expected that there will be no major change in the topography of EMD even for other geometries on the C_{2v} dissociative path of water molecule.

3. Concluding remarks

The distinctive topography and the hierarchical structure of molecular EMD's discussed in section 1 has prompted us to carry out a systematic investigation of a reaction in momentum space viz. the C_{2v} dissociation of H_2O . For this purpose, the value of EMD at $\mathbf{p} = \mathbf{0}$ as well as the eigenvalues of the Hessian matrix (and its trace, viz. $\nabla^2\gamma(\mathbf{0})$) have been employed. It has been observed that $\gamma(\mathbf{0})$ as well as $\nabla^2\gamma(\mathbf{0})$ follow the path of a chemical reaction under investigation and such a behaviour of EMD is observed to be independent of choice of basis-set beyond dzp basis. This is

an interesting feature which warrants further detailed investigations before a generalization is made. The inclusion of correlation effects does not, in general, affect the qualitative critical structure of a molecular species when compared to one within Hartree-Fock theory.

That the information around $\mathbf{p} = \mathbf{0}$ suffices for a momentum space analysis of a chemical reaction is the most remarkable feature brought out by the present work. The region near $\mathbf{p} = \mathbf{0}$ indeed refers to the "valence region" which is of supreme importance in understanding chemical reactions. For a corresponding study in position space, a search for various bond-, ring- and cage-type critical points has to be carried out in three dimensions. In the momentum space, the information around a single point ($\mathbf{p} = \mathbf{0}$) could be used as a practical tool for probing chemical reactions. In order to generalize this, a study of some isomerization reactions such as HCN, CH_3CN , etc. wherein a transition state occurs on the reaction path has been taken up (Kulkarni and Gadre 1993b). Interestingly enough, the EMD and its Laplacian follow the path of the reaction in these cases also.

Acknowledgements

We thank Professor F Illas (Barcelona, Spain) for providing us with the natural orbitals for some molecules. We also thank the Centre for Development of Advanced Computing (C-DAC), Pune for financial assistance.

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