Proc. Indian Acad. Sci. (Chem. Sci.), Vol. 102, No. 2, April 1990, pp. 189–192.

Nonexistence of local maxima in molecular electrostatic potential maps

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MS received 11 January 1990

Abstract. It has been rigorously established by means of classical electrostatic arguments, that molecular electrostatic potential maps are devoid of local maxima. This forms a generalization of the earlier works of Politzer and co-workers which were restricted to the case of atoms.

Keywords. Electrostatic potential; electron density; molecular electrostatic potential maps; local maxima.

Molecular electrostatic potentials (MESP) have been widely employed for studies of structure and reactivity of organic, inorganic as well as biomolecules (Politzer and Truhlar 1981). However, rigorous results on MESP of general interest are rather rare in the literature: the only ones, so far, are due to Politzer and co-workers (Weinstein *et al* 1975; Sen and Politzer 1989). Weinstein *et al* (1975) proved the nonexistence of maxima in the electrostatic potential for one-centre, spherically symmetric (atomic) systems. This fact readily follows from the Poisson equation for such a system, as seen below. Define the atomic electrostatic potential, $V(r)$, (in Hartree units) as

$$V(r) = Z/r - \int d^3r' \rho(r') |\mathbf{r} - \mathbf{r}'|^{-1}, \tag{1}$$

where Z is the nuclear charge and $\rho(r)$, the single-particle, spherically symmetric electron density. The Poisson equation for this case yields (except at the nuclear sites)

$$V'' + 2V'/r = 4\pi\rho(r), \tag{2}$$

the prime denoting differentiation with respect to r. The necessary and sufficient conditions for the occurrence of a local maximum at r_0 in this case are given by $V'(r_0) = 0$ and $V''(r_0) < 0$, by virtue of which, $\rho(r_0)$ would turn out to be negative, leading to a contradiction (Weinstein *et al* 1975), since $\rho(r)$ is *always non-negative*. More recently, Sen and Politzer (1989) established that for a monoatomic negative ion, $V(r)$ indeed reaches a minimum at $r = r_m$ (say), such that the charge density outside a sphere centred at the nucleus with radius r_m integrates to the ionicity of the respective negative ion.

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A suitable generalization of the above results to arbitrary molecular systems is not immediately apparent owing to the complicated nature of the necessary and sufficient conditions for extrema in the calculus of several variables. In particular, *a set* of necessary conditions for the occurrence of local maxima suited to the problem at hand, is furnished by

$$V_x = V_y = V_z = 0$$

and

$$V_{xx} < 0, \quad V_{yy} < 0, \quad V_{zz} < 0; \tag{3}$$

at the (possible) local maximum. Here, the suffixes denote partial differentiation with respect to the corresponding Cartesian coordinates. These conditions, not usually encountered in the literature *in this form*, are obtained via a suitable Taylor-series expansion of V

$$\begin{aligned}\Delta V &= V(x, y, z) - V(x_0, y_0, z_0)\\ &= \sum_i V_i \Delta x_i + (1/2!) \sum_{i,j} V_{ij} \Delta x_i \Delta x_j + \cdots,\end{aligned} \tag{4}$$

where $\Delta x = x - x_0$, etc. and i and j run through x, y, z (thus x_1, x_2 and x_3 respectively denote x, y and z). Making a particular choice $\Delta x = \varepsilon \rightarrow 0$, $\Delta y = 0$, $\Delta z = 0$ etc. and noting that $\Delta V < 0$, one readily obtains the above mentioned conditions. It may be pointed out that the above requirements (3) are one of the possible sets of necessary conditions, and are by no means sufficient. (Incidentally, the sufficiency involves the eigenvalues of the Hessian matrix, in that *all* the eigenvalues should be strictly negative.) Now, let us apply these criteria for scrutinizing the MESP maps for possible local maxima. The MESP for a molecula case at $\mathbf{r}$, is defined as

$$V(\mathbf{r}) = \sum_A Z_A / |\mathbf{r} - \mathbf{R}_A| - \int \mathrm{d}^3 r' \rho(\mathbf{r}') / |\mathbf{r} - \mathbf{r}'|, \tag{5}$$

wherein Z_A and R_A denote the nuclear charges and locations, respectively, $\rho(\mathbf{r})$ being the electron density, not restricted to any particular symmetry. Invoking the Poisson equation for this case, leads to

$$\nabla^2 V(\mathbf{r}) = 4\pi\rho(\mathbf{r}) - \sum_A Z_A \delta(\mathbf{r} - \mathbf{R}_A). \tag{6}$$

If $\mathbf{r}$ coincides with one of the nuclear locations, $\mathbf{R}_B$, say, then the term involving $\mathbf{R}_B$ is to be dropped from the r.h.s. of (5) and (6). In view of the above set of conditions (3) for a possible appearance of a local maximum in $V(\mathbf{r})$, one must have $\nabla^2 V = V_{xx} + V_{yy} + V_{zz} < 0$. However, once again, the non-negativity of $\rho(\mathbf{r})$ rules out this possibility, vide (6), proving the general theorem of non-occurrence of strict local maxima for MESP maps.

While strict maxima are forbidden, minima as well as other types of critical points, e.g. saddle points, may make their appearance in the MESP plots. Several such instances are depicted in the MESP-maps in the literature (Politzer and Truhlar 1981). As an illustration of the above theorem, we present, in figure 1, variations of $V(\mathbf{r})$ along three mutually perpendicular directions, viz. the x, y and z axes, for the cyclopropane molecule (Synder and Basch 1972). A local *directional* maximum at the origin is clearly discernible as one sweeps along the z-axis. However, this is seen to

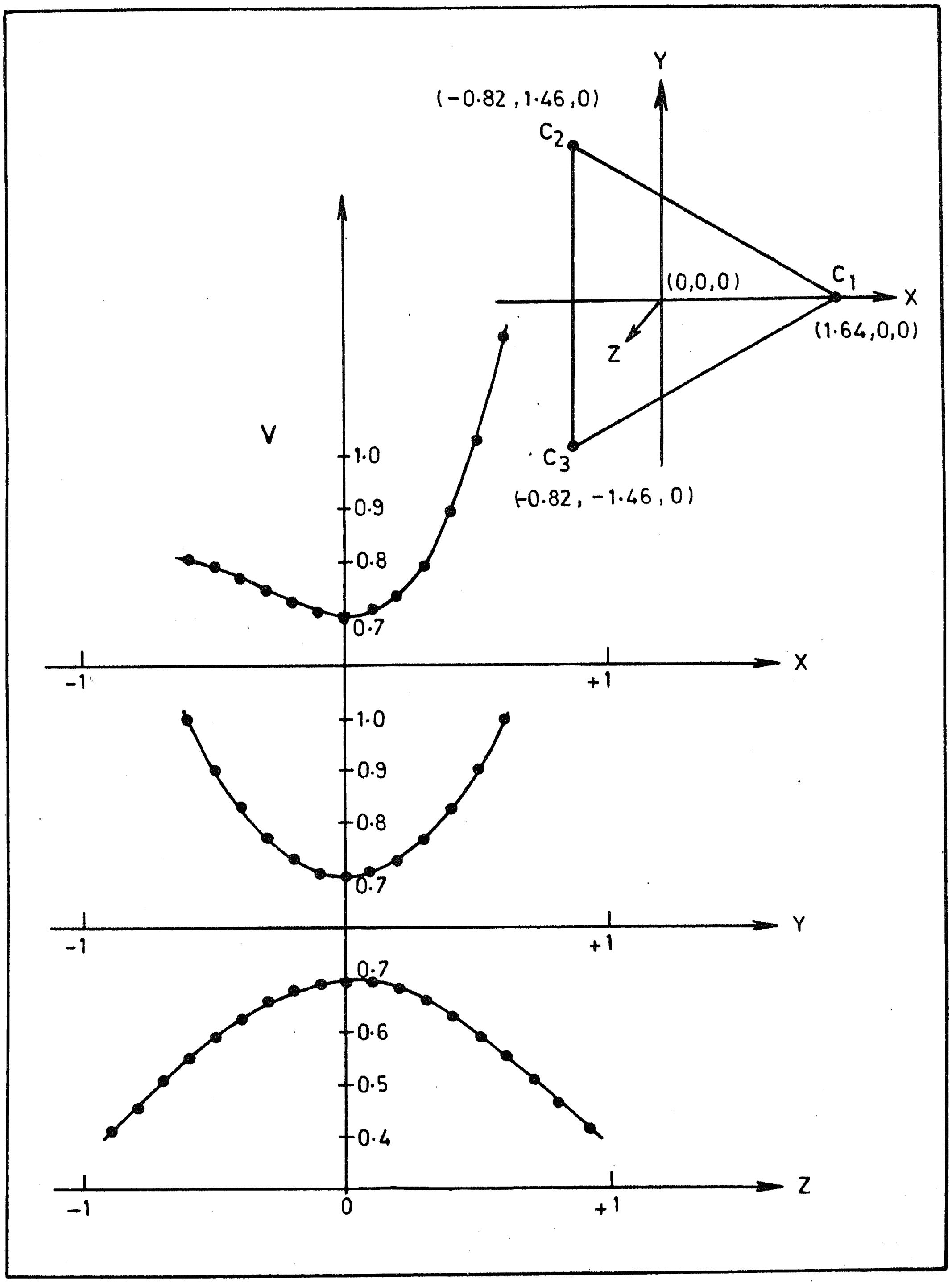

Figure 1. Variation of the molecular electrostatic potential for the cyclopropane molecule along the x, y and z axes. The reference co-ordinate frame along with the $C_1C_2C_3$ plane is also shown. (All values in Hartree a.u.)

be a local minimum along the concurrent perpendicular directions, viz. the x and y axes, thereby exhibiting a saddle point structure. It may further be remarked that the occurrence of relative minima renders MESP useful for prediction of electrophilic sites in molecules. On the other hand, the present study clearly brings out why these maps cannot be fruitfully employed for the prediction of favourable nucleophilic sites, since strict local maxima are totally absent.

It is thus gratifying to note that theorems of general validity for quantal systems are brought out through the application of classical electrostatic arguments to molecular electrostatic potentials.

Acknowledgements

The authors thank Mr. Sudhir Kulkarni and Ms. Indira Shrivastava for their computational assistance. SRG is grateful to the Department of Science and Technology and the Indian National Science Academy for financial support.

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