CHAPTER - V

Similarities in the Contour Maps of Molecular Electron Densities, Electrostatic Potentials and Bare Nuclear Potentials

* The material presented in this Chapter has partly been published as a research article:
Introduction

Recently there has been substantial interest [1-4] in the relationship between the distributions of molecular electron density, \( \rho(r) \) and bare nuclear potential, \( V \), where

\[
V(r) = - \sum_{i}^{\text{atoms}} \frac{Z_i}{r_i}
\]  

(5.1)

This aspect of the similarity between the scalar fields of \( V(r) \) and \( \rho(r) \) has been discussed earlier in chapter I section 1.8. Parr, Gadre and Bartolotti [1], while developing a local density functional model for atoms and molecules, have shown that within this model, the electron density \( \rho(r) \) emerges naturally as a point function of \( V \). It may be noted that for the spherically symmetric case of an atom the contours of \( \rho(r) \), \( V \) and electrostatic potential, \( V^* \) would be identical.

Within the local density functional theory [1], the contours of \( V \) are also contours of \( \rho(r) \) even in the molecular case. The similarity of these scalar function has been pictorially demonstrated [1,2] for the Hartree-Fock case for some molecules. Tal et al [3] studied the topological relationship between these two scalar fields of \( \rho(r) \) and \( V \) for molecular systems, and demonstrated through a detailed study that the structure diagrams for the ground state electron density \( \rho \) and the bare nuclear potential, \( V \) of the water molecule are homemorphic. They further conjectured that this homeomorphism exists for any molecular system.
Parr and Berk [4] further explored the hypothesis best represented by

$$\rho = \int (V)$$

which implies that the contours of molecular electron density $\rho$ and $V$ are identical in general. They pictorially demonstrated the similarity of contours of Hartree-Fock $\rho(r)$ and the corresponding $V$ for BeH, BH, $B_2H_6$ and water molecules, leading to the conjecture that the molecular $V$ acts as a 'harbinger' for the electron density. As a direct application of this observation they developed a variation treatment for the $H_2^+$ ion. For this purpose, they constructed a wavefunction which was a point function function of $V$, the bare nuclear potential alone. It is interesting to note that the total binding energy predicted by the model is typically 80% of the true binding energy. The corresponding wavefunction is also inferior to even a simple LCAO-MO wavefunction around the equilibrium internuclear separation. However, that such a function leads to binding at all is gratifying indeed.

More recently, Politzer and Zilles [5] have carefully examined the hypothesis that the electron density distribution in a molecule is qualitatively similar to the bare nuclear potential as suggested by the relation (5.2). They found that this hypothesis is in error in at least two cases, viz. oxirane and cubane molecules, though it holds good in a number of other cases. For the oxirane ring system the similarity between $\rho$ and $V$ breaks down in the central part.
of the ring (See Fig. V.6 and V.7). Electron density contours show a saddle point in this region, whereas the V does not. In the case of cubane molecule, the contours of \( \rho \) and V in the diagonal plane of the molecule differ markedly [5].

Politzer and Zilles [5] pointed out an intrinsic difference between \( \rho (r) \) and V for the molecular case, viz.

\[
\Delta V(r) = V_{\text{mol}}(r) - \sum_{\text{at}} V_{\text{at}}(r)
\]

is identically zero. However, the difference electron density \( \Delta \rho (r) = \rho_{\text{mol}}(r) - \sum_{\text{at}} \rho_{\text{at}}(r) \) is certainly non-zero, in general. Thus \( V_{\text{mol}}(r) \) would not reflect the effects associated with molecule formation. They also further conjectured failures in similarity between \( \rho (r) \) and V for small ring systems containing heteroatoms and for cage-systems.

In the following sections the validity of the hypothesis (5.2) will be explored for the case of the \( \text{H}_2 \) molecule employing a variety of wavefunctions. A companion scalar field of electron density is that of electrostatic potential. Prompted by the considerations in the Thomas-Fermi model and the recent work of Politzer and Zilles [5], the similarity between \( \rho \) and V* has also been investigated for homo- and heteronuclear ring systems.

V.2. Computational Details:

In the present work the Gaussian wavefunctions used were of double zeta quality, as tabulated by Synder and Basch [6]. For these wavefunctions the electron density \( \rho (r) \) is given by the expression
\[ \rho(\vec{r}) = \sum_{i=1}^{\text{occ.}} |\Phi_i|^2 n_i \]  

where \( \Phi_i \)'s are the molecular orbitals (MO) with occupancies of \( n_i \). These MO's when expanded in terms of the contraction coefficients and primitive Gaussian functions give:

\[ \rho(\vec{r}) = \sum_{i=1}^{\text{occ.}} \left\{ \sum_{j=1}^{N} \sum_{k=1}^{M} \sum_{l=1}^{P} C_{jk}^{\lambda} \eta_{jkl} \right\}^2 n_i \]  

Here \( N \) being the number of atoms constituting the molecule, \( M \) the total number of contractions per atom and \( P \) the number of primitive gaussians, \( \eta_{jkl} \) per contraction,

\[ \eta_{jkl}(r_A) = N_{jkl} X_\lambda^A Y_\mu^A Z_\nu^A e^{-\alpha_i r_A^2} \]

Here since molecules with the constituent atoms of the first row of the periodic table are considered, only s- and p-type gaussians have are involved and one has \( \lambda = \mu = \nu = 0 \) for the s-type and for the p-type \( \lambda = 1 \) for \( p_x \), \( \mu = 1 \) for \( p_y \) and \( \nu = 1 \) for the \( p_z \) function. Here \( r_A \) is the distance from the center \( A \) and the corresponding cartesian components of \( r_A \) are \( x_A, y_A \) and \( z_A \).

The electrostatic potential \( V^*(r) \) is expressed as:

\[ V^*(\vec{r}) = \int \frac{\rho(\vec{r}_1)}{|\vec{r}_1 - \vec{r}_2|} d\vec{r}_1 - \sum_{A=1}^{\text{atoms}} \frac{Z_A}{r_A} \]

which may be broken down to a sum of integrals over various atomic
orbitals. The various integrals are listed in Table V.1.A and V.1.B in compact form. As can be seen from the Table V.1.A and table V.1.B, the result of the integration is expressed in terms of the reduced form of the incomplete gamma function $F_0$ [7]. This function $F_0$ is related to the error function through the relation:

\[
F_0(t) = \frac{1}{\sqrt{t}} \int_{0}^{t} e^{-x^2} dx = \frac{1}{2} \sqrt{\frac{\pi}{t}} \text{erf}(\sqrt{t})
\]  

(5.7)

For ease and speed of computation the function $F_0$ was evaluated using a three term rational approximation to the error function [8] of the form given below:

\[
\text{erf}(x) = 1 - (a_1 u + a_2 u^2 + a_3 u^3) e^{-x^2} + \epsilon(x),
\]

\[
u = \frac{1}{1 + px}; \quad |\epsilon(x)| < 2.5 \times 10^{-5}
\]

(5.8)

where $p = 0.47047$, $a_1 = 0.3480242$, $a_2 = -0.958798$ and $a_3 = 0.7478556$

The first and second order derivatives of $F_0$ which appear as $F_1$ and $F_2$ in the evaluation of the electrostatic integrals involving p- and s-type orbital cross products are obtained by the formula

\[
F_{m+1}(t) = -\frac{d}{dt} F_m(t)
\]

(5.8a)

and may be evaluated using the recursion relation [7] :

\[
F_m(t) = \frac{1}{2m+1} \left\{ 2t F_{m+1}(t) + e^{-t} \right\}
\]

(5.9)
Table V.1.A

Table showing the expressions for the electrostatic potential over primitive Gaussians at different centers.

<table>
<thead>
<tr>
<th>Type</th>
<th>Expression $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$s^A s^B$</td>
<td>$2K F_0$</td>
</tr>
<tr>
<td>$s^A p^B_x$</td>
<td>$2K \left[ (x_2 - C_x)^2 F_1 + \frac{\alpha}{\alpha + \beta} (A_x - B_x) F_0 \right]$</td>
</tr>
<tr>
<td>$p^A_x s^B$</td>
<td>$2K \left[ (x_2 - C_x)^2 F_1 - \frac{\beta}{\alpha + \beta} (A_x - B_x) F_0 \right]$</td>
</tr>
<tr>
<td>$p^A_x p^A_x$</td>
<td>$K \left[ 2(\alpha - \beta)(A_x - B_x)(x_2 - C_x) - 1 \right] F_1/(\alpha + \beta) + 2(x_2 - C_x)^2 F_2 + \left[ 1 - 2 \frac{\alpha \beta}{(\alpha + \beta)} (A_x - B_x)^2 \right] F_0/(\alpha + \beta))$</td>
</tr>
<tr>
<td>$p^A_x p^A_y$</td>
<td>$2K \left[ (A_x + B_x)(x_2 - C_x) - (A_x - B_x)(y_2 - C_y) \right] F_1/(\alpha + \beta) - \frac{\alpha \beta}{(\alpha + \beta)} (A_x - B_x)(A_y - B_y) F_0 + (x_2 - C_x)(y_2 - C_y) F_2 \right]$</td>
</tr>
</tbody>
</table>

$^a$ Here $s^A$ and $p^A$ are $s$ and $p$ type Gaussians centered at point $A$ with coordinates $(A_x, A_y, A_z)$. The constant $K$ is given by:

$K = \frac{\pi}{(\alpha + \beta)} \exp \left( - \frac{\alpha \beta}{(\alpha + \beta)} \sum_{x,y,z} (A_x - B_x)^2 \right)$.

$C$ represents the center of the product of the gaussians centered at $A$ and $B$ with exponents $\alpha$ and $\beta$ respectively. The coordinates of point $C$ being given by $C_x = (\alpha A_x + \beta B_x)/(\alpha + \beta)$, and similarly for $C_y$ and $C_z$. The arguments of the function $F_0$ are

$F_0 \equiv F_0\left\{ (\alpha + \beta) \sum_{x,y,z} (x_2 - C_x)^2 \right\}$.
Table V.1.B

Table showing the expressions for the electrostatic potential over primitive Gaussians on the same center.

<table>
<thead>
<tr>
<th>Type</th>
<th>Expression^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>s^A_s^A</td>
<td>( \frac{2 \pi}{(\alpha + \beta)} F_0 )</td>
</tr>
<tr>
<td>s^A_p_x^A</td>
<td>( \frac{2}{(\alpha + \beta)} \left[ (x_2 - A_x) F_1 \right] )</td>
</tr>
<tr>
<td>p_x^A_p_x^A</td>
<td>( \frac{\Pi}{(\alpha + \beta)} \left[ F_0 / (\alpha + \beta) - F_1 / (\alpha + \beta) + 2(x_2 - A_x)^2 F_2 \right] )</td>
</tr>
<tr>
<td>p_x^A_p_y^A</td>
<td>( \frac{2 \pi}{(\alpha + \beta)} \left[ (x_2 - A_x) (y_2 - A_y) F_2 \right] )</td>
</tr>
</tbody>
</table>

^a The arguments of the function \( F_0 \) are similar to the ones where the gaussians are situated at different centers. (see Table V.1.A)
The contours of \( \rho(r) \) were obtained by employing a method based on interpolating polynomials, where continuous single valued functions \( f(x,z) \) with non infinite slope, for constant \( z \) are fit to a cubic polynomial. For a given set of ordered points \((x,z)\) for a contour, the multivalued function \( z(x) \) is resplined by alternately splining \( z(x) \) and \( x(z) \) and finally linearly interpolating between the generated points. The splining method is based on the method of Ahlberg et al. [9].

V.3 Similarity between \( \rho(r) \) and \( V(r) \); the case for the \( H_2 \) molecule

As mentioned earlier Parr and Berk [2] have explored the hypothesis that the contours of \( V(r) \) and \( \rho(r) \) appear similar in general. They pictorially demonstrated the similarity of the contours of Hartree-Fock \( \rho(r) \) and the corresponding \( V(r) \) for \( \text{BeH, BH, B}_2\text{H}_6 \) and \( \text{H}_2\text{O} \) molecules. In their [2] work on the \( \text{H}_2^+ \), they employed a wavefunction which is a point function of \( V(r) \) alone and is of the type

\[
\Psi(V, R) = \sum_{n=1}^{N} C_n L_n \frac{1}{\alpha V}
\]

where \( N \) is the number of basis functions and \( R \), the internuclear separation. Here, the bare nuclear potential is given by

\[
-\sqrt{V(r)} = \frac{1}{\gamma_A} + \frac{1}{\gamma_B}
\]
\( r_A \) and \( r_B \) being the distance of the point \( r \) from the nuclei \( A \) and \( B \), and

\[
L_n(x) = \frac{x^n}{n!} e^{-x/2}
\]  

(5.12)

The electron density generated from this wavefunction has contours identical, by construction, to those of the bare nuclear potential. The total binding energy computed with this limiting wavefunction (5.10) is predicted to within 80 percent of the experimental binding energy of the \( H_2^+ \) ion. It is noteworthy that this limiting wavefunction is slightly inferior to even a simple LCAO-MO wavefunction, around the equilibrium internuclear separation. In this section we shall examine the similarity among the contours of \( \Psi(r) \) and \( V(r) \) for the \( H_2 \) molecule using various wavefunctions.

The problem of comparison between the similarity of two scalar fields \( \phi \) and \( \eta \) is one of examining the validity of the relation

\[
\phi = f(\eta)
\]  

(5.13)

which implies that the contours of \( \phi \) and \( \eta \) are exactly identical. For the case of molecules the model relationship in (5.13) may not be true. If \( \phi \) is loosely related to \( \eta \) then in such a case what can be said about the similarity between the contours of \( \phi \) and \( \eta \)? A semi-quantitative method for testing the similarity between \( \phi \) and \( \eta \) for a homonuclear diatomic molecule as an example may be formulated as follows:

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1) For a molecule, consider, say the $x-y$ plane through the molecule in a cartesian frame.

2) Construct contours of $\phi$ and select one such contour. Locate the points $(x_i, z_i)$ on the contour.

3) Evaluate $\eta_i = (x_i, z_i)$ at all the points on the contour.

4) Calculate the quantity $\zeta$ for this contour, where

$$
\zeta = \frac{1}{N} \sqrt{\frac{1}{N} \sum_{i=1}^{N} (\eta_i - \overline{\eta})^2}
$$

(5.14)

$N$ is the number of points, and $\overline{\eta}$ is the average of all $\eta_i$.

5) Repeat steps (2) - (4) for all contours.

From (5.14) it may be noted that the quantity $\zeta$ will be rather small if the relation (5.13) is obeyed closely, and extremely large if (5.13) is poorly satisfied. In the present work the validity of the relation (5.13) has been tested by calculating the $\zeta$ values for the bare nuclear potential along the contours of $\rho(r)$ for contour values ranging from 0.025 to 0.4 a.u. The various wavefunctions employed are listed in Table V.2. It may be noted that these wavefunctions lead to strong binding of the $H_2$ molecule. Hence, it was felt worthwhile to incorporate in this study some models exhibiting weak binding. One such model (abbreviated as NTHA) employing the relation

$$
\rho = \rho_A + \rho_B
$$

(5.15)
Table V.2

A Table showing the binding energy and equilibrium internuclear distance in case of H₂ molecule for the various models used.

<table>
<thead>
<tr>
<th>Wavefunction</th>
<th>B.E. a</th>
<th>R  b</th>
<th>Other details</th>
</tr>
</thead>
</table>
| Hurley Floating VB [12]| 4.14   | 1.44 | $\psi=ls_c ls_d+ls_a ls_c$  
c and d inside the molecule at a distance $x=0.08$ from the nuclei |
| Weinbaum VB [11]      | 4.024  | 1.42 | $\psi=(ls_a ls_b+ls_a ls_b)+$  
$\lambda (ls_a ls_a+ls_b ls_b)$  
orbital exponent $\xi =1.193$  
and $\lambda =0.256$               |
| Coulson MO [10]       | 3.488  | 1.38 | $\psi = \varphi(1) \varphi(2)$  
$\varphi(y)=ls_a +ls_b; \xi =1.197$ |
| Kolos and Roothaan 50 term wavefunction⁷ | 4.7082 | 1.4009 |                                                                       |
| NIHA-I                | 0.2    | 1.38 | $\rho = \rho_A + \rho_B$                                |
| NIHA-II               | -      | 10   | $\rho = \rho_A + \rho_B$                                |

a Binding energy in eV.  
b Internuclear distance R in a.u.  
e The internuclear distance, R, was fixed at the equilibrium R for the MO function. See text for other details.  
where \( \rho_A \) and \( \rho_B \) are individual Hydrogen atom densities, is known to show weak binding. The NIHA model with the internuclear separation of 10 and 1.38 a.u. has also been scrutinized in the present work.

The contours of \( \rho(r) \) were generated for the five functions used, viz. the MO [10], the Weinbaum VB [11], Hurley floating VB [12], NIHA-I at an internuclear distance of 10 a.u. and NIHA-II at \( R = 1.38 \) a.u. corresponding to the internuclear distance in the MO model. Fig. V.1 shows the contours of \( \rho(r) \), for the values ranging from 0.025 to 0.3 a.u. to be symmetric around the nucleus B, for the NIHA-I model. Fig. V.2 displays the weak binding situation (binding energy 0.2 eV) within the NIHA-II model at \( R=1.38 \). Here, the inner contours are almost symmetric around the nucleus B with barely perceptible distortion due to polarization. The overlap region shows contours somewhat reminiscent of a bonding situation. On the other hand the contours for the relatively stronger binding MO function, depicted in Fig. V.3 show polarized contours for the inner region. Also, the outer contours (e.g., corresponding to \( \rho(r) \) values of 0.025 and 0.05 a.u.) are compressed along the bond axis. Fig. V.4 exhibits similar trends for the floating VB function except that the contours are more polarized since the orbital center has been displaced inwards from the nuclear positions.

Consider the NIHA-I model (\( R=10 \) a.u.). Due to the large internuclear separation, there is a negligible interaction between the atoms, leading to 'atomic like' contours for moderately large \( \rho(r) \) values. Now, from the expression (5.11) for \( V(r) \), one may see that
Fig. VI : The contours of electron density, $\rho(\mathbf{r})$, for the NIHA-I model ($R=10$ a.u.). Nucleus B is positioned at 5 a.u. on the X-axis. The values of $\rho(\mathbf{r})$ are marked for each contour. See text for further details.
Fig. V.2: The contours of electron density, $\rho(r)$, for the NIHA-II model ($r=1.383$ a.u.). Nucleus B is positioned at 0.693 a.u. on the $x$-axis. The values of $\rho(r)$ are marked for each contour. See text for further details.
Fig.V3 : Contours of $\rho(r)$ for the Coulson MO [10] model (R=1.383 a.u.) for one quadrant (see text for details) with the nucleus B at 0.693 q.u. on the X-axis.
the term $1/r_B$ dominates for lower values for $r_B$. Thus, $V(r)$ evaluated along the inner contours will be reasonably constant leading to low $\zeta$ values. The contours of low $\rho(r)$ value, e.g. 0.025 a.u. are still symmetric around the atomic nucleus. The $1/r_B$ term is practically constant over these contours, but their contribution from the $1/r_A$ term increases on tracing the contours towards the nucleus $A$, leading to higher $\zeta$ values. This accounts for the steadily decreasing $\zeta$ values with the increasing $\rho(r)$ values within the NIHA-I model, as may be noted from Table V.3. Now consider the NIHA-II model ($R=10$ a.u.), the contours for which are presented in Fig. V.2. The atomic like contours for this weak binding case exhibit rather small polarization effect. However, for these contours the contribution of $1/r_A$ term becomes significant due to the relatively small internuclear separation as compared to the one in the NIHA-I model. A similar argument holds for contours with $\rho(r)$ values of 0.025 and 0.05 a.u. as well. Thus, the $\zeta$ values for this model are expected to be higher than the corresponding ones within the NIHA-I.

The Coulson MO function is a case of relatively stronger binding (binding energy 3.5 eV). The electron density shows larger overlap and polarization effects. This attribute coupled with the significant contribution from $1/r_A$ term leads to relatively smaller $R$, causes $\zeta$ to take low values for the 'atomic like' region as compared to the NIHA models. Now consider the contours with $\rho(r)$ values of 0.025 and 0.05 a.u. for the MO case as an illustration. These contours are axially compressed as compared to the NIHA-II model, leading to higher $1/r_B$ contributions. As one proceeds towards the
overlap region along such contours, $V(r)$ becomes progressively higher. Thus the MO model is expected to yield higher $C$ values for such contours as compared to their NIHA counterparts. The Weinbaum VB function being energetically similar to the MO function, is expected to show a parallel trend. These predictions are clearly borne out by the values reported in Table V.2.

The floating VB function of Hurley [12] is rather different from the MO [10] and the VB [11] functions since here the orbitals are not anchored on the nuclei. The nucleus B is located at (0.72,0), as has been marked on Fig. V.4, with the contours displaced towards the overlap region. The atomic like contours are thus expected to lead to higher $C$ values: the outer contours also reflecting comparatively similar trends. This feature can readily seen from Table V.2.

Let us now examine the contours of $\rho(r)$ obtained from a highly accurate wavefunction such as the fifty term Kolos - Roothaan [13] wavefunction. For ease of manipulation, the natural expansion of this function has been used, as tabulated by Davidson and Jones [14]. The equilibrium separation being 1.4009 a.u. and the total energy $-1.17303$ Hartrees. The corresponding $C$ values are presented in Table V.3. The contours of $\rho(r)$ extracted from this wavefunction are depicted in Fig. V.5. From Table V.3 it is discernable that the $C$ value increases steadily as one goes towards regions of higher $\rho(r)$. These $C$ values are quite comparable to those from the floating VB function corresponding to the outer regions of low $\rho(r)$. Notably the inner regions show $C$ values resembling those corresponding to the MO function. Thus for the inner "atomic-like" region, a highly
Fig.V4: Contours of $\rho(r)$ for the Hurley VB [11] model with the orbital center displaced inwards from the nuclear center. The nucleus B is positioned at 0.72 a.u. on the X-axis.
Fig.W.5: Contours of $\rho(\mathbf{r})$ for the Natural expansion of the fifty term Kolos - Roothaan wavefunction ($R=1.4009$ a.u.).
Table V.3

A table showing the $\tau$ values$^a$ for the $\text{H}_2$ molecule within various models.

<table>
<thead>
<tr>
<th>Electron density contour value (a.u.)</th>
<th>0.025</th>
<th>0.05</th>
<th>0.10</th>
<th>0.15</th>
<th>0.2</th>
<th>0.25</th>
<th>0.3</th>
<th>0.35</th>
<th>0.4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hurley floating VB</td>
<td>0.0133</td>
<td>0.0317</td>
<td>0.0727</td>
<td>0.1236</td>
<td>0.1949</td>
<td>0.304</td>
<td>0.4149</td>
<td>0.7813</td>
<td>0.5465</td>
</tr>
<tr>
<td>Weinbaum floating VB</td>
<td>0.00483</td>
<td>0.00971</td>
<td>0.0292</td>
<td>0.059</td>
<td>0.1032</td>
<td>0.1314</td>
<td>0.1499</td>
<td>0.1279</td>
<td>0.1242</td>
</tr>
<tr>
<td>Coulson floating MO</td>
<td>0.00169</td>
<td>0.00942</td>
<td>0.0362</td>
<td>0.0971</td>
<td>0.1032</td>
<td>0.1556</td>
<td>0.1499</td>
<td>0.1486</td>
<td>0.1456</td>
</tr>
<tr>
<td>Non-Interacting Hydrogen Atoms model incorporating $\rho = \rho_A + \rho_B$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NIHA-I$^b$</td>
<td>0.00273</td>
<td>0.0200</td>
<td>0.0362</td>
<td>0.0856</td>
<td>0.04824</td>
<td>0.04824</td>
<td>0.1499</td>
<td>0.1486</td>
<td>0.1456</td>
</tr>
<tr>
<td>NIHA-II$^b$</td>
<td>0.0103</td>
<td>0.0059</td>
<td>0.00296</td>
<td>0.00097</td>
<td>0.000375</td>
<td>0.000115</td>
<td>0.000153</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$K$-$R^c$</td>
<td></td>
<td></td>
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<td></td>
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<td></td>
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</tr>
</tbody>
</table>

$^a$See equation (5.5) in text for details.

$^b$Non-Interacting Hydrogen Atoms model incorporating $\rho = \rho_A + \rho_B$

$^c$Employing the natural expansion of the fifty term Kolos and Roothaan wavefunction. See text for details.
correlated wavefunction is expected to deviate maximally from the relation (5.11) as is evident from the intense polarization of the contours depicted in Fig. V.5.

For wavefunctions which represent the binding situation very accurately, the \( C \) values are comparatively larger for contours corresponding to a high \( \rho(r) \) implying the very loose validity of the relation (5.13). A strong case against the relation (5.13) is the physical picture for the models incorporating \( \rho = f(V) \). Consider a diatomic molecule AB, in which the distance between the nuclei is fixed at the equilibrium separation, with the atomic nature of A and B retained. On application of relation (5.13), it is obvious that there is no charge build up in the internuclear region, whereas if the electrons were allowed to 'interact', as in a normal molecule, an increase in charge density in the internuclear region results. This seems to be the physical reason for the weak binding shown by the models incorporating the relation (5.2). The Thomas-Fermi theory, however, points towards a relation of the form, \( \rho = \rho(V^*) \) where \( V^* \) is the total molecular electrostatic potential. Though molecules are not stable within the realm of the Thomas-Fermi theory, such a relation prompted by this indeed seems intuitively attractive.

In the next section, we present some tests of the similarity of the scalar fields of \( V^* \), \( V \) and \( \rho \) for some molecular systems. We include here our studies on three membered ring systems prompted by the work of Politzer and Ziles [4].
V.4. Similarity among Bare Nuclear Potential, Electron Density and Electrostatic Potential: Some Three Membered Ring Systems

The geometries as well as double - zeta quality Gaussian wavefunctions of the molecules used as test cases in this section have been taken from the tabulations due to Snyder and Basch [6]. The contours of $\rho$, $V$, and $V^*$ were generated using a method to fit the function $F(x,y)$ to a cubic spline as outlined in section V.2. Some test checks were carried out on $\rho(r)$ and $V^*(r)$ for some molecules, by evaluating these quantities at the nuclear positions. At the nuclei, $V^*$ shows a local minimum whereas $\rho(r)$ has a local maximum. The values for $V^*$ are generally quite insensitive to the local environment of the atom. The $\rho(r)$ values at the nucleus however do differ by as much as 8 percent at different levels of approximations. Our values bear a good agreement with those reported by Politzer [15] and are displayed in table V.4.

As seen earlier, Politzer and Zilles [4] have discussed the case of oxirane in detail, in the light of the dissimilarities between contours of $\rho(r)$ and $V$. The difference among the contours being most prominent in the C-C bonding region and the central region of the ring. Here they have shown that there is no saddle point in the C-C bonding region for $V$ contours, but is present in the contours of $\rho(r)$ in the same region. For the case of the homonuclear ring system, viz cyclopropane, they have shown that the characteristic feature of a saddle point in the $\rho(r)$ distribution is also seen in the distribution of $V$. At this juncture, let us test our earlier
Table V.4

Some tests for $\rho$ and $V^*$ at nuclear positions of atoms in molecules using molecular wavefunctions as tabulated by Snyder and Basch [6]. (All values in a.u.).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Atom</th>
<th>$\rho$</th>
<th>$V^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxirane</td>
<td>O</td>
<td>289.248</td>
<td>-22.3511</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>116.362</td>
<td>-14.669</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.426</td>
<td>-1.082</td>
</tr>
<tr>
<td>Diazirine</td>
<td>N</td>
<td>189.776</td>
<td>-18.256</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>116.298</td>
<td>-14.644</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.418</td>
<td>-1.0578</td>
</tr>
<tr>
<td>Cyclopropane</td>
<td>C</td>
<td>116.278</td>
<td>-14.732</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.420</td>
<td>-1.1116</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>N</td>
<td>189.950</td>
<td>-18.233</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(205.591)</td>
<td>(-18.273)</td>
</tr>
<tr>
<td>Water</td>
<td>O</td>
<td>288.704</td>
<td>-22.348</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-22.348)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>0.416</td>
<td>0.9722</td>
</tr>
</tbody>
</table>

The values in parentheses are taken from Ref. [15]
prediction regarding the similarity between the contours of $V^*$ and $\rho(r)$.

In the case of the oxirane molecule, contours of $V$, $\rho(r)$ and $V^*$ are displayed in Figs. V.6, V.7 and V.8 respectively. The contours of $\rho(r)$ and $V^*$ show strikingly similar qualitative features. The unique topological feature of the saddle point in the C-O and C-C bonding region is conspicuous in both the contours of $V^*$ and $\rho(r)$ as can be seen readily from figures V.6, V.7 and V.8. A closer analysis of $V$, $\rho(r)$ and $V^*$ (Fig. V.6-13) shows that contours of $\rho(r)$ and $V^*$ show similar characteristic polarization of 'atomic' like (almost spherical) contours. This is present to a lesser extent in the contours of $V$.

In the case of the cyclopropane molecule the similarity in the gross qualitative features of bonding is seen in all the three distributions of $V$ and $V^*$ from figures V.9 and V.10. The contours of $\rho(r)$ may be referred to from Ref.[4]. In this case too, focusing our attention on the 'atomic' like contours, it is apparent from the polarization of these contours that the distributions of $\rho(r)$ show markedly more similarity with $V^*$ than with those of $V$. Here the saddle point in all the C-C bonding regions is seen in all three distributions. Another interesting feature is the small closed contour in the central region of the ring which is present in all the three distributions.

The prediction by Politzer and Zilles [4] that small ring molecules containing heteroatoms will fail to obey the relation

$\rho_{mol}(r) = f( V_{mol}(r) )$ implies that the distributions
Fig.V.6 : The contours of Bare nuclear Potential, $V$, of oxirane molecule in the plane of the ring.
Fig.V.7 : Contours of Electron density, $\rho(r)$, of oxirane in the
Fig. 18 : Contours of Electrostatic potential, $V^*$, of oxirane in the plane of the ring. (All values are in a.u.).
Fig. V9: Contours of Bare Nuclear Potential, $V$, of cyclopropane molecule in the plane of the ring.
Fig.V.10 : Characteristic closed contours of $\Psi^*$ of cyclopropane in the central region of the plane of the ring.
(All values are in a.u.).
of $\rho(r)$ and $V$ will be dissimilar prompted examination of the case of the diazirine molecule, an unsaturated strained ring system. The contours of $V$, $\rho(r)$ and $V^*$ are displayed in Figures V.11, V.12 and V.13 respectively. Figures V.11 and V.12 clearly bear out their [4] prediction of the dissimilarity of the $V$ and $\rho(r)$ contours. Here too, similar to the case of oxirane, the saddle point is not seen in the N-N bonding region in $V$ contours, is clearly present in that of $\rho(r)$ and $V^*$ contours. Though it may be noted that the polarization of 'atomic' like contours of $\rho(r)$ is not reflected to any large extent in contours of $V^*$ and $V$.

A strong case for the similarity between $\rho(r)$ and $V^*(r)$ would be the presence of critical as well as saddle points of $V^*$ in the vicinity of those corresponding to $\rho(r)$. Table V.5 shows the location of the saddle points as well as critical point in the central part of the ring for $\rho(r)$ and $V^*(r)$ for the three molecules considered. For the case of cyclopropane, the critical point is located at the ring center for both the distributions. For all the other cases it may be clearly noticed that these points of $V^*(r)$ lie in the vicinity (located within an average distance of 0.2 a.u.) of the corresponding ones for $\rho(r)$ in the region under investigation.

From this semiquantitative analysis of these test cases it is eminent that a further rigorous analysis, as done by Tal et al [3], for $V^*$ and $\rho(r)$ would prove enlightening. We have not probed the regions outside the rings. Such an analysis would prove useful for obtaining useful information on chemical reactivity.
Fig. V.11 : Contours of $V$ of diazirine in the plane of the ring.
Fig.V.12: Electron density contours of diazirine in the plane of the ring.
Fig. V.13: Electrostatic potential contours of diazirine in the plane of the ring. (All values are in a.u.).
Table V.5

A comparison of saddle and critical points of $\rho(r)$ and $V^*(r)$ for the molecular cases considered$^a$

<table>
<thead>
<tr>
<th>Molecule/Region</th>
<th>$\rho$</th>
<th>Location</th>
<th>$-V^*$</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxirane</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Central ring</td>
<td>0.185</td>
<td>(0, 0, -0.68)</td>
<td>0.862</td>
<td>(0, 0, -0.8)</td>
</tr>
<tr>
<td>C - O</td>
<td>0.226</td>
<td>(0.871, 0, -0.945)</td>
<td>0.978</td>
<td>(0.55, 0, -1.1)</td>
</tr>
<tr>
<td>C - C</td>
<td>0.239</td>
<td>(0, 0, 0.165)</td>
<td>0.960</td>
<td>(0, 0, -0.175)</td>
</tr>
<tr>
<td><strong>Diazirine</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Central ring</td>
<td>0.193</td>
<td>(0, 0, 1.295)</td>
<td>0.103</td>
<td>(0, 0, 1.475)</td>
</tr>
<tr>
<td>C - N</td>
<td>0.217</td>
<td>(0.62, 0, 1.04)</td>
<td>1.046</td>
<td>(0.34, 0, 1.39)</td>
</tr>
<tr>
<td>N - N</td>
<td>0.450</td>
<td>(0, 0, 2.598)</td>
<td>1.603</td>
<td>(0, 0, 2.479)</td>
</tr>
<tr>
<td><strong>Cyclopropane</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Central ring</td>
<td>0.173</td>
<td>(0, 0, 0)</td>
<td>0.698</td>
<td>(0, 0, 0)</td>
</tr>
<tr>
<td>C - C</td>
<td>0.218</td>
<td>(-0.936, 0, 0)</td>
<td>0.804</td>
<td>(-0.68, 0, 0)</td>
</tr>
</tbody>
</table>

$^a$ The wavefunctions and geometries of the molecules studied were taken from Ref.[6]
The purpose of the present work has been to explore the similarity between the scalar fields of $V, \rho(r)$ and $V^*$. This has been studied with simple diatomic, polyatomic and some three membered molecular ring systems as test cases. For the case of the $H_2$ molecule only the similarity between the electron density and bare nuclear potential was studied. From Table V.3 it may be observed that wavefunctions leading to strong binding and consequently a higher delocalization or pile up of electrons in the internuclear region show a comparatively higher $\mathcal{C}$ value for $V$ evaluated over contours in this region. The $\mathcal{C}$ values corresponding to $V$ evaluated over contours in the outer region of the molecule, i.e. enclosing the molecule are much lower.

In the case of weak bonding situations as depicted by the NIHA models it may be observed that $\mathcal{C}$ values are consistently lower in both the outer as well as the inner regions of the molecule indicating that the hypothesis that $\rho = f(V)$ is valid for weak binding situations. At this juncture it may be more illuminating to consider a heuristic picture of molecule formation. Consider the nuclei to be rigidly fixed at their respective equilibrium positions and allow the electrons to flow in. Initially the electrons would distribute themselves around the nuclei according to the bare nuclear potential felt by them. As more electrons flow in the potential felt by them would be numerically smaller due to the screening by the inner electrons. Thus, from this crude picture one may infer that in a
molecule in the region around the nuclei, where the contribution \( Z_i/r \) towards the bare nuclear potential \( V \), from the other nuclei is negligible, the relation \( \rho = f(V) \) would be better. In the internuclear region where there is a pile up of charge the relation \( \rho = f(V^*) \) is expected to be a better one.

The clear similarity between \( \rho(r) \) and \( V^* \) even for heteronuclear ring systems may be noticed from the case of the oxirane ring system. Here for the distribution of \( V \), no characteristic closed contour is found as in the case of \( \rho(r) \) and \( V^* \). In this same region for both \( \rho(r) \) and \( V^* \), a critical point, viz. a minimum, is present. Consider the relation \( \nabla^2 V^* = 4\pi\rho \), implying that \( \nabla^2 V > 0 \) at all points in space. Hence the critical points of \( V^* \) must be minima.

At the nucleus, \( V^* \) shows a minimum. For \( \rho(r) \), the nucleus is more a singularity than a critical point since \( \nabla \rho \) is not defined at the nucleus, though numerically \( \rho(r) \) attains the largest value at nuclear site in the near neighbourhood.

These aspects have led to a conclusion which perhaps may be made more general that \( XXO \) and \( V^* \) are topologically more similar than \( V \) and \( XXO \). The observations made in the present work indeed induce one to further investigate the use of electron density maps instead of electrostatic potential maps for the conventional prediction of chemical reactive sites in molecules or path of approach for protonation in molecules as done for \( V^* \) by Tomasi [16]. The similarity among the contours of molecular electron densities and electrostatic potentials, though prompted by semiclassical (Thomas-Fermi) considerations, thus seems to be much more deep rooted
and worth investigating further.

It is felt that in the regions where \( V^*(r) \) is a minimum, \( \rho(r) \) may also exhibit some special features. However, more work (which requires computations with larger molecules and more accurate densities) in this direction remains to be done. It is hoped that the work embodied in this Chapter will provide an impetus to further studies in this direction.
References


