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Some Observations Concerning Electronic Densities, Electrostatic Potentials and Chemical Potentials

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The hypothesis that the electronic density distribution in a molecule is qualitatively similar to the nuclear potential is shown to be in error in at least two cases—oxirane and cubane—although it does hold true in a number of other systems. Its emphasis upon the dominant role played by electrostatic interactions with the nuclei is consistent with some approximate molecular energy formulas. However, taking the nuclear potential as an approximation to the electronic density misses the small effects that correspond to the formation of chemical bonds. It is suggested that the electronic density difference function should provide a rough picture of the local variations in the chemical potential that occur as atoms combine to form a molecule. Finally, the common practice of representing the energy and electronegativity of an interacting atom as functions only of the number of electrons associated with the atom is shown to be inadequate; some account should be taken of the changing internuclear separations.

I. THE NUCLEAR POTENTIAL AS A DETERMINANT OF THE MOLECULAR ELECTRONIC DENSITY DISTRIBUTION AND THE TOTAL ENERGY

There has recently been presented the intriguing hypothesis that the electronic density distribution in a molecule, $\varrho^{mol}(\vec{r})$, is qualitatively similar, in its general features, to the electrostatic potential due to the nuclei, $V_N^{mol}(\vec{r})$.[1-3] The latter is given by,

$$V_N^{mol}(\vec{r}) = \sum_A{}' \frac{Z_A}{|\vec{R}_A - \vec{r}|} \tag{1}$$

in which Z_A is the charge on nucleus A, located at $\vec{R}_A$, and the summation is taken over all of the nuclei in the molecule. According to this hypothesis, it should be a good approximation to assume that there exists a functional relationship of the form,[3]

$$\varrho^{mol}(\vec{r}) = f[V_N^{mol}(\vec{r})] \tag{2}$$

The analogous equation for atoms, $\varrho^{at,A}(\vec{r}) = g[V_N^{at,A}(\vec{r})]$, is exact; this can be shown by noting that $V_N^{at,A}(\vec{r}) = Z_A/r$, so that
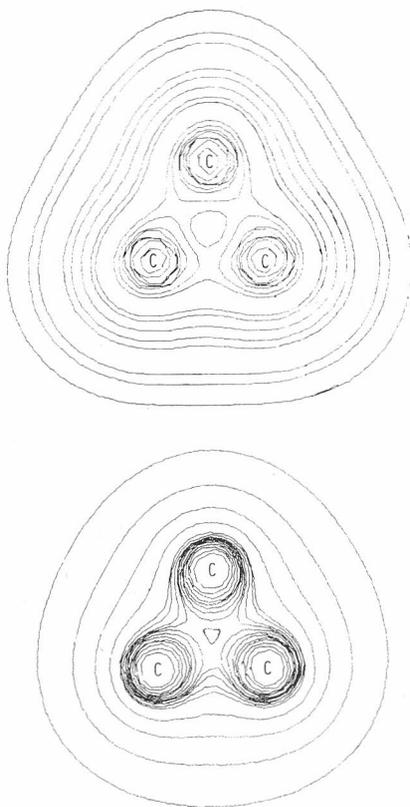
Figure 1. Top: Electronic density of cyclopropane in the plane of the ring, calculated with an *ab initio* SCF-MO wave function computed at the 6-31G level. The contours correspond to the following electronic densities, in electrons/bohr³: 0.001, 0.003, 0.005, 0.020, 0.030, 0.050, 0.080, 0.100, 0.200, 0.230, 0.270, 0.300, 0.400, 0.500, 1.000 and 5.000. Bottom: Electrostatic potential due to the nuclei in cyclopropane, in the plane of the ring. The contours correspond to the following potential values, in atomic units (1 a. u. = 27.21 eV): 5.5, 7.0, 8.5, 10.0, 11.6, 12.0, 12.5, 12.8, 13.1, 13.5, 14.0, 14.5, 15.0, 16.0, 17.5 and 20.0. Both plots have a local minimum in the center of the ring, which means that there is a saddlepoint in each C—C internuclear region.

$$\varrho^{at, A} (\vec{r}) = \varrho^{at, A} (r) = \varrho^{at, A} [Z_A/V_N^{at, A} (\vec{r})] = g [V_N^{at, A} (\vec{r})] \tag{3}$$

Eq. (3) invokes the spherical symmetry of the electronic charge distribution of the atom.[4]

The situation for molecules is not as straightforward, however, as shall be shown. Parr and Berk have compared contour diagrams of $\varrho^{mol} (\vec{r})$ and $V_N^{mol} (\vec{r})$ for several diatomic and triatomic molecules, and found that there is indeed a qualitative similarity.[3] Another supporting example, cyclopropane (I), is shown in Figure 1. Thus there is certainly evidence indicating the approximate validity of Eq. (2), although Tal *et al.* point out that in some instances it is necessary to consider geometries other than the equilibrium ones.[2]
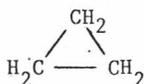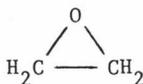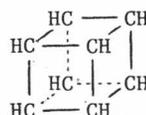
I   II   III

To the extent that Eq. (2) is obeyed, it shows that the interactions between the nuclei and the electrons are the dominant factor in determining the electronic density distribution in a molecule. This interesting conclusion is consistent in spirit with two relationships that have been found to be good approximations to the total energy of a molecule:[5-7]

$$E^{\text{mol}} = \frac{3}{7} \sum_A Z_A V_{0,A} \tag{4}$$

and

$$E^{\text{mol}} = \sum_A k_A Z_A V_{0,A} \tag{5}$$

$V_{0,A}$ is the total electrostatic potential that is produced at the nucleus of atom A by the electrons and the other nuclei in the molecule:

$$V_{0,A} = \sum_{B \neq A} \frac{Z_B}{|\vec{R}_B - \vec{R}_A|} - \int \frac{\varrho^{\text{mol}}(\vec{r}) \, d\vec{r}}{|\vec{r} - \vec{R}_A|} \tag{6}$$

Eq. (5) is simply a generalized form of Eq. (4), in which the universal factor 3/7 has been replaced by a parameter k_A that is specific to each atom A. Eq. (4) gives molecular energies to within an error of generally less than 2%,[5] and even considerably greater accuracy can be obtained with Eq. (5), depending upon how the values for the parameters k_A are chosen.[6-10]

Eqs. (4) and (5) show that a good approximation to the total energy can be obtained by considering explicitly only the electrostatic interactions of the nuclei with each other and with the electrons (modified by a numerical factor*), while the evidence mentioned earlier indicates that the distribution of the electrons can also be predicted, qualitatively, with reasonably good accuracy by considering only the electrostatic potential created by the nuclei. The unifying theme is that only electrostatic interactions involving the nuclei are explicitly being taken into account.

II. SOME FAILURES OF EQ. (2)

While there is clearly reason to believe that Eq. (2) will very often be a good approximation, there are at least two instances in which it fails.**

Figure 2 compares $\varrho^{\text{mol}}(\vec{r})$ and $V_N^{\text{mol}}(\vec{r})$ for oxirane (II). They differ quite markedly in the C—C bonding region; if $V_N^{\text{mol}}(\vec{r})$ were being used to predict $\varrho^{\text{mol}}(\vec{r})$, it would erroneously be concluded that there is no bond between the carbons. The saddlepoint in the C—C internuclear region that is present in the nuclear potential of cyclopropane and in the electronic densities of both cyclopropane and oxirane is absent in the nuclear potential of the latter. This

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* One of the functions of this factor is to take approximate account of interelectronic repulsion.
** One of these has already been mentioned briefly in reference 11.

is because the positive charges in the CH_2 group of cyclopropane have been replaced by one that is both more concentrated (8 *vs.* 6 + 1 + 1) and also closer to the C—C region. (Our optimized C—O bond lengths in oxirane are 1.43 Å, compared to the 1.51 Å in cyclopropane.)

Another molecule in which there is a significant qualitative difference between $\varrho^{mol}(\vec{r})$ and $V_N^{mol}(\vec{r})$ is cubane (III). In the plane presented in Figure 3, $\varrho^{mol}(\vec{r})$ has a saddlepoint between each pair of neighbouring carbons (even those that are not ordinarily regarded as being bonded to each other) and a minimum in the center of all four; $V_N^{mol}(\vec{r})$, on the other hand, shows no saddlepoints between neighboring carbons and a central plateau.
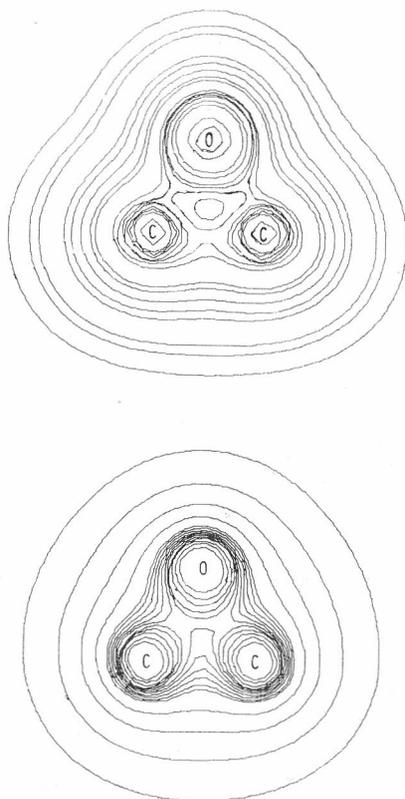
Figure 2. Top: Electronic density of oxirane in the plane of the ring, calculated with an *ab initio* SCF-MO wave function computed at the 6-31G level. The contours correspond to the following electronic densities, in electrons/bohr³: 0.001, 0.003, 0.005, 0.020, 0.030, 0.050, 0.080, 0.100, 0.200, 0.230, 0.270, 0.300, 0.400, 0.500, 1.000 and 5.000. Bottom: Electrostatic potential due to the nuclei in oxirane, in the plane of the ring. The contours correspond to the following potential values, in atomic units (1 a. u. = = 27.21 eV): 5.5, 7.0, 8.5, 10.0, 11.6, 12.0, 12.5, 13.0, 13.5, 14.0, 14.5, 15.0, 16.0, 17.5 and 20.0. Whereas the electronic density shows a local minimum near the center of the ring, there is no corresponding one in the nuclear potential. The latter decreases monotonically along the line leading from the oxygen nucleus and passing through the midpoint of the C—C bond. Accordingly, unlike the electronic density of oxirane, the nuclear potential has no saddlepoint in the C—C internuclear region.
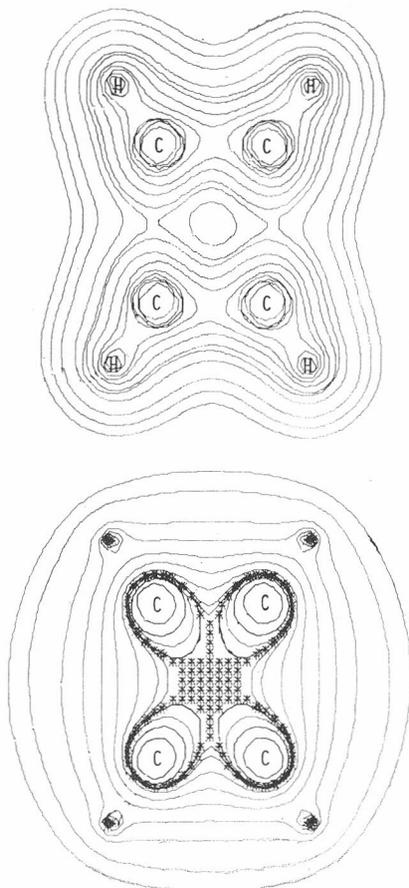
Figure 3. Top: Electronic density of cubane in the mirror plane passing through two opposite C—C bonds (diagonal plane), calculated with an *ab initio* SCF-MO wave function computed at the STO-5G level. The contours correspond to the following electronic densities, in electrons/bohr³: 0.005, 0.010, 0.020, 0.050, 0.080, 0.100, 0.150, 0.200, 0.250, 0.300, 0.350, 0.500 and 1.000. Bottom: Electrostatic potential due to the nuclei in cubane, in the same plane as above. The contours correspond to the following potential values, in atomic units (1 a. u. =27.21 eV): 10.0, 11.0, 13.0, 14.5, 16.0, 17.5, 19.0, 20.0, 20.3, 20.6, 21.0, 22.0 and 25.0. The asterisks indicate points at which the potential is 20.5. The electronic density has a local minimum in the center of the cube, with a saddlepoint in each of the four C—C internuclear regions. There are no corresponding saddlepoints in the nuclear potential.

Further failures of Eq. (2) may be anticipated for other small-ring molecules containing heteroatoms, as well as for other cage-type systems.

III. AN INTRINSIC DIFFERENCE BETWEEN $\rho^{mol}(\vec{r})$ AND $V_N^{mol}(\vec{r})$

Since $V_N^{mol}(\vec{r})$ is simply a superposition of the individual nuclear potentials of the atoms that constitute the molecule, placed at the same positions as they occupy in the molecule, it follows that the difference $\Delta V_N(\vec{r})$, defined as,

$$\Delta V_N \vec{(r)} = V_N^{mol} \vec{(r)} - \underset{A}{\Sigma} V_N^{at,A} \vec{(r)} \tag{7}$$

is identically zero at all $\vec{r}$. (In Eq. (7), $V_N^{at,A} \vec{(r)}$ is defined as $Z_A / |\vec{R_A} - \vec{r}|$.)
On the other hand, the density difference function,

$$\Delta \varrho \vec{(r)} = \varrho^{mol} \vec{(r)} - \underset{A}{\Sigma} \varrho^{at,A} \vec{(r)} \tag{8}$$

is certainly not zero everywhere. ($\varrho^{at,A} \vec{(r)}$ is the electronic density of free atom A, placed at its position in the molecule but assumed to undergo no interaction with any other atom.) The function $\Delta \varrho \vec{(r)}$ indicates the overall rearrangement of electronic charge density that occurs when atoms combine to form a molecule, and it has been used very extensively in studying chemical bonding.[12-17]

The preceding considerations bring out the fact that $V_N^{mol} \vec{(r)}$ will invariably fail to reflect the effects associated with the formation of chemical bonds. Of course these effects are very small, and may be regarded as simply perturbations of the free atoms; they give rise to $\Delta \varrho \vec{(r)}$ and ΔE (the interaction energy), both of which are normally very small fractions of the total electronic density and total energy of the system.

IV. THE CHEMICAL POTENTIAL AND THE ELECTRONIC DENSITY DIFFERENCE FUNCTION

In conjunction with the recent advances in density functional theory, a great deal of attention has been focused upon the chemical potential, μ.[18,19] For a system of N electrons, with nuclear charges Z_i and internuclear distances R_j, μ is defined by

$$\mu = \left(\frac{\partial E}{\partial N} \right)_{Z_i, R_j} \tag{9}$$

It has been shown that the chemical potential is a guide to the movement of electronic charge within a system of nuclei and electrons; electron migration occurs from regions of high potential to regions in which μ is low, continuing until, at equilibrium, the chemical potential is uniform throughout the system.[20,21] (This is an alternate statement of the principle of electronegativity equalization.[22])

This process, as it occurs in the formation of heteronuclear molecules from their constituent atoms, can easily be visualized. A major feature is presumably the shifting of some quantity of electronic charge previously associated with the atom(s) of higher μ to the vicinities of atoms with lower μ values. In the course of whatever charge transfer and charge rearrangement take place, the chemical potentials of the constituent atoms change to some uniform final value.

However this simple picture is incomplete. It is useful to examine in detail the formation of homonuclear systems, because this can bring out certain important general points that may be overlooked in dealing with heteronuclear examples. Consider, for instance, the interaction of two like atoms to produce a homonuclear diatomic molecule. Here the chemical potential is already uniform throughout the system even before any interaction has begun, and there is clearly no net charge transfer from either atom to the other. However it is

known from both theoretical and experimental studies[13,14,23,24] that rearrangement of electronic charge does take place. This means that there must be local variations in the chemical potential in at least some regions of the space around the two atoms as they come together.

It seems reasonable to suggest that a rough picture of these local variations can be obtained from an examination of the electronic density difference function, $\Delta\varrho\,(\vec{r})$, for the ground state of the molecule. As explained in section III, $\Delta\varrho\,(\vec{r})$ shows how the molecular electronic density differs, at each point in space, from the superposed free atom densities. Speaking strictly qualitatively, those regions in which $\Delta\varrho\,(\vec{r}) > 0$ presumably had low chemical potentials during at least some portion of the interaction process, while $\Delta\varrho\,(\vec{r}) < 0$ should show where μ_1 had been high.

For many diatomic molecules, heteronuclear as well as homonuclear, $\Delta\varrho\,(\vec{r})$ has certain characteristic features: There are buildups of electronic charge ($\Delta\varrho > 0$) in the internuclear and lone pair regions, and diminutions ($\Delta\varrho < 0$) in the regions perpendicular to the molecular axis near the positions of the nuclei. As an example, Figure 4 shows the density difference for the nitrogen
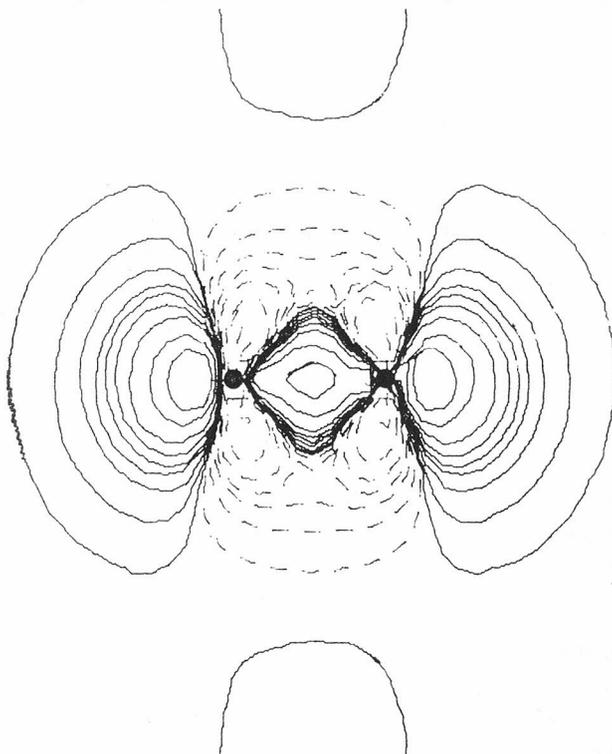
Figure 4. Electronic density difference function for the ground state of the nitrogen molecule. The positions of the nuclei are indicated by solid circles. The contours correspond to the following density differences, in electrons/bohr³: Solid contours: 0.000, 0.001, 0.004, 0.008, 0.012, 0.018, 0.030, 0.060, and 0.100. Dashed contours: —0.001, —0.004, —0.008, —0.012, —0.018, —0.030, —0.060 and —0.100.

molecule. These characteristic features of diatomic $\overrightarrow{\Delta\varrho}(r)$ diagrams should reflect, at least approximately, the local variations in the chemical potential of the system that accompany the formation of such molecules from their atoms.

This proposed rough relationship between $\Delta\varrho$ and μ should not be carried too far, however. For example, it is rigorously true, by definition, that $\int \overrightarrow{\Delta\varrho}(r)\,\overrightarrow{dr} = 0$, for any molecule. If an equivalent statement were true for the chemical potential, it would mean that μ for a homonuclear diatomic molecule should be the same as for the free atoms. The approximate chemical potentials given in Table I indicate that this is not so.

TABLE I

Comparison of Some Atomic and Molecular Chemical Potentials

Atom	μ/eV	Molecule	μ/eV
O	7.5	O_2	6.3
Cl	8.3	Cl_2	7.0
I	6.8	I_2	6.0

* All of these chemical potentials have been calculated using the approximate formula, $\mu = 0.5\,(I + A)$, where I and A are the ionization potential and electron affinity of the system, respectively.[20] The atomic μ values are taken from reference 30; those for the molecules were determined using I from reference 31 and A from references 32 and 33.

V. ENERGY EXPRESSIONS FOR INTERACTING ATOMS

In conclusion, it is instructive to consider another aspect of the formation of homonuclear molecules from their atoms. The fact that the number of electrons associated with each atom remains unchanged throughout this process means that it is not valid to represent the energy of an interacting N-electron atom by any function of N alone, such as the commonly-used,

$$E^{at} = A + BN + CN^2 \tag{10}$$

in which A, B and C are constants. Eq. (10) would imply that the energies of the atoms in homonuclear molecules are exactly the same as those of the free atoms, so that the binding energy would be equal to zero. In the context of atomic interactions, the expression for E^{at} must contain a dependence upon the internuclear separations.*

It follows that the electronegativity of an atom, X, given by $X = -\mu$,[20] is not really properly represented by the formula,

$$X = \alpha + \beta N \tag{11}$$

obtained by inserting Eq. (10) into Eq. (9), even though some useful results and insights have indeed been attained, for heteronuclear systems, with Eq. (11) (or its equivalent written in terms of the net charge on the atom).[25-29]

* For a related discussion, see reference 21.

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SAŽETAK

Neka zapažanja o elektronskim gustoćama, elektrostatskim potencijalima i kemijskim potencijalima

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Pokazano je da hipoteza prema kojoj je raspodjela elektronske gustoće u molekuli kvalitativno slična potencijalu što ga proizvode jezgre nije dobra barem u dva slučaja — oksiranu i kubanu. Ona je, ipak, točna, za čitav niz drugih molekula, što se može objasniti aproksimativnim formulama za energiju u kojima elektrostatska inter- ·

akcija jezgri igra dominantnu ulogu. Međutim, uzimanjem u obzir jedino potencijala jezgri zanemaruju se finiji detalji promjena gustoće elektrona koje su posljedica stvaranja kemijskih veza, što posebno dolazi do izražaja kod spomenute dvije molekule. Nadalje, predlaže se da se za opis varijacija kemijskog potencijala do kojega dolazi uslijed spajanja atoma koristi deformacija raspodjele gustoće elektrona. Konačno, pokazano je da uobičajeno određivanje elektronegativnosti atoma, prema broju elektrona koji su tom atomu pripisani, nije sasvim adekvatno, već treba uzeti u obzir i promjene u međuatomskim udaljenostima.