Molecular Surfaces, van der Waals Radii and Electrostatic Potentials in Relation to Noncovalent Interactions*

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Abstract. We investigate two questions relating to the use of electrostatic potentials in interpreting and predicting noncovalent interactions. First, is the molecular surface defined by the 0.001 au contour of the electronic density a reasonable one, in terms of its relationship to the van der Waals radii of the component atoms? Second, how does the electrostatic potential vary with distance in different directions from the nuclei of covalently-bonded atoms? We address these questions computationally, at the density functional B3PW91/6-31G(d,p) level.

Keywords: molecular electrostatic potential, isodensity molecular surface, distance-dependence of electrostatic potential, van der Waals radii

INTRODUCTION

The electronic density $\rho(r)$ and the electrostatic potential $V(r)$ are two of the most basic molecular properties. They are related, through Coulomb's Law,

$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')dr'}{|r' - r|} \qquad (1)$$

and through Poisson's equation,

$$\nabla^2 V(r) = 4\pi\rho(r) - 4\pi\sum_A Z_A \delta(r - R_A) \qquad (2)$$

In Eqs. (1) and (2), Z_A is the charge on nucleus A, located at R_A. Both $\rho(r)$ and $V(r)$ are physical observables; they can be determined by diffraction techniques[1,2] as well as computationally. Note however that $V(r)$ does not reflect $\rho(r)$ alone; it explicitly contains the contribution of the nuclei.

Two fundamental theorems, the Hohenberg-Kohn[3] and the Hellmann-Feynman,[4,5] link the energy E of an atom or molecule, in principle, to $\rho(r)$ and $V(r)$, respectively. While actual rigorous formulations of $E[\rho(r)]$ are yet to be achieved, some are already known for $E[V(r)]$, specifically in terms of $V(r)$ at the positions of the nuclei.[6–9] For a general overview of the significance of the electrostatic potential with regard to molecular properties, see Politzer and Murray.[10]

Our focus in this paper is on the use of $V(r)$ in interpreting and predicting molecular reactivity, particularly in noncovalent interactions; this goes back to the pioneering work of Scrocco and Tomasi,[11,12] and has been reviewed several times.[2,13–18] For these purposes, it is now quite common to compute and analyze $V(r)$ on an appropriate three-dimensional surface of the molecule; this will be labeled $V_S(r)$. While any definition of a molecular surface is necessarily arbitrary, a seemingly reasonable one was proposed by Bader *et al.*:[19] an outer contour of the molecule's electronic density $\rho(r)$. This has the advantage of reflecting the specific features of that particular molecule, *e.g.* lone pairs, π electrons, strained bonds, *etc.* We use the 0.001 au (electrons/a_0^3) contour of $\rho(r)$, which encompasses more than 95 % of the molecule's electronic charge.

Our objective in this paper is to examine certain features of molecular $V(r)$ and $V_S(r)$ in order to better characterize these properties, especially in the context of noncovalent interactions. Our results have been obtained computationally; geometry optimizations and calculation of $V(r)$ and $V_S(r)$ were carried out at the density functional B3PW91/6-31G(d,p) level. As examples, Figures 1 and 2 show the electrostatic potentials $V_S(r)$ plotted on the $\rho(r) = 0.001$ au surfaces of HCN and NH_3.

Figure 1. Computed electrostatic potential $V_S(r)$ on the $\rho(r) =$ 0.001 au surface of HCN. The nitrogen atom is at the right. Color ranges, in kcal mol^{-1} are: red, more positive than 30; yellow, between 15 and 30; green, between 0 and 15; blue, between -20 and 0; purple, more negative than -20.
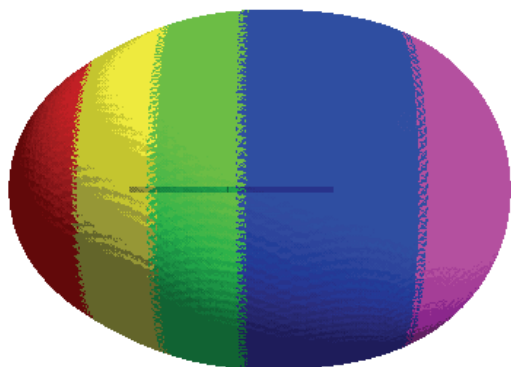

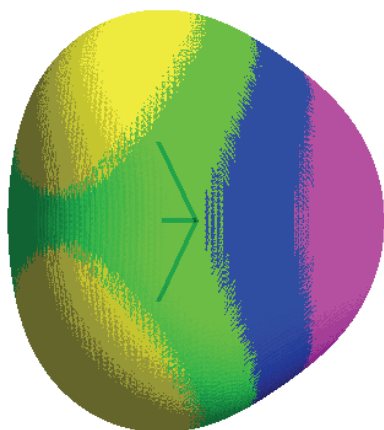**Figure 2.** Computed electrostatic potential $V_S(r)$ on the $\rho(r) =$ 0.001 au surface of NH$_3$. The nitrogen atom is at the right. Color ranges, in kcal mol^{-1} are: yellow, between 15 and 30; green, between 0 and 15; blue, between -20 and 0; purple, more negative than -20.

RESULTS AND DISCUSSION

Distances to $\rho(r) = 0.001$ au Surfaces *vs.* van der Waals Radii

A reasonable initial question is: Where is the $\rho(r) =$ 0.001 au surface around an atom in a molecule in relation to that atom's van der Waals radius? To answer this, we look at some key points on the surface, those at which the electrostatic potential $V_S(r)$ has its most positive and most negative values, the local maxima $V_{S,max}$ and the local minima $V_{S,min}$, respectively. The relevance of these to noncovalent interactions is well established.

The $V_{S,max}$ of hydrogens and the $V_{S,min}$ of Lewis bases have been shown to correlate with empirical measures of hydrogen bond donating and accepting tendencies,[20] while the $V_{S,max}$ on the extensions of covalent bonds to Group IV−VII atoms indicate the possibilities for σ-hole bonding (often called halogen bonding in the case of Group VII).[21]

In Table 1 are listed, for a group of representative molecules, the distances from the nuclei of some of the component atoms to the $V_{S,max}$ and/or $V_{S,min}$ that are clearly associated with them. (A given atom in a molecule may have from zero to several $V_{S,max}$ and/or $V_{S,min}$; it also often happens that some $V_{S,max}$ and $V_{S,min}$ cannot be assigned unambiguously to any one atom.) The distances to the $V_{S,max}$ and $V_{S,min}$ serve as convenient indicators of how far the surfaces are from the nuclei in different regions of the molecule. For comparison, the van der Waals radius of each atom is presented. The sum of the van der Waals radii of two atoms is a rough guide to the distance at which significant noncovalent interaction begins.

In every instance in Table 1, the distance from a nucleus to the $\rho(r) = 0.001$ au surface – specifically to its local $V_{S,max}$ and/or $V_{S,min}$ – is greater than the atom's van der Waals radius. Thus the features of the electrostatic potential on that surface are relevant already to the very early stages of an incipient interaction.

The data in Table 1 illustrate some of the advantages of representing a molecular surface by an outer contour of $\rho(r)$. One of these is that the shape of the contour around each atom reflects its actual molecular environment. This can readily be seen by comparing the positions and magnitudes of the $V_{S,max}$ for a given atom in different molecules. Thus the $V_{S,max}$ of Br is 22.6 kcal mol^{-1} at 2.00 Å in Br−C≡C−CH$_3$, but 47.5 kcal mol^{-1} at 1.90 Å in BrF. For the hydrogens in pyrazine, it is 19.2 kcal mol^{-1} at 1.34 Å, but 43.6 kcal mol^{-1} at 1.19 Å for the hydroxyl hydrogen in H$_3$COH. As any portion of the $\rho(r) = 0.001$ au surface around an atom becomes more positive, it tends to move closer to that atom's nucleus.

Another realistic feature of a surface defined by a contour of $\rho(r)$ is that it reflects anisotropies in the charge distributions of covalently-bonded atoms.[22,23] One manifestation of this, for those atoms in Table 1 that have both a $V_{S,max}$ and a $V_{S,min}$, is that the former is closer to the nucleus.

The $V_{S,max}$ of the non-hydrogen atoms in Table 1 are approximately on the extensions of the covalent bonds to those atoms; they are a consequence of a deficiency of electronic charge in the outer lobe of the p-type orbital involved in the bond. This is known as a σ-hole,[21,24] and accounts for their anisotropic charge distributions. If the σ-hole is strong enough, it can produce

Table 1. Magnitudes of $V_{S,max}$ and $V_{S,min}$ (expressed in kcal mol^{-1}) and distances /Å from nuclei of indicated atoms compared to their van der Waals radii /Å [a]

Molecule	Atom	$V_{S,max}$	Distance	$V_{S,min}$	Distance	vdW Radius [b]
NH_3	H	25.5	1.27			1.17
	N			−46.3	1.96	1.55
H_2O	H	43.3	1.20			1.17
	O			−39.6	1.75	1.52
H_2S	H	24.0	1.38			1.17
	S			−21.0	2.29	1.83
HCN	H	49.5	1.24			1.17
	N			−32.9	1.85	1.55
BrF	Br	47.5	1.90	−1.7	2.22	1.85
	F			−11.9	1.59	1.50
OF_2	O	13.8	1.63	−3.7	1.75	1.52
	F	6.6	1.53	−4.3	1.59	1.50
SCl_2	S	25.1	2.00	−5.9	2.26	1.83
	Cl	13.3	1.94	−5.9	2.11	1.76
$S(CH_3)_2$	S			−25.4	2.28	1.83
	H	14.5	1.34			1.17
CH_3OH	O			−36.2	1.75	1.52
	H (hydroxyl)	43.6	1.19			1.17
$(H_3C)_2CO$	O			−36.7	1.72	1.52
	H	19.2	1.36			1.17
$Cl-NO_2$	Cl	16.4	1.93	−5.4	2.10	1.76
	N	27.9	1.76			1.55
	O			−8.1, −5.4	1.72, 1.71	1.52
$HC{\equiv}C-Cl$	H	35.9	1.25			1.17
	Cl	20.6	1.88	−5.5	2.09	1.76
$H_2C(OH)CH_2Cl$	O			−26.3	1.75	1.52
	Cl			−16.2	2.11	1.76
	H (hydroxyl)	51.1	1.18			1.17
	H	14.8	1.33			1.17
$Br-C{\equiv}C-CH_3$	Br	22.6	2.00	−7.9	2.22	1.85
	H	17.2	1.34			1.17
C_6H_5Br	Br	9.7		−13.7	2.24	1.85
	C (*p*)			−11.9	2.05	1.70
	H	16.3−18.3	1.34			1.17
pyrazine	N			−31.3	1.91	1.55
	H	19.2	1.34			1.17
$Se(CN)_2$	Se	46.9	2.04			1.87
	N			−26.8	1.84	1.55
$P(CH_3)_3$	P			−30.8	2.40	1.80
	H	11.2−11.8	1.35−1.37			1.17
AsF_3	As	34.7	2.05			1.85
	F			−15.6	1.58	1.50
$SiCl_4$	Si	20.2	2.27			2.1
	Cl	9.3	1.96	−1.7	2.10	1.76

[a] If an atom has more than one $V_{S,max}$ or $V_{S,min}$ with the same value, only one of these is reported.
[b] A. Bondi, *J. Phys. Chem.* **68** (1964) 441−451.

a positive $V_{S,max}$ even on the surface of an electronegative atom (Table 1), which can then interact in a highly directional manner with Lewis bases (noncovalent σ-hole bonding).[21] In the case of the halogens, the electronic charge anisotropy has been called "polar flattening".[23]

As can be seen in Table 1, many covalently-bonded atoms have regions of both positive and negative electrostatic potential on their surfaces. They can accordingly interact attractively with both nucleophiles and electrophiles, as has been observed crystallographically[25,26] and computationally.[27,28] In such cases, which are quite common,[29] it is certainly not valid to assign to the

atom a single global atomic charge. As has been pointed out,[28,30] this should be considered in designing force fields. For instance, the Br in C_6H_5Br can interact through its $V_{S,max}$ of 9.7 kcal mol^{-1} and also its $V_{S,min}$ of -13.7 kcal mol^{-1}; no single point charge could account for both possibilities.

Variation of $V(r)$ with Distance from Covalently-bonded Atoms

How does the electrostatic potential $V(r)$ vary with distance from the nuclei of covalently-bonded atoms? Near a nucleus, it is large and positive, its magnitude being determined primarily by the nuclear charge. As the distance approaches infinity, $V(r)$ goes to zero. What happens between these extremes? Does $V(r)$ go through maxima and/or minima, and how rapidly does it go to zero? For a free neutral atom, $V(r)$ is positive everywhere and decreases radially monotonically.[31] For a monatomic anion, $V(r)$ decreases monotonically to a negative minimum and then increases to zero.[32]

To gain more detailed insight into what happens in molecules, we have computed $V(r)$ as a function of distance from a nucleus in various directions, starting at a point less than the atom's van der Waals radius and evaluating $V(r)$ at increments of 0.2 Å. This was done for F_2, Cl_2, Br_2, HCN, NH_3, C_6H_6 and CH_3OH. The results are in Figures 3−13.

F_2, Cl_2 and Br_2

Looking first at the three halogen molecules, Figures 3−5 show that their $V(r)$ are quite positive on the extensions of the bonds to the outsides of the internuclear regions, well past the respective van der Waals radii. These are the σ-hole potentials, mentioned earlier, which are involved in the noncovalent interactions of these molecules, particularly Cl_2 and Br_2, with Lewis bases.[33] The σ-holes of the less polarizable fluorine atoms are considerably weaker and diminish more rapidly than those of the chlorines and bromines; in fact, the σ-holes of covalently-bonded fluorines usually are not positive, as can be seen from the absence of $V_{S,max}$ values for them in BrF and AsF_3 (Table 1). (It should be pointed out that the σ-holes of Cl_2 and Br_2, while quite positive with $V_{S,max}$ of 23.8 and 29.1 kcal mol^{-1}, are not among the strongest for these atoms;[21,28,29] for instance, the Br in BrCN has $V_{S,max} = 42.1$ kcal mol^{-1}.)

In the directions perpendicular to the bonds at the positions of the nuclei, $V(r)$ is initially positive but then becomes negative, at or before the van der Waals radius, reaching a shallow minimum before starting to approach zero. Thus these atoms can interact laterally (but weakly) with electrophiles. For example, in the crystal lattice of solid Cl_2, the positive σ-holes of one Cl_2 molecule are positioned toward the negative lateral sides of the chlorines in its neighbors.[34,35]
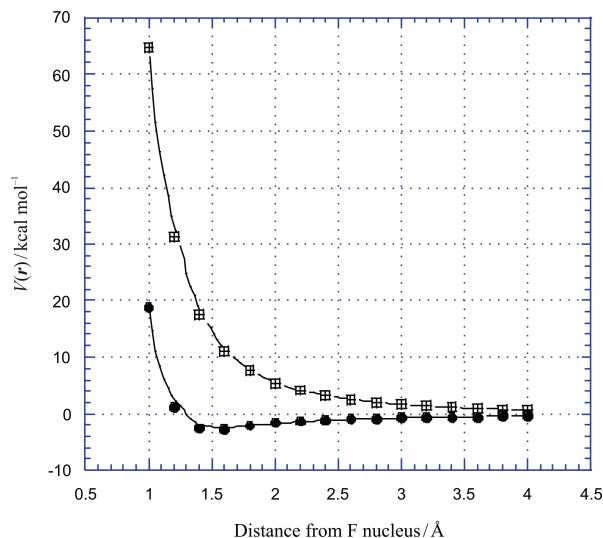
Figure 3. Computed electrostatic potential $V(r)$ of F_2 as a function of distance from F nucleus along extension of F−F bond (upper curve) and perpendicular to F−F bond (lower curve). The van der Waals radius of the F atom is 1.50 Å.
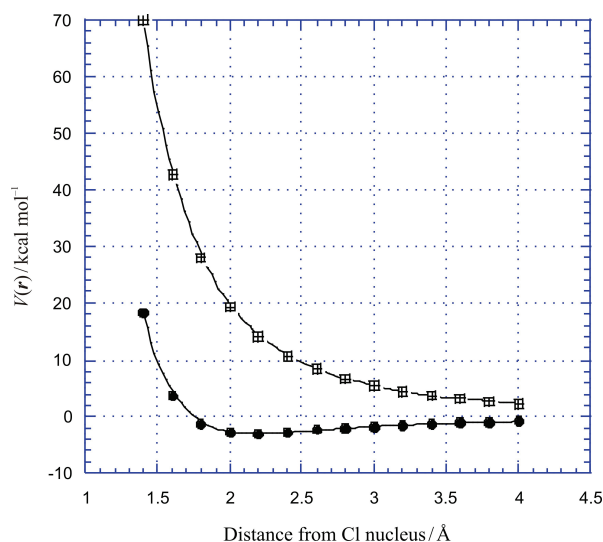
Figure 4. Computed electrostatic potential $V(r)$ of Cl_2 as a function of distance from Cl nucleus along extension of Cl−Cl bond (upper curve) and perpendicular to Cl−Cl bond (lower curve). The van der Waals radius of the Cl atom is 1.76 Å.

HCN

The HCN molecule is a strong hydrogen bond donor. Reasons for this are evident in Figure 6; $V(\mathbf{r})$ along the extension of the C−H bond is still nearly 20 kcal mol^{-1} at double the van der Waals radius of 1.17 Å. What is particularly interesting is that $V(\mathbf{r})$ perpendicular to the molecular axis at the hydrogen is also strongly positive considerably beyond the van der Waals radius (Figures 1 and 6). This is in contrast to the negative potentials on the lateral sides of many other covalently-bonded atoms
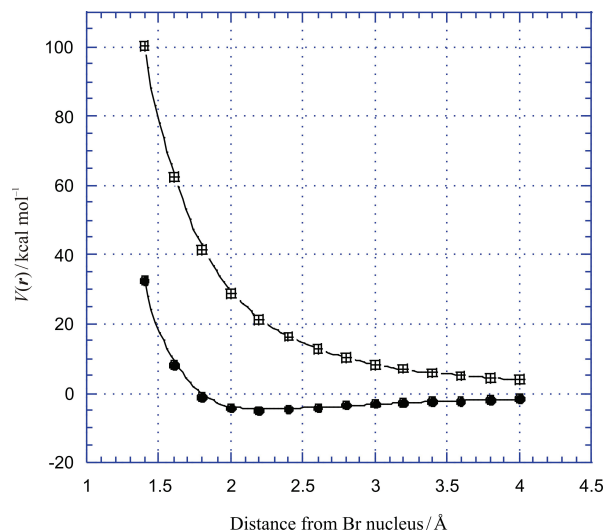
Figure 5. Computed electrostatic potential $V(r)$ of Br_2 as a function of distance from Br nucleus along extension of Br−Br bond (upper curve) and perpendicular to Br−Br bond (lower curve). The van der Waals radius of the Br atom is 1.85 Å.
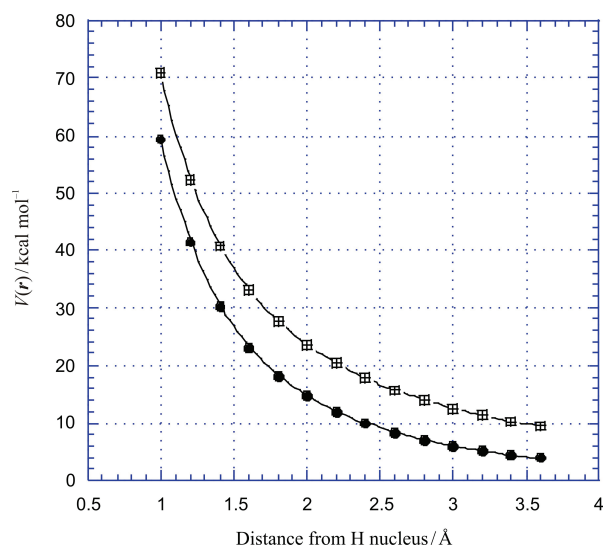

Figure 7. Computed electrostatic potential $V(r)$ of HCN as a function of distance from C nucleus perpendicular to molecular axis (upper curve), from N nucleus perpendicular to axis (middle curve) and from N nucleus along extension of C≡N bond (lower curve). The van der Waals radii of the C and N atoms are 1.70 and 1.55 Å, respectively.

is perpendicular to the axis at the nitrogen reflects the π electrons of the C≡N triple bond; Figure 1 shows that on the surface their negative potential blends into that of the nitrogen lone pair. Perpendicular to the carbon, however, $V(r)$ remains positive (Figure 7) and quickly decreases.

NH₃

Ammonia is also a hydrogen bond donor, although not as strongly so as HCN; $V(r)$ along the extensions of the bonds to the hydrogens is much weaker in NH_3 than in HCN. (Compare Figures 8 and 6, and Figures 2 and 1.) When $V(r)$ is plotted perpendicular to an N−H bond of NH_3 at the H (Figure 8), toward the symmetry axis, it is initially less than along the N−H extension but then becomes greater as the effects of the other hydrogens are felt. However going in the opposite perpendicular direction at H, away from the symmetry axis, an outer portion of the very extended lone pair region of the nitrogen is entered, as can be seen in Figure 2, and $V(r)$ becomes negative (Figure 8).

NH₃ should be a better hydrogen bond or σ-hole bond acceptor than HCN; Figure 9 shows $V(r)$ along the symmetry axis in the nitrogen lone pair region to be much more negative in NH_3 than in HCN, Figure 7. In each case, the overall $V(r)$ minimum is located within the van der Waals radius, 1.55 Å, and hence within the $\rho(r) = 0.001$ au molecular surface. The $V_{S,min}$ on this surface, given in Table 1, are −46.3 kcal mol⁻¹ (NH_3) and −32.9 kcal mol⁻¹ (HCN).

Figure 6. Computed electrostatic potential $V(r)$ of HCN as a function of distance from H nucleus along extension of C−H bond (upper curve) and perpendicular to molecular axis (lower curve). The van der Waals radius of the H atom is 1.17 Å.

(Figures 3−5 and Table 1), and is due to the hydrogen atom having just a single electron, which is involved in the bond. Figures 1 and 6 account for the fact that hydrogen bonding (unlike σ-hole bonding) is often nonlinear.[33]

When moving along the molecular axis in the other direction, away from the nitrogen, its negative lone pair potential is quickly encountered, at less than 1 Å (see Figure 7). It also persists past twice the van der Waals radius (1.55 Å). The weaker negative region that
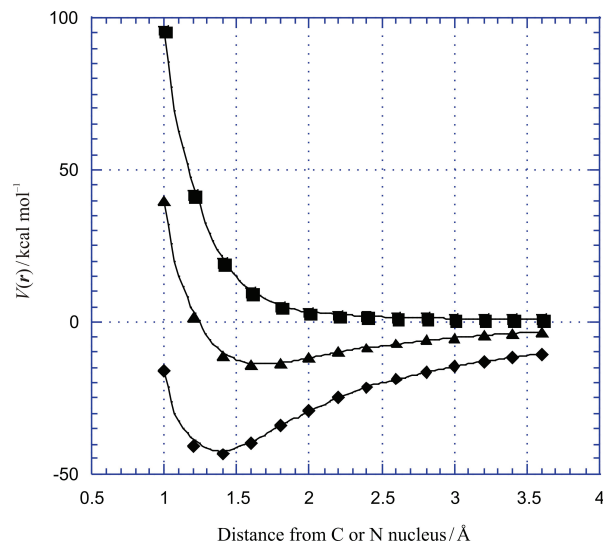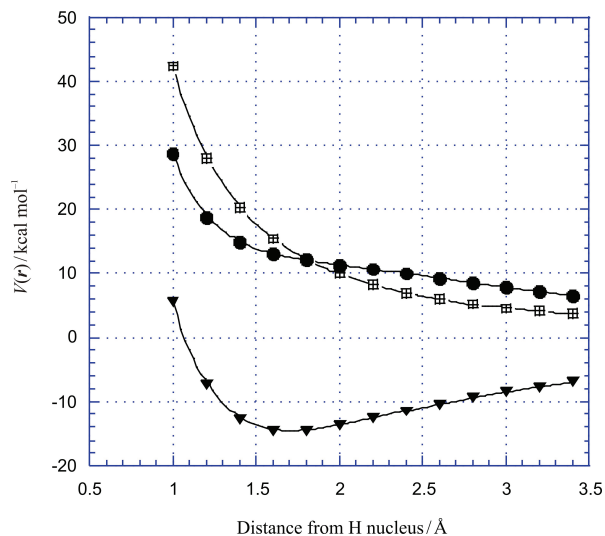
Figure 8. Computed electrostatic potential $V(r)$ of NH_3 as a function of distance from an H nucleus along extension of N−H bond (upper curve, squares), perpendicular to N−H bond toward symmetry axis (middle curve, circles), and perpendicular to N−H bond away from symmetry axis (lower curve). The van der Waals radius of the H atom is 1.17 Å.
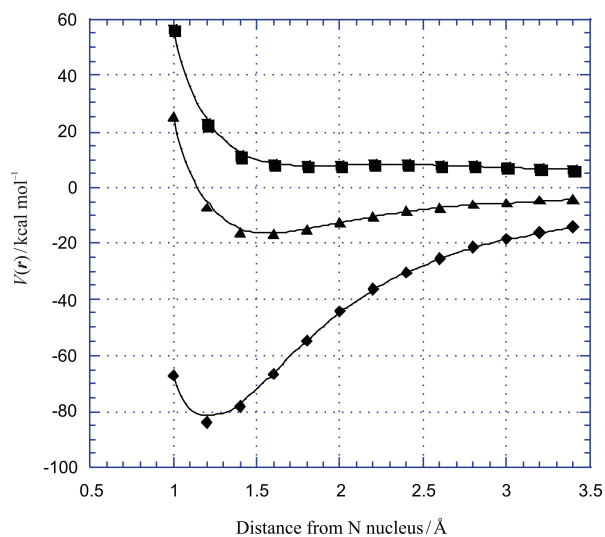

Figure 9. Computed electrostatic potential $V(r)$ of NH_3 as a function of distance from N nucleus along symmetry axis away from lone pair region (upper curve), along extension of H−N bond into lone pair region (middle curve), and along symmetry axis into lone pair region (lower curve). The van der Waals radius of the N atom is 1.55 Å.

Figures 2 and 9 also bring out the size of the lone pair region in NH_3. On the extension of each H−N bond away from the nitrogen, which makes an angle of 67° with the symmetry axis, $V(r)$ still reaches −16 kcal mol^{-1} at the van der Waals radius (Figure 9). On the other hand, along the symmetry axis away from the lone pair region, $V(r)$ drops to 10 kcal mol^{-1} and then levels off.

C_6H_6

A noteworthy feature of benzene is the extent of the negative potential due to the π electrons. Above or below the ring, once past the carbon van der Waals radius of 1.70 A, $V(r)$ is approximately uniform, nearly as negative above the carbons as above the center of the ring, Figure 10. It still becomes weakly negative even above the hydrogens, Figure 11. Along the extensions of the C−H bonds, Figure 11, $V(r)$ is similar in form to the
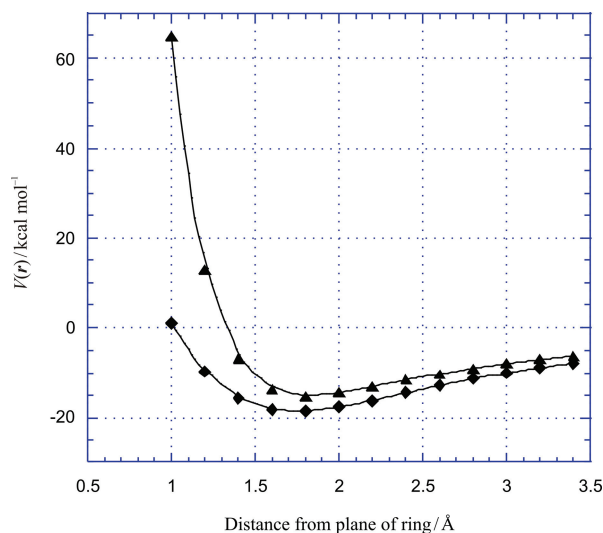

Figure 10. Computed electrostatic potential $V(r)$ of C_6H_6 as a function of perpendicular distance from the plane of the ring, at a carbon nucleus (upper curve) and at the midpoint of the ring (lower curve). The van der Waals radius of the C atom is 1.70 Å.
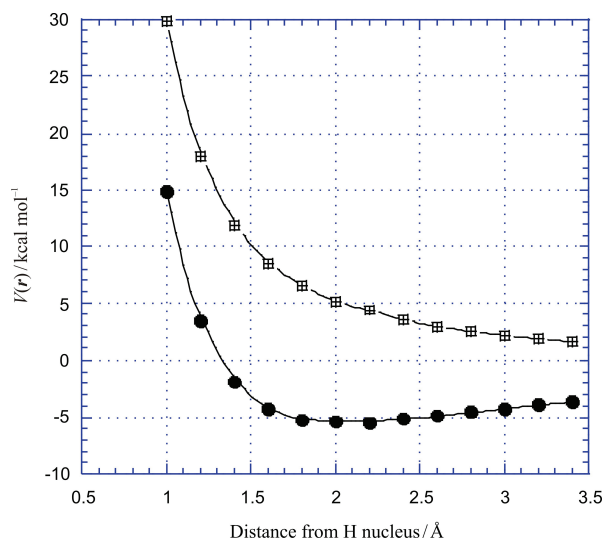

Figure 11. Computed electrostatic potential $V(r)$ of C_6H_6 as a function of distance from an H nucleus along extension of C−H bond (upper curve) and perpendicular to molecular plane (lower curve). The van der Waals radius of the H atom is 1.17 Å.
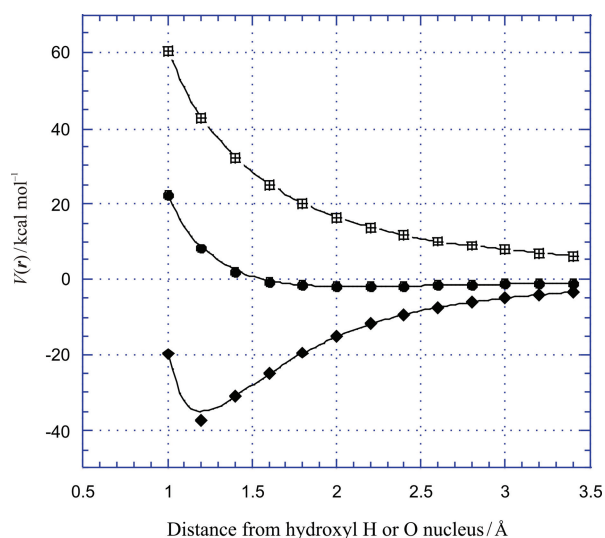
Figure 12. Computed electrostatic potential $V(r)$ of CH_3OH as a function of distance from hydroxyl H nucleus along extension of O−H bond (upper curve), perpendicular to C-O-H plane at H nucleus (middle curve) and perpendicular to C-O-H plane at O nucleus (lower curve). The van der Waals radii of the H and O atoms are 1.17 and 1.52 Å, respectively.
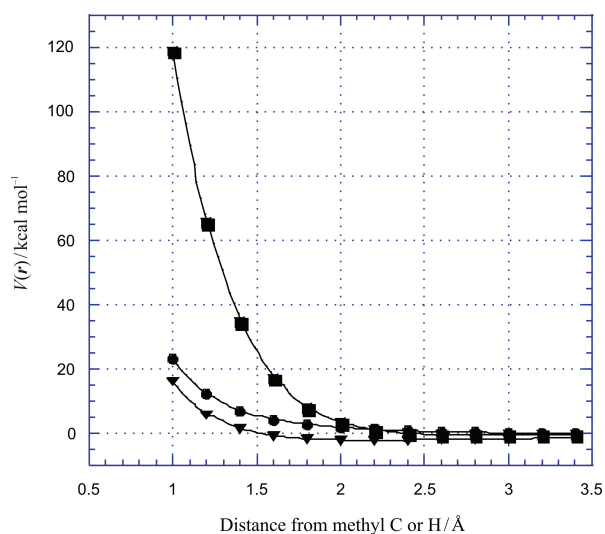

Figure 13. Computed electrostatic potential $V(r)$ of CH_3OH as a function of distance from C nucleus perpendicular to C-O-H plane (upper curve), from a methyl H nucleus along extension of C−H bond (middle curve) and from a methyl H perpendicular to C-O-H plane (lower curve). The van der Waals radii of the C and H atoms are 1.70 and 1.17 Å, respectively.

corresponding curve for the N−H bond in NH_3, but less positive. Overall, the $V(r)$ of benzene does not reach the magnitudes, beyond its van der Waals radii, of those of NH_3 and HCN. (For a recent discussion of the $V(r)$ of benzene and some of its derivatives, see Suresh and Gadre.)[36]

CH₃OH

Figures 12 and 13 focus, respectively, upon the hydroxyl and the methyl groups of methanol. On the extension of the O−H bond, $V(r)$ resembles its counterpart in NH_3, but is stronger. However going away from the hydrogen in the direction perpendicular to the C-O-H plane, $V(r)$ soon becomes quite weak and even slightly negative, reflecting the influence of the oxygen lone pairs. Thus a hydrogen bond in which this OH group is the donor is likely to be closer to linearity than one involving the hydrogens of NH_3 and HCN. The $V(r)$ curve perpendicular to the C-O-H plane at the oxygen is qualitatively like those going into the lone pair regions of HCN, Figure 7, and NH_3, Figure 9, but weaker, since it does not go into the most negative parts of the oxygen lone pairs.

Finally, the methyl hydrogen $V(r)$ in Figure 13 are somewhat similar to those of benzene, Figure 11. Here the slightly negative values in one direction are due to a nearby oxygen lone pair.

CONCLUSIONS

We have confirmed that the 0.001 au contour of a molecule's electronic density typically lies beyond the van der Waals radii of its component atoms. The importance of this is in providing assurance that the electrostatic potential on this molecular surface, $V_S(r)$, is indeed relevant to the onset of noncovalent interactions. $V_S(r)$ is what another moiety "sees" as it initially approaches the molecule.

From how far away can a molecule's electrostatic potential be "seen" to a significant degree? This was addressed by plotting $V(r)$ along lines in various directions away from the individual atoms in a group of molecules. The results, in Figures 3−13, show that the key features of $V(r)$ remain evident for some distances after the van der Waals radii and the $\rho(r) = 0.001$ au surfaces, but the details for a given type of atom vary considerably from one molecule to another. For example, compare the changes in the $V(r)$ of HCN (Figure 7) and NH_3 (Figure 9) in advancing 1.00 Å along their symmetry axes in the nitrogen lone pair regions, from the van der Waals radii at 1.55 Å to 2.55 Å. $V(r)$ goes from −40 to −18 kcal mol⁻¹ for HCN, and from −70 to −27 kcal mol⁻¹ for NH_3. The effect is nearly twice as great in the latter case.

The rate of change of $V(r)$ in a particular direction, as just discussed for HCN and NH_3, is important because it represents the electric field exerted upon whatever may be approaching:

$$\varepsilon(\boldsymbol{r}) = -\frac{\partial V(\boldsymbol{r})}{\partial \boldsymbol{r}} \tag{3}$$

Indeed, the stronger field in its lone pair region is why NH_3 is more likely than HCN to produce a decreased stretching frequency ("red shift") in a hydrogen bond or σ-hole bond donor.[37] On the other hand, the field created by the hydrogen in HCN is expected to be stronger than that due to any one of the hydrogens in NH_3. (Compare the slopes of the respective curves in Figures 6 and 8.)

Plots of $V(\boldsymbol{r})$ in different directions, as in Figures 3−13, are a useful complement to representations of $V_S(\boldsymbol{r})$ on molecular surfaces, as in Figures 1 and 2. The former relate to the approach to a site, the latter to the interaction at the site. A good example of these separate roles is provided by Figure 6, which shows two pathways to the hydrogen in HCN; one is along the extension of the C−H bond, the other is perpendicular to it. It is clear that interaction along the C−H extension should eventually yield the more stable complex, by about 10 kcal mol^{-1}. But during much of the approach, the two pathways have similar curvatures, and thus are approximately equally likely from the standpoint of the attracting force being exerted.

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SAŽETAK

Molekulske površine, van der Waalsovi radijusi i elektrostatski potencijali povezani s nekovalentim interakcijama

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Istražena su dva pitanja povezana s korištenjem elektrostatskih potencijala u interpretaciji i predviđanju nekovalentnih interakcija. Prvo, da li je molekulska površina definirana s konturom elektronske gustoće od 0.001 atomskih jedinica razumna i u skladu s njenim odnosom prema van der Waalsovim radijusima atoma koji ju izgrađuju? Drugo, kako se elektrostatski potencijal mijenja s udaljenošću u raznim smjerovima od jezgre kovalentno-povezanih atoma? Pitanja su razmatrana računski, koristeći funkcional gustoće B3PW91/6-31G(d,p).