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Improved electrostatic properties using combined Mulliken and hybridization-displaced charges for radicals

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Abstract Effects of explicit consideration of charges displaced from atomic sites due to atomic orbital hybridization called hybridization-displaced charges (HDC) on dipole moments and surface molecular electrostatic potentials of certain radicals and their complexes with closed-shell molecules have been studied. HDC were computed for several radicals and their complexes at the B3LYP/6–31G** level of theory. At this level, HDC consist of three point charges associated with hydrogen atoms and seven point charges associated with heavy atoms belonging to the second row of the periodic table. HDC are so calculated that the contribution of each atom to the component of molecular dipole moment arising due to atomic orbital hybridization is preserved. It is found that dipole moments and electrostatic potentials of the systems studied here can be obtained with a significantly improved accuracy using a combination of Mulliken charges and HDC over that obtained by Mulliken charges only.

Keywords Atomic orbital hybridization · Dipole moment · Hybridization-displaced charges · Molecular electrostatic potential · Pointcharge distribution

Introduction

The concept of point charges located on atomic sites in molecules has proved to be very useful in the study of molecular properties and intermolecular interactions [1–4]. These charges are widely used in molecular mechanical and molecular dynamics simulation studies [1–5]. Point charges located at atomic sites may be obtained by theoretical or experimental methods or by fitting to surface molecular electrostatic potentials (MEP) [6–11]. The different theoretical methods partition the total electron density in various ways and assign the different portions to the individual atoms. The Mulliken population analysis scheme [6] belongs to this category and is one of the commonly used ones. The experimental methods are based on interpretation of experimental data, e.g., those based on X-ray diffraction intensity distribution, IR intensity distribution, and NMR spectral features [8]. The Mulliken and the other electron density partitioning schemes have a serious inbuilt weakness each. That is, they preserve only the total electron count and place the calculated point charges exactly at the atomic nuclear sites. It cannot be justified since on molecular formation, the electronic charge centers may be significantly shifted from the nuclear sites. Wherever off-nuclear site charges have been properly considered, improvement in calculated electrostatic properties has been obtained [2, 4]. The existence of lone pairs demands that we go beyond the atomic site-based point charge schemes.

A point charge distribution cannot be considered to be satisfactory until it satisfies the following conditions: (i) It reproduces the total molecular dipole moment obtained at the SCF level satisfactorily; and (ii) It reproduces the surface MEP features obtained using the continuous electron density distribution on the van der Waals surfaces of molecules satisfactorily. As MEP is intimately related to intrinsic molecular properties and is quite sensitive to chemical changes [12, 13], the (ii) condition serves as a rigorous test of accuracy of charge distribution. The point charges calculated using the theoretical methods mentioned above usually do not satisfy the two conditions consistently. However, the MEP-derived charges [10, 11] fulfill the two

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above-mentioned criteria except in certain respects, e.g., for MEP features of homonuclear diatomics and π-electron systems. To improve the theoretical description of point charges, we have introduced the concept of hybridization displacement charges that are renamed here as hybridiza-tion-displaced charges (HDC), and used the same to calculate electrostatic properties of several molecules using both semiempirical and *ab initio* wave functions [2, 14–17]. HDC arise due to hybridization of atomic orbitals and correspond to the hybridization dipole moment [14–17]. A satisfactory point charge distribution consisting of both the on- and off-nuclear site components may be obtained by combining HDC with the atomic site-based charges, e.g., the Mulliken charges [15–17]. HDC have been shown to be related to atomic dipole polarizability and bonding in molecules [16, 17]. It has been found that many covalently bonded atoms of groups V-VII have regions of both positive and negative MEP on their surfaces [18]. It shows that the practice of assigning single point charges to atoms is not always valid [18]. An alternative to it is provided by the HDC scheme that associates several different point charges with each atom.

Removal of a hydrogen atom of a molecule would cause a change in the valence state of the atom to which the hydrogen atom was attached. One of the possible ways to quantify this change is provided by HDC. An important question in this context is whether a combination of HDC with the charges obtained by other popular methods, e.g., the Mulliken scheme can provide an improved charge distribution or not. We have shown here that a combination of HDC with Mulliken charges improves the calculated dipole moments and surface MEP values of radicals and their complexes with closed shell molecules over those obtained using the Mulliken charges alone significantly. We preferred to consider a combination of HDC with the Mulliken charges since the latter are frequently used.

Some of the radicals studied here are of great impor-tance. The HO˙ radical occurs in the atmosphere, acts as a detergent by reacting with many pollutants in the tropo-sphere [19] and oxidizes biomolecules causing harmful effects [20]. The HC˙ radical is an important intermediate in many types of reactions including combustion and those involved in atmospheric and interstellar processes [21]. The H$_3$C˙ radical is one of the most important compounds of hydrocarbon plasma and plays a key role in the decompo-sition of diamond layers [22]. Abstraction of certain hydrogen atoms of the nucleic acid bases or nucleotides and fission of the NR (R=H or carbon atom of the sugar ring) bonds have been observed [23, 24]. These processes generally involve the N9H9 bonds of the purine bases and the N1H1 bonds of the pyrimidine bases [23, 24]. Due to these reasons, the radicals formed by removal of the H9 atoms of the purine bases and H1 atoms of the pyrimidine

bases of nucleic acids were considered here. Importance of other radicals in different contexts is discussed elsewhere [25].

Definition of HDC

The total dipole moment (μ^t) of a molecule is a vector sum of two components, i.e., μ^{net} and μ^h. The first one of these components arises due to the net charges located at the atomic sites while the second one arises due to the shifted electronic charges from the atomic sites owing to atomic orbital hybridization. We can calculate μ^{net} using the net Mulliken charges located at the atomic sites. The αth Cartesian component of μ^h can be written as [14–17]

$$\mu_\alpha^h = (KD_\alpha)(Q_\alpha/K) = D'_\alpha Q'_\alpha \qquad (\alpha = x, y, z) \qquad (1a)$$

where,

$$D_\alpha = (ns|\alpha|mp_\alpha) \quad (n = 1, 2, 3 \text{ etc. and } m = 2, 3, 4 \text{ etc.}) \qquad (1b)$$

$$Q_\alpha = -P_{ns,mp\alpha} \qquad (1c)$$

where n and m are principal quantum numbers associated with the s and p_α atomic orbitals of a given atom respectively, and P represents the density matrix which is obtained from the linear combination coefficients of atomic orbitals in molecular orbitals [26]. As the elements of the density matrix represent different components of electron density, we need a definition that combines the different components suitably yielding the electron density shifted from the given atomic site in terms of which the corresponding hybridization dipole moment can be defined. K in Eq. (1a) is a parameter that may be adjusted to reproduce an appropriate physical property. D'_α is the distance of charge Q'_α along the α (α=x, y or z) direction. The magnitude of the total hybridization dipole moment μ^h and the HDC displacement (D) are given in terms of their Cartesian components as follows:

$$\mu^h = \left(\mu^h{}_x{}^2 + \mu^h{}_y{}^2 + \mu^h{}_z{}^2\right)^{1/2} \qquad (2)$$

and

$$D = \left(D_x^2 + D_y^2 + D_z^2\right)^{1/2} \qquad (3)$$

A straightforward procedure would involve calculation of the above-mentioned quantities using Gaussian-type orbitals. However, for computational convenience, we

evaluated these quantities using Slater type atomic orbitals (STOs). Using STOs we find

$$D_\alpha = \frac{2^a \zeta_s^b \zeta_{p\alpha}^c (a!)}{\sqrt{3}\sqrt{(2n(s)!)}\sqrt{(2m(p_\alpha)!)} d^{a+1}} \quad (4)$$

$$(\alpha = x, \ y, \ z)$$

where $a = n(s) + m(p_\alpha) + 1$, $b = n(s) + 1/2$, $c = m(p_\alpha) + 1/2$, $d = \zeta_s + \zeta_{p\alpha}$. Here $n(s)$ and $m(p_\alpha)$ are the principal quantum numbers of the s and p_α ($\alpha = $ x,y,z) atomic orbitals respectively while ζ_s and $\zeta_{p\alpha}$ are the corresponding Slater exponents. As shown by Eq. (4), for given $n(s)$ and $m(p_\alpha)$ values, D_α (α=x,y,z) depends only on the exponents of the s and p_α STOs. Thus D_α (α=x,y,z) and hence D are fixed for given s and p_α orbitals having specific Slater exponents. Since $\zeta_{px}=\zeta_{py}=\zeta_{pz}$, we get $D_x=D_y=D_z$. Then the total HDC value (Q) is obtained as

$$Q = \mu^h/R = \left[\left(Q_x^2 + Q_y^2 + Q_z^2 \right) \big/ 3 \right]^{1/2}. \quad (5)$$

Thus Q is the root-mean-square of Q_x, Q_y and Q_z. Obviously, Eq. (5) would hold true even if the s orbital belongs to a different quantum number than that to which the three orbitals p_X, p_Y and p_Z belong.

The electronic charge Q (HDC) would be displaced from the given atom in the direction specified by the following angles in spherical polar coordinates

$$\varphi = \tan^{-1}\left(\mu_y \big/ \mu_x \right) \quad (6)$$

and

$$\theta = \cos^{-1}\left(\mu_z / \mu^h \right) \quad (7)$$

Details of HDC calculations

Density matrices of some radicals, neutral molecules and their complexes were obtained using the density functional theory (DFT) employing the B3LYP hybrid density functional [27, 28]. In one case, additional calculations were also performed using the BHandH and BHandHLYP functionals [29]. In each case, the 6–31G** basis set was used. As the results computed employing the BHandH and BHandHLYP functionals [29] were similar, those obtained using the latter functional only are presented here. When the 6–31G** basis set is used, HDC consist of three point charges associated with hydrogen atoms and seven point charges associated with heavy atoms belonging to the second row of the periodic table. The parameter K was fixed for different atoms employing the criterion of best possible agreement between the surface MEP values obtained using (Mulliken + HDC) charges and those obtained using MEP-derived CHelpG charges at the van der Waals surfaces of molecules [15–17]. To calculate HDC, as an approximation, the density matrix elements were considered as having been obtained using STOs as basis functions. This approximation is justified as contractions of gaussians are similar to the corresponding STOs. The Slater exponents of STOs of the innermost (n=1) atomic shells of atoms were taken to be the same as those given in the literature [26]. However, the ζ values of higher shells were adjusted so as to obtain the best possible agreement between the dipole moments of several molecules calculated using the (Mulliken + HDC) charges and those obtained by rigorous calculations. It must be noted that we adjusted ζ values of STOs only for HDC calculations, and no changes in the exponents of gaussians used in the DFT calculations were made. The adjusted values of K and ζ for different atoms have already been reported [16]. Due to displacement of the negative charge (Q) from an atomic site, an equal amount of positive charge would be acquired by it, and thus the overall charge state (e.g., neutral, anionic, or cationic) of the molecule under consideration would remain unchanged. In the present calculations, mixing of only s and p types of atomic orbitals was considered, and d or higher atomic orbitals were not included.

A limitation of the present computational approach may be noted. That is, here the HDC are so calculated that the atomic contributions to only the total molecular dipole moment are preserved (approximately), and there is no provision to preserve the atomic contributions to the higher electric molecular moments. Therefore, the present approach would show weakness where quadrupole and/or higher electric moments would control molecular electrostatic properties, e.g., MEP, strongly. The Windows version of the Gaussian 98 program (G98W) [30] was used to obtain density matrices while the GaussView program [31] was used to visualize molecular structures. HDC were computed and maps of MEP on van der Waals surfaces visualized using locally developed software.

Results and discussion

The calculated dipole moments of 28 systems that are either isolated radicals or complexes of radicals with closed-shell molecules obtained by the following four different methods are presented in Table 1: (a) As expectation values of the electric dipole operator at the B3LYP/6–31G** level of theory (and also at the BHandHLYP/6–31G** level in one case), (b) Using the classical definition and point charges calculated using the CHelpG algorithm, (c) As in (b) but using (Mulliken + HDC) point charges, and (d) As in (b) but using Mulliken point charges alone. The last column

Table 1 Dipole moments (Debye) of radicals and complexes calculated using various methods or charges obtained at the B3LYP/6–31G** level, unless otherwise specified

S.No.	Radical/complex	Rigorous calculation	CHelpG charge	Mulliken + HDC charge	Mulliken charge	% change[a]
1	HO·	1.73	1.73	1.65	1.53	7.8
2	HOO·	2.26	2.25	2.25	2.15	4.7
3	$H_2N·$	1.97	2.05	1.85	1.56	18.6
4	HC·	1.37	1.21	0.98	0.47	108.5
5	$H_3C·$	0.0	0.0	0.0	0.0	0.0
6	OHC·	1.65	1.62	2.09	2.23	6.3
7	$O_3C^{·-}$	0.20	0.19	0.03	0.03	0.0
8	H_2O-HO·	3.87	3.89	3.78	3.59	5.3
9	NH_3-HO·	4.62	4.64	4.36	4.05	7.7
10	H_2O-OHC·	0.93	0.95	0.80	1.49	46.3
11	H_2O-$O_3C^{·-}$	0.22	0.28	0.11	0.04	175
12	NH_3-$O_3C^{·-}$	1.42	1.45	1.39	1.47	5.4
13	HF-$O_3C^{·-}$	0.33	0.37	0.24	0.17	41.2
14	NH_3-OHC·	4.42	4.28	4.60	4.20	9.5
15	HF-HO·	1.87	1.95	1.78	1.72	3.5
16	HF-OHC·	2.47	2.27	2.90	2.32	25.0
17	$NH_2COH_2C·$	3.68	3.71	3.71	3.53	5.1
18	$CH_3COHN·$	1.61	1.64	2.03	2.13	4.7
19	$NH_2CO·$	3.62	3.49	3.29	3.23	1.9
20	COHHN·	2.37	2.31	2.20	2.85	22.8
21	$NH_2CONH·$	2.46	2.45	2.33	2.33	0.0
22	$CH_3H_2C·$	0.26	0.23	0.35	0.26	34.6
23	$CH_3O·$	1.98	1.98	2.69	2.67	-0.7
24	U·[b]	2.93	2.95	3.95	3.98	0.8
25	C·[b]	7.26	7.30	7.72	7.41	-4.2
26	T·[b]	3.80	3.81	4.82	4.84	0.4
27	A·[c]	5.04	5.02	4.50	4.19	7.4
28	G·[c]	7.28[d]	7.25[d]	6.25[d]	5.84[d]	7.0
		(7.09)[e]	(7.05)[e]	(5.98)[e]	(5.58)[e]	(7.2)[e]

[a] Percentage difference between the dipole moments obtained using Mulliken charges and (Mulliken + HDC) charges. For the meaning of % change and its sign, see text

[b] In uracil, thymine and cytosine radicals, the hydrogen atom was removed from the N1 position. See Ref. [35] for atomic numbering

[c] In adenine and guanine radicals, the hydrogen atom was removed from the N9 position. See Ref. [35] for atomic numbering

[d] Obtained by B3LYP/6–31G** method [27, 28]

[e] Obtained by BHandHLYP/6–31G** method [29]

presents the percentage changes in dipole moments obtained in going from Mulliken to the (Mulliken + HDC) charges. The signs of the percentage changes were decided as follows. If, in going from the Mulliken charges to the (Mulliken + HDC) charges in a given case, the agreement of the calculated dipole moment with that obtained rigorously as defined in (a) above is improved, the percentage change is given the '+' sign, otherwise it is given the '-' sign. The calculated most negative surface MEP values are shown in Table 2 while the locations of different HDC components in some cases with respect to the corresponding atoms are given in Table 3.

The case of $CO_3^{·-}$ deserves a special mention. A time-resolved resonance Raman spectroscopic study has shown that the geometry of this radical conforms to the C_2v point group [32]. The geometry of this radical optimized at the B3LYP/6–31G** level of theory had D_3h symmetry while that optimized at the MP2/6–31G** level had C_2v symmetry. Therefore, in this case, for the B3LYP/6–31G** calculations of dipole moment, charges and surface MEP, the geometry optimized at the MP2/6–31G** level was used.

The calculated MEP maps on the van der Waals surfaces of some cases are shown in Figs. 1(a-d) and 2(a-d) for the sake of a detailed comparison of surface MEP features obtained using CHelpG and (Mulliken + HDC) charges. In these maps, different ranges of MEP values including the most negative and highest ones are shown using color codes. Further, the green patches located near the atomic sites (almost coincident with the atomic sites or somewhat displaced from the same) in the surface MEP maps obtained using (Mulliken + HDC) charges correspond to HDC. From

Table 2 MEP values (kcal mol⁻¹) (V^x) on the van der Waals surfaces of molecules calculated using charges denoted by x where x = CHelpG, M + HDC and M (M stands for Mulliken) obtained at the B3LYP/ 6–31G** level of theory, unless otherwise specified

S.No.	Radical/complex	Near atom	MEP			% Change[a]
			V^{CHelpG}	$V^{HDC + M}$	V^M	
1	HO·	O	-32.3	-31.8	-28	12.0
2	HOO·	O	-33.7	-31.1	-30.5	2.0
3	H_2N·	N	-45.3	-42.6	-35.1	21.4
4	HC·	C	-16.3	-18.7	-6.40	192.2
5	H_3C·	C	-12.1	-10.2	-10.2	0.0
6	OHC·	O	-20.9	-31.4	-32.0	3.1
7	O_3C·⁻	O1[b]	-139.4	-139.8	-141.6	1.3
		O2[b]	-174.2	-174.8	-177.1	1.3
8	H_2O-HO·	O(HO·)	-46.0	-45.7	-42.5	7.5
9	NH_3-HO·	O(HO·)	-51.8	-50.5	-46.8	7.9
10	H_2O-OHC·	C(OHC·)	-42.6	-38.3	-34.1	12.3
11	H_2O-O_3C·⁻	C(O_3C·⁻)	-151.2	-150.8	-153.3	1.6
12	NH_3-O_3C·⁻	C(O_3C·⁻)	156.7	-156.1	-158.7	1.6
13	HF-O_3C·⁻	C(O_3C·⁻)	-151.4	-150.7	-152.7	1.3
14	NH_3-OHC·	C(OHC·)	-33.2	-39.7	-39.4	-0.8
15	HF-HO·	O(HO·)	-39.2	-37.6	-35.3	6.5
16	HF-OHC·	C(OHC·)	-26.8	-31.9	-32.2	0.9
17	NH_2COH_2C·	O	-56.1	-58.4	-54.5	7.2
18	CH_3COHN·	O	-40.3	-41.9	-40.1	4.5
19	NH2CO·	O	-38.1	-42.1	-42.5	0.9
20	COHHN·	O	-47.9	-38.8	-50.9	23.8
21	NH_2COHN·	O	-49.3	-46.7	-44.1	5.9
22	CH_3H_2C·	C	-11.0	-22.1	-18.9	-16.9
23	CH_3O·	O	-32.0	-41.2	-38.9	-5.9
24	U·[c]	O2	-46.2	-46.2	-43.0	7.4
26	T·[c]	O2	-48.6	-48.7	-45.6	6.8
25	C·[c]	O2	-54.7	-56.7	-53.5	-6.0
27	A·[d]	N9	-53.0	-46.7	-44.4	5.2
28	G·[d]	i	-53.1(N9) [j]	-48.3(O6)[j]	-45.4(O6)[j]	
			-56.1(N9)[k]	-50.4(N9)[k]	-46.9(N9)[k]	7.5

[a] Percentage change in MEP in going from Mulliken charges to (Mulliken + HDC) charges. For the meaning of sign, see text

[b] In O_3C·⁻, the oxygen atom lying on the C_2 axis is O1 while any of the other two oxygens is O2

[c] In uracil, thymine and cytosine radicals, the hydrogen atom was removed from the N1 position. See Ref. [35] for atomic numbering

[d] In adenine and guanine radicals, the hydrogen atom was removed from the N9 position. See Ref. [35] for atomic numbering

[i] Atomic positions are given below the most negative MEP values. See text for explanation

[j] Obtained by B3LYP/6–31G** method Ref. [27, 28]

[k] Obtained by BHandHLYP/6–31G** method Ref. [29]

Figs. 1 and 2, it is clear that the surface MEP features obtained using CHelpG and (Mulliken + HDC) charges are very similar. The effects of combining HDC with Mulliken charges on molecular dipole moments and most negative surface MEP values in different cases are discussed below.

1. Dipole moments

   The data presented in Table 1 reveal the following information:

   (i) In some cases, e.g., HC·, CH3O· and U·, the dipole moments obtained using Mulliken charges are quite different from those calculated rigorously at the B3LYP/6–31G** level. The experimental dipole moments [33, 34] of the HO·, HC· radicals are 1.66 and 1.45 Debye, respectively. The calculated dipole moments of these radicals rigorously at the B3LYP/6–31G** level are 1.73 and 1.37 Debye, those obtained using CHelpG charges are 1.73 and 1.21 Debye, those obtained using Mulliken charges are 1.53 and 0.47 Debye while those obtained using (Mulliken + HDC) charges are 1.65 and 0.98 Debye, respectively. Thus in going from Mulliken to (Mulliken + HDC) charges, the dipole moment of the HC· radical gets more than doubled,

Table 3 Amounts of HDC (in the unit of magnitude of electric charge) associated with different atoms in some molecules and their locations in terms of distances (Å) and directions of displacements from the corresponding atoms

S.No.	Radical	Atom and orbital mixing	Amount of HDC[a]	Distance of HDC from the atom	HDC location and displacement direction
1.	HO·	O 1 (1s, 2p)	-0.022 (-0.057)	0.114	Inside OH bond
		2 (2s, 2p)	-0.124 (-0.312)	0.040	Outside OH bond
		3 (1s, 3p)	-0.017 (-0.054)	0.073	Inside OH bond
		4 (2s, 3p)	-0.106 (-0.340)	0.021	Outside OH bond
		5 (3s, 2p)	-0.544 (-1.384)	0.021	Outside OH bond
		6 (3s, 3p)	-0.330 (-1.033)	0.022	Outside OH bond
		Total HDC	-1.143 (-3.180)		
		NS	0.818 (2.571)		
		H 1 (1s, 3p)	-0.008 (-0.017)	0.082	Towards O
		2 (2s, 3p)	-0.008 (-0.022)	0.003	Towards O
		Total HDC	-0.016 (-0.040)		
		NS	0.340 (0.345)		
2.	HC·	C 1 (1s,2p)	-0.025 (-0.063)	0.058	Inside C-H bond
		2 (2s,2p)	-0.124 (-0.339)	0.265	Outside C-H bond
		3 (1s,3p)	-0.013 (-0.054)	0.151	Inside C-H bond
		4 (2s,3p)	-0.093 (-0.380)	0.061	Outside C-H bond
		5 (3s,2p)	-0.665 (-1.550)	0.061	Outside C-H bond
		6 (3s,3p)	-0.337 (-1.169)	0.093	Outside C-H bond
		Total HDC	-1.257 (-3.555)		
		NS	1.171 (3.356)		
		H 1 (1s,3p)	-0.004 (-0.009)	0.082	Towards C
		2 (2s,3p)	-0.006 (-0.018)	0.003	Towards C
		Total HDC	-0.010 (-0.028)		
		NS	0.097 (0.128)		
3.	H₂N·	N 1(1s, 2p)	-0.028 (-0.051)	0.073	Inside HHN angle
		2 (2s, 2p)	-0.201 (-0.343)	0.165	Outside HNH angle
		3 (1s, 3p)	-0.021 (-0.057)	0.111	Inside HNH angle
		4 (2s,3p)	-0.171 (-0.409)	0.011	Outside HNH angle
		5 (3s,2p)	-0.594 (-1.156)	0.011	Outside HNH angle
		6 (3s,3p)	-0.449 (-1.074)	0.035	Outside HNH angle
		Total HDC	-1.464 (-3.090)		
		NS	0.948 (2.374)		
		H 1 (1s,3p)	-0.008 (-0.012)	0.082	Towards N
		2 (2s,3p)	-0.010 (-0.017)	0.003	Towards N
		Total HDC	-0.018 (-0.029)		
		NS	0.276 (0.268)		
4.	OHC· (∠HCO=152˚, A = HDC compo- nent)	C 1(1s,2p)	-0.044 (-0.009)	0.058	Inside ∠HCO (∠HAO=157)
		2(2s,2p)	-0.263 (-0.010)	0.265	Outside∠HCO(∠HAO=130)
		3 (1s,3p)	-0.047 (-0.035)	0.151	Inside ∠HCO(∠HAO=162)
		4 (2s,3p)	-0.294 (-0.199)	0.061	Outside∠HCO(∠HAO=148)
		5 (3s,2p)	-1.037 (-0.328)	0.061	Outside∠HCO(∠HAO=147)
		6(3s,3p)	-0.810 (-0.194)	0.093	Outside∠HCO(∠HAO=145)
		Total HDC	-2.495 (-0.775)		
		NS	2.679 (0.951)		
		O 1 (1s,2p)	-0.025 (-0.052)	0.114	Inside C-O bond
		2 (2s,2p)	-0.167 (-0.295)	0.040	Outside C-O bond
		3 (1s,3p)	-0.021 (-0.044)	0.073	Inside C-O bond
		4 (2s,3p)	-0.143 (-0.270)	0.021	Outside C-O bond
		5 (3s,2p)	-0.583 (-1.338)	0.021	Outside C-O bond
		6 (3s,3p)	-0.339 (-0.779)	0.022	Outside C-O bond
		Total HDC	-1.278 (-2.778)		
		NS	0.990 (2.439)		
		H 1(1s,3p)	-0.006 (-0.011)	0.082	Towards C
		2 (2s,3p)	-0.029 (-0.024)	0.003	Towards C
		Total HDC	-0.035 (-0.035)		
		NS	0.136 (0.116)		

NS stands for nuclear site. The HDC values in the corresponding closed shell molecules are also given

[a] The values given in parentheses in the cases of HO· , H₂N· , HC· and OHC· belong to the corresponding atom in the closed shell molecules, i.e., H₂O, NH₃, CH₂ and HCHO respectively

Fig. 1 Surface MEP maps obtained using CHelpG and (Mulliken + HDC) charges as indicated on the different parts. (**a**) and (**b**): H_2O-$HO^{\cdot}$ radical complex where the most negative MEP value is found near the oxygen atom of the $HO^{\cdot}$ radical; (**c**) and (**d**): $CH_3COHN^{\cdot}$ radical where the most negative MEP value is found near the oxygen atom of the CO group
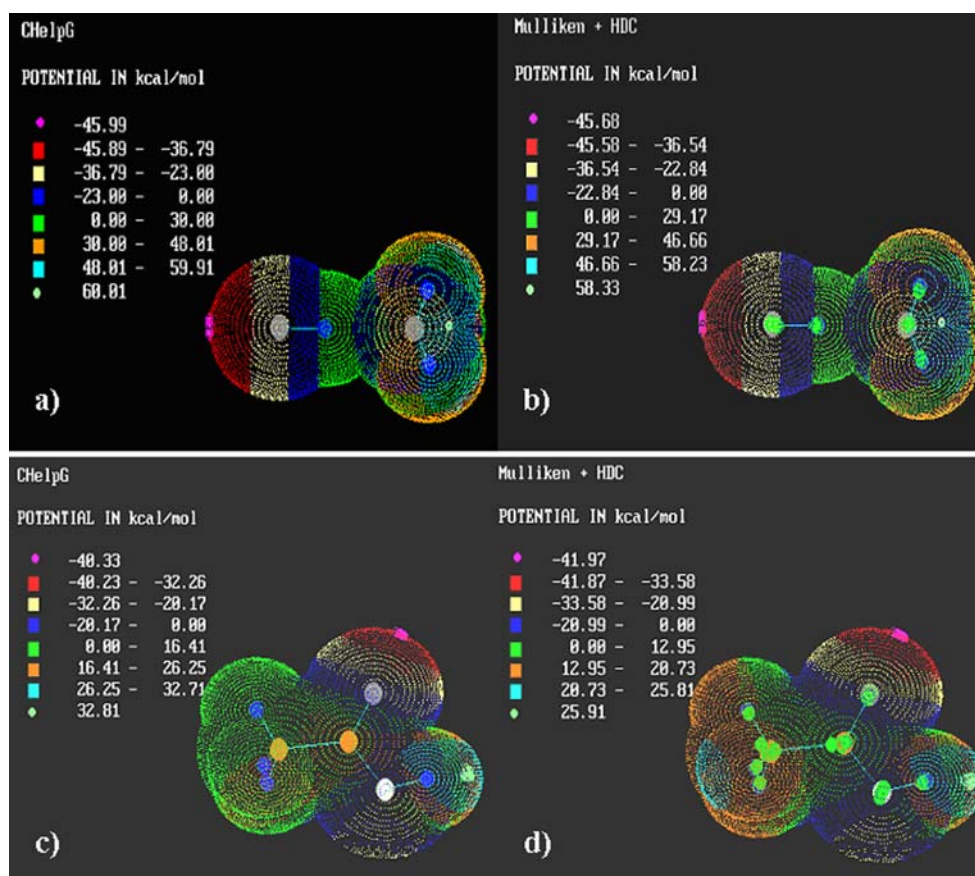
becoming much closer to the experimental or rigorously calculated values [34] than that obtained using Mulliken charges alone.

(ii) As shown by the positive signs of the percentage changes given in Table 1, the agreement with the rigorously calculated dipole moments is improved in all the cases except two, in going from Mulliken to (Mulliken + HDC) charges. Further, the percentage changes are quite large and positive in some cases, e.g., $H_2N^{\cdot}$, $HC^{\cdot}$, $H_2O - OHC^{\cdot}$, $H_2O - CO_3^{-}$, $HF - CO_3^{-}$, $CH_3H_2C^{\cdot}$ and $HCOHN^{\cdot}$. Thus the combination of Mulliken charges with HDC rectifies the shortcoming of the former to a great extent. In two cases, the percentage changes given in Table 1 are negative, but both of these are small. These negative percentage changes may be ascribed to the fact that the Slater exponents of atomic orbitals adjusted considering closed shell atoms [16] may not be equally suitable for radicals.

(iii) For the guanine radical ($G^{\cdot}$), for the reason given in the next subsection, dipole moments and charges were calculated using the B3LYP and BHandH-LYP functionals along with the 6–31G** basis set. The results obtained using both the fuctionals in this case are qualitatively similar (Table 1).

2. MEP values

The calculated most negative MEP values on the van der Waals surfaces of the radicals using the three types of point charges mentioned earlier along with the atomic sites near which these MEP features are located are presented in Table 2. In this table, MEP is denoted by V^x where x represents the charge scheme used, i.e., CHelpG, (Mulliken + HDC) or Mulliken. The MEP values obtained using the CHelpG charges were taken to be standard for comparison with those obtained employing the other two charge distributions. The last column of this table gives the percentage change in MEP in going from Mulliken to (Mulliken + HDC) charges. The signs of percentage changes in MEP given in this column are also based on the criterion adopted for the corresponding column of Table 1. We make the following observations from the MEP maps presented in Figs. 1, 2 and the data presented in Table 2:

(i) The surface MEP features obtained using CHelpG and (Mulliken + HDC) charges are very similar as revealed by Figs. 1 and 2.

(ii) The positive signs of percentage changes in MEP values show that in all except four cases, in going from Mulliken to (Mulliken + HDC) charges, the agreement of the calculated MEP values with

Fig. 2 Surface MEP maps obtained using CHelpG and (Mulliken + HDC) charges as indicated on the different parts. (**a**) and (**b**): Uracil radical where the hydrogen atom attached to the N1 site has been removed and the most negative MEP value is found near the O2 site; (**c**) and (**d**): Adenine radical where the hydrogen atom attached to the N9 site has been removed and the most negative MEP value is also found near the same site. Standard atomic numbering was used (Ref. 35)
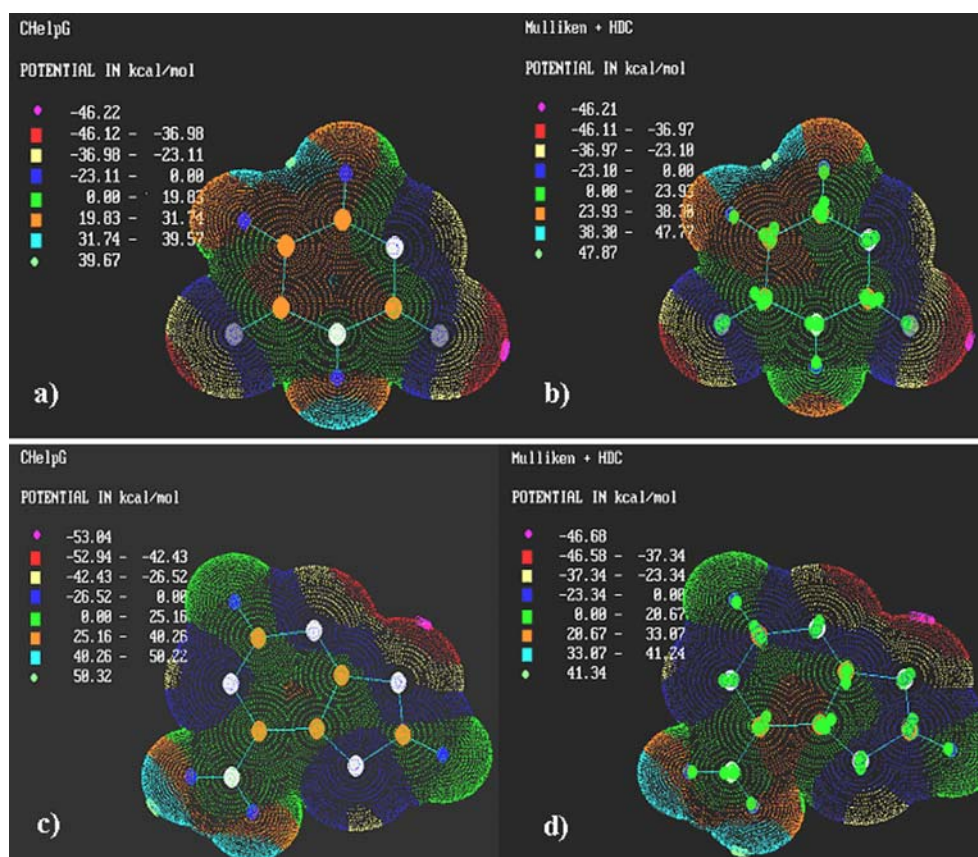
those obtained using CHelpG charges is improved to different extents in different cases. Further, in some cases, e.g., $H_2N^{\cdot}$, $HC^{\cdot}$ and $HCOHN^{\cdot}$, the improvements are quite significant.

(iii) In the case of $CO_3^{\cdot-}$, there are two types of oxygen atoms in view of the C_2v symmetry of the radical [32]. The magnitude of the most negative MEP value near the oxygen atom that lies on the C_2 axis is much less than those near the other two equivalent oxygen atoms. Since the Mulliken charges already reproduce the MEP values obtained using the CHelpG charges quite satisfactorily, the combination of HDC with the same brings about only a small but positive change in this regard.

(iv) In four cases, i.e., NH_3-$OHC^{\cdot}$, $CH_3H_2C^{\cdot}$, $CH_3O^{\cdot}$, and cytosine radical, the calculated percentage changes are negative, that in the case of $CH_3H_2C^{\cdot}$ being quite appreciable. The radical $CH_3H_2C^{\cdot}$ is obtained by removal of a hydrogen atom from one of the carbon atoms of ethane. While the valence state of one of the two carbon atoms of $CH_3H_2C^{\cdot}$ would be sp3, that of the other carbon atom would be sp2. Thus, there will be a π-electron associated with the carbon atom of the $H_2C^{\cdot}$ group of $CH_3H_2C^{\cdot}$. Occurrence of this π-electron would not as much affect the dipole moment as it would affect the quadrupole and higher electric moments as well as the surface MEP values of the radical. The appreciable negative percentage change in MEP in this case (Table 2) may be understood in terms of the fact that the present HDC scheme does not preserve atomic contributions to the molecular electric quadrupole and octupole moments. The negative percentage changes of MEP values in the other three cases are appreciably smaller, and can be understood broadly on a similar basis.

(v) The standard atomic numbering was used for radicals of the nucleic acid bases [35]. The case of guanine radical requires an explanation as follows. In this case, the most negative surface MEP value computed using CHelpG charges obtained from B3LYP/6–31G** calculations was found near the N9 atom. However, the most negative surface MEP values obtained using Mulliken and (Mulliken + HDC) charges computed at the B3LYP/6–31G** level were found to be located near the O6 atom of the radical. However, when the Mulliken and (Mulliken + HDC) charges obtained employing the BHandHLYP/6–31G** method [29] were employed, the most negative

surface MEP values were found near the N9 atom. Thus the shortcoming of the Mulliken charges is not adequately rectified by the HDC correction at the B3LYP/6–31G** level but it is achieved when the BHandHLYP fuctional is used instead of the B3LYP fuctional. Since the location of the most negative MEP region is not correctly predicted by the Mulliken and (Mulliken + HDC) charges obtained at the B3LYP/6–31G** level, the corresponding percentage change is not given for the guanine radical in Table 2.

3. Locations of HDC components

Values of HDC (in the unit of magnitude of electronic charge) associated with different atoms in some of the radicals and their locations in terms of distances and directions of displacements from the corresponding atoms along with the charges located at nuclear sites are presented in Table 3. The HDC values in radicals and those in the corresponding closed shell molecules (e.g., NH_3 corresponding to $H_2N^.$) are also given in this table for comparison. We make the following observations from this table:

(i) There are two HDC components associated with each hydrogen atom and six HDC components associated with each heavy atom. Thus including the nuclear site charges, there are three and seven charge components associated with the hydrogen and heavy atoms, respectively.

(ii) For heavy atoms, the HDC values associated with (1s,np) (n=2,3) orbital hybridization are much smaller than those associated with (ms,np) (m,n= 2,3) orbital hybridization. It shows that the 1s orbitals of the heavy atoms are relatively very weakly involved in bond formation as compared to those of the higher shells. It is in accordance with the common concept about contributions of different atomic shells to bonding in molecules or radicals.

(iii) In the 6–31G** basis set, 1s, 2s and 3p orbitals are provided for hydrogen atoms. The non-zero HDC values associated with (1s,3p) and (2s,3p) orbital mixing on hydrogens show that the atomic orbitals of these atoms are also hybridized in the radicals. However, the extent of orbital hybridization on hydrogen atoms is usually much less than that on the heavier atoms as shown by the corresponding HDC values.

(iv) As mentioned earlier, in the present computational approach, distances of the different HDC components from the corresponding atoms are fixed for given combinations of atomic orbitals. These distances are usually small but not negligible, the largest one being 0.265 Å corresponding to the (2s, 2p) orbital mixing on oxygen atoms.

(v) In going from closed-shell molecules to the corresponding radicals, hybridization of atomic orbital is appreciably changed as shown by the HDC values. For example, in $HC^.$ the (3s, 2p) and (3s, 3p) HDC components for the carbon atom are -0.665 and -0.337 while the corresponding HDC components in CH_2 are -1.550 and -1.169 respectively. This is not surprising since one CH bond is missing in $HC^.$ as compared to CH_2.

(vi) In $HO^.$ and $HC^.$, the different components of HDC associated with the H, O and C atoms are displaced along the bonds, being located inside or outside the bonds. Further, in each of $HO^.$, $HC^.$ and $H_2N^.$, the directions of displacements of (1s,2p) and (1s,3p) HDC components that involve 1s orbitals of O, C and N atoms are opposite to those of the other HDC components. It shows that 1s orbitals behave differently from the 2s and 3s orbitals with regard to directions of HDC displacements.

(vii) In $H_2N^.$ and $OHC^.$ that have bent structures, the HDC components associated with the central heavy atoms are located either on the acute or on the obtuse angle sides. The (1s,2p) and (1s,3p) HDC components associated with the N atom of $H_2N^.$ that involve the 1s orbital of the atom are displaced inside the acute HNH angle while the other HDC components of the atom are displaced on the obtuse HNH angle side. In the case of $OHC^.$ also, a similar observation is made (in this case, in Table 3, A stands for an HDC component). These results show an interesting difference between the displacement directions of (1s, np) (n=2,3 etc.) and (ms, np) (m>1, n=2,3 etc.) HDC components in bent systems. The HDC components associated with the H atoms of $H_2N^.$ and $OHC^.$ are displaced along the NH and CH bonds respectively towards the corresponding heavy atom. However the HDC components associated with the O atom of $OHC^.$ are displaced along the CO bond direction, either toward the C atom or away from it, the latter corresponding to lone pairs.

Conclusions

The present study shows that a combination of Mulliken charges and HDC offers a much more reliable approach than that based on Mulliken charges alone to calculate electrostatic properties of molecules and radicals.

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