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The molecular electrostatic potential of some simple molecules

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The calculation of the molecular electrostatic potential from simplified models of the electron density is considered. Results are shown for water, hydrogen fluoride and ammonia. Little loss of accuracy is evident when the density is represented by a linear sum of well-chosen Gaussians. When these are further simplified into sets of point charges the inner parts of the molecule are poorly represented. More elaborate point moments make the representation worse. On the other hand a mixed representation with point charges and one diffuse Gaussian gives all the essential features of the potential of these molecules.

Key words: Molecular electrostatic potential — Gaussian models — Point charge models — Water molecule

1. Introduction

In earlier papers from this laboratory practical methods of deriving Gaussian models of the electron density have been described (Smith and Hall [1]) and applied to water as a test case [2]. These have shown that a modest number of Gaussians with optimized exponents and coefficients can produce useful and compact representations of the electron density. The Gaussian positions are not optimized freely but some of them are allowed to move along prescribed lines. In a further application the Gaussians were "shrunk" into delta functions (cf. [3], [4]) and the resulting point charge models compared with some of those in current use.

In this paper the same types of models are used to calculate the Molecular Electrostatic Potential (MEP). The MEP has proved to be a most suggestive quantity indicating the affinity of the molecule to attack of various kinds (e.g., Politzer and Truhlar [5]). Its calculation from a complicated wavefunction can be tedious and so simplified methods using localized orbitals have been developed by Bonaccorsi et al. [6], [7] and Naray-Szabo et al. [8]. A calculation from the Gaussian models instead of the original density is much simpler since the number of terms is drastically reduced. As will be seen in Sect. 2, these results are essentially identical with the full results. On the other hand the point charge results distort the MEP in the penetration region although the outer region is well represented. The suggestion of using point dipoles, quadrupoles and octupoles to improve the potential (Sokalski and Poirier [9]) results in an improvement in the outer region at the expense of the inner region which develops an alternating potential not found in the MEP. The solution to this problem described in Sect. 4 is to append one diffuse Gaussian at the centre of the molecule to the point charges in calculating the MEP. The result is a potential showing the characteristic minimum in the lone pair MEP and giving considerable improvements to the potential in other regions. The significance of this model of the electron density is discussed in the final section.

2. Some Gaussian models

The programs already described [1] were amended slightly to enable the fitting to be carried to higher accuracy and were then used to calculate a Gaussian model for water. The original electron density for the fitting came from a wavefunction calculated using the 4-31G* basis set in the Gaussian 80 program. The details of the Gaussians in the fit are given in Table 1. In addition to Gaussians on each nucleus they are in the OH bonds, in the lone pairs, and two lie on the axis just below the O atom. As an indication of the accuracy of this fit, the expectation values of some operators are shown in Table 2 together with the mean square error *U*, in the notation of [1]. The MEP for the original wavefunction in the molecular plane (*yz*) and through the lone pairs (*xz*) is shown in Fig. 1

Table 1. Gaussians used for water

	Position				
	x	*y*	*z*	Exponent	Charge
Lone pair	0.3234	0.0	−0.3724	2.0002	1.1318
	−0.3234	0.0	−0.3724	2.0002	1.1318
O atom	0.0	0.0	−0.2214	404.7601	0.0778
	0.0	0.0	−0.2214	86.8883	0.6227
	0.0	0.0	−0.2214	27.3052	1.1218
Below O	0.0	0.0	−0.1849	0.4616	3.1376
	0.0	0.0	−0.0180	1.2787	1.6608
In OH	0.0	1.2381	0.7369	3.1325	0.1944
	0.0	−1.2381	0.7369	3.1325	0.1944
H atom	0.0	1.4304	0.8857	1.1111	0.3635
	0.0	−1.4304	0.8857	1.1111	0.3635

Table 2. Expectation values using Gaussian models

	Water		Hydrogen fluoride		Ammonia	
	Fitted[a]	Calc.[a]	Fitted[a]	Calc.[a]	Fitted[a]	Calc.[a]
$\langle z\rangle$	−0.9259	−0.8634	0.9257	0.9585	−0.8234	−0.7527
$\langle x^2\rangle$	5.2638	5.3329	4.0579	3.9938	9.2546	9.2123
$\langle y^2\rangle$	7.1107	7.1420	4.0579	3.9938	9.2546	9.2123
$\langle z^2\rangle$	6.3196	6.3599	5.0934	5.1789	7.4850	7.6189
$\langle z^3\rangle$	−1.0573	−0.6654	3.2356	3.7382	−2.5910	−2.1311
$\langle x^2z\rangle$	−0.6087	−0.5105	0.4660	0.4640	0.6249	1.0373
$\langle y^2z\rangle$	1.2363	1.6919	0.4660	0.4640	0.6249	1.0373
$\langle x^4\rangle$	13.0810	13.3951	8.2443	7.5134	34.7157	35.2002
$\langle y^4\rangle$	21.2459	22.6160	8.2443	7.5134	34.7157	35.2002
$\langle z^4\rangle$	16.2330	16.8191	13.1086	14.3453	24.5706	25.1429
$\langle x^2y^2\rangle$	5.0575	5.3069	2.7481	2.5045	11.5719	11.7334
$\langle y^2z^2\rangle$	6.9753	7.2787	3.0324	3.0522	9.4173	9.5158
$\langle z^2x^2\rangle$	4.8121	4.9619	3.0324	3.0522	9.4173	9.5158
$\langle 1/r_X\rangle$	23.3913	23.4236	27.1389	27.1608	19.9050	19.9371
$\langle 1/r_H\rangle$	5.7564	5.7702	6.0884	6.1074	5.3547	5.3775
U	0.001634		0.001145		0.001836	

[a] The columns headed calc. use the full calculated density while those with fitted use the Gaussian models

and the MEP for this fitted density in Fig. 2. There is very little difference apparent between them.

Similar calculations have been done for hydrogen fluoride and for ammonia. These are described in Tables 2-4. The accuracy of the fitting is comparable to that for water. The MEP for the wavefunction is shown in Fig. 3 for HF and in Fig. 4 for NH_3.

3. Point charge models

The shrinking of the Gaussians into delta functions preserves all the spherical moments of the density so the angular dependence of the MEP at large distances should be reproduced by a point charge model. It is clear that the delta functions will introduce singularities into the MEP which are not in the original so that in the inner regions of the molecule the MEP will be considerably different. This is seen in Figs. 5-7 which are the point charge MEPs. Their outer contours remain good representations of Figs. 1, 3, 4 but the lone pairs and bonds are treated quite differently. The original MEP has a shallow minimum for the lone pair at some distance from the nucleus while the point charge MEP shows one much closer to the nucleus and infinitely deep. The original MEP has the bond region surrounded by smooth positive iso-potentials but the point charge MEP shows the bonds as dipoles. The MEP near a nucleus is dominated by the nuclear potential because, as the electron cloud is penetrated, its outer parts cease to affect the potential and the inner electrons only partly screen the nucleus. Such an effect is difficult to reproduce using a modest number of point charges. The

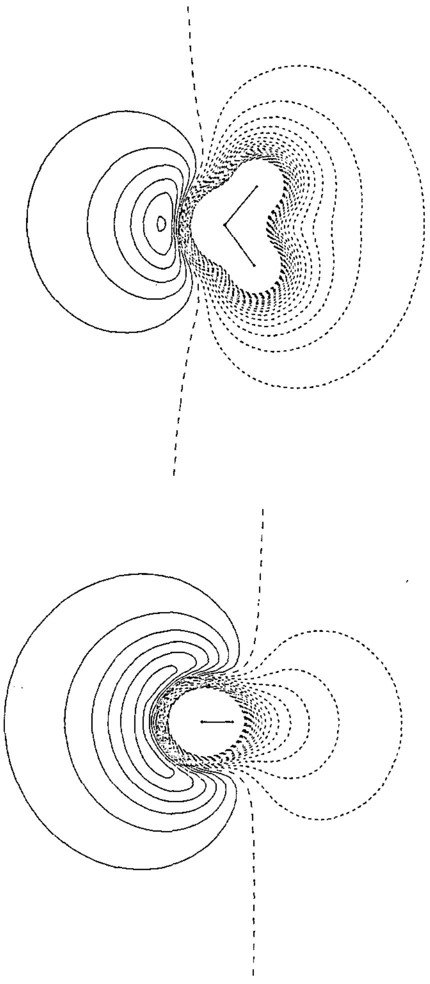
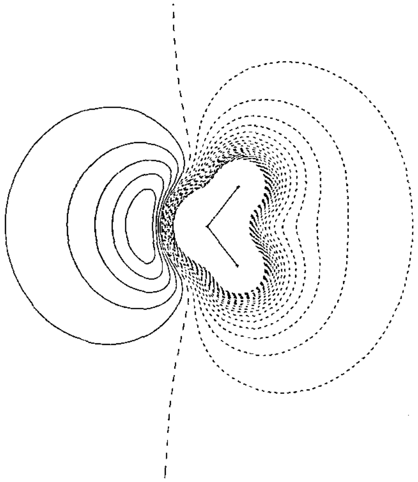


Fig. 1. The molecular electrostatic potential for water. The contour interval is 10 kcal/mol. Contours outside ±200 kcal/mol are not shown. *Solid lines* show negative potential, *dotted lines* show positive potential and a *dashed line* shows the zero

screening due to tightly-bound inner shells can be represented by a neutralizing charge on the nucleus. A cluster of point charges (cf. [10]) can give a penetration effect but at least four are needed for this.

It has been suggested by Sokalski and Poirier [9] that segmented moment expansions can be used to represent the outer potential to high accuracy. Since these use many more parameters to fit the potential this is not surprising. The MEP produced by these expansions is shown in Fig. 8 for water. A close examination shows that the potential outside 4.5 bohr from the nuclei is indeed represented more accurately than with the Gaussian fit. On the other hand the potential inside this distance becomes very bad. Part of the reason for this is the use of point dipoles, quadrupoles, octopoles... Since their potentials become even more singular than that of a point charge they, instead of the nuclear potentials, will dominate the potential near the nuclei. Another reason is that the penetration, which is the principal missing effect, cannot be represented in such



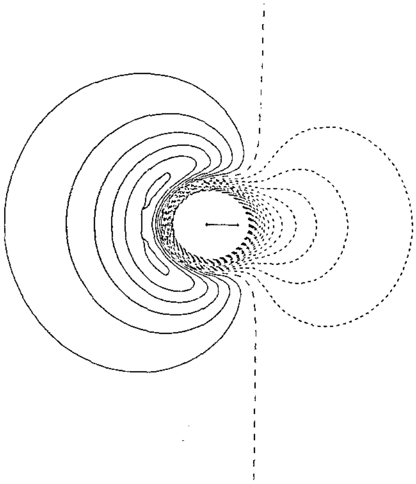


Fig. 2. The MEP for H_2O calculated using the Gaussian model. Contours are as in Fig. 1

Table 3. Gaussians used for hydrogen fluoride

	Position				
	x	y	z	Exponent	Charge
Lone pairs	0.0	−0.2930	−0.0584	4.1199	0.5034
	0.2538	0.1465	−0.0584	4.1199	0.5034
	−0.2538	0.1465	−0.0584	4.1199	0.5034
F atom	0.0	0.0	0.0	682.7818	0.0469
	0.0	0.0	0.0	138.3677	0.4912
	0.0	0.0	0.0	40.1253	1.2256
HF bond	0.0	0.0	0.0276	1.2906	4.3853
	0.0	0.0	0.1440	0.4951	1.9907
H atom	0.0	0.0	1.7329	2.1030	0.3498

Table 4. Gaussians used for ammonia

	Position			Exponent	Charge
	x	y	z		
Lone pair	0.0	0.0	−0.5295	1.2418	2.0610
Above N	0.0	0.0	−0.2423	0.3326	2.5183
Below N	0.0	0.0	0.1833	1.1204	1.3485
N atom	0.0	0.0	−0.2160	292.9156	0.0847
	0.0	0.0	−0.2160	63.1278	0.6478
	0.0	0.0	−0.2160	20.0333	1.1020
NH bonds	0.0	1.5340	0.4074	2.3063	0.3468
	−1.3285	−0.7670	0.4074	2.3063	0.3468
	1.3285	−0.7670	0.4074	2.3063	0.3468
H atoms	0.0	1.7717	0.5040	0.8854	0.3991
	−1.5343	−0.8858	0.5040	0.8854	0.3991
	1.5343	−0.8858	0.5040	0.8854	0.3991

a form. Figure 8 shows clearly how seriously this model misrepresents the inner potentials. It shows oscillations in the inner potential which are not present in the true MEP. The use of such a potential to estimate the electrostatic intermolecular forces can give misleading results when the molecules are close. In particular at the separation of H-bonding there may be appreciable errors.

4. Mixed models

A feature of many Gaussian models is the presence of one or more diffuse Gaussians in the model. These may be defined as ones whose exponents are less than 1. They spread over more than one atom and have to be divided before their charges can be related to individual nuclei [11]. Because of their small

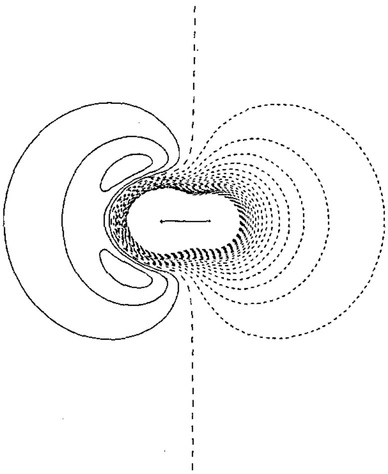


Fig. 3. The MEP for HF

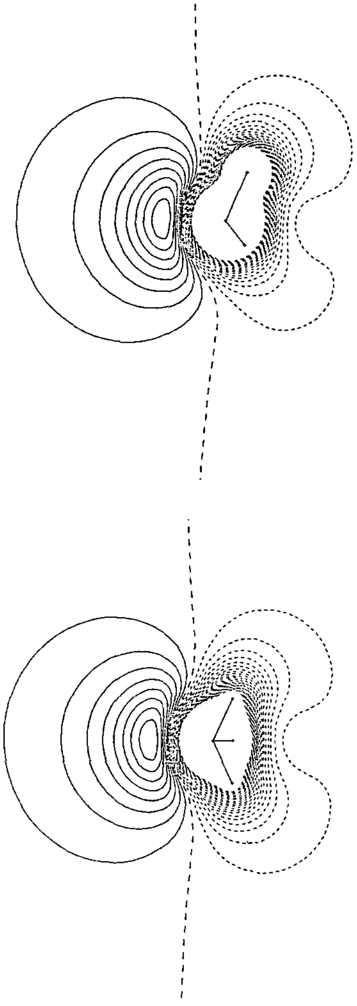


Fig. 4. The MEP for NH_3

exponent these functions reprsesent the outer part of the electron density which is the part to be penetrated first. An improvement on the point charge model of a molecular density would allow for these in some different way. The suggestion now presented is to exclude these functions from the shrinking and keep them as continuous distributions. Thus the model would consist of some point charges and a small number of diffuse functions.

The MEP for a model of this kind for water is shown in Fig. 9. It is almost indistinguishable from the original MEP. Only one diffuse function was used, situated very close to the centre of nuclear charge. Even with one diffuse function the penetration effect is well represented. The minimum in the lone pairs is also well represented. For purposes of evaluating intermolecular forces even at close

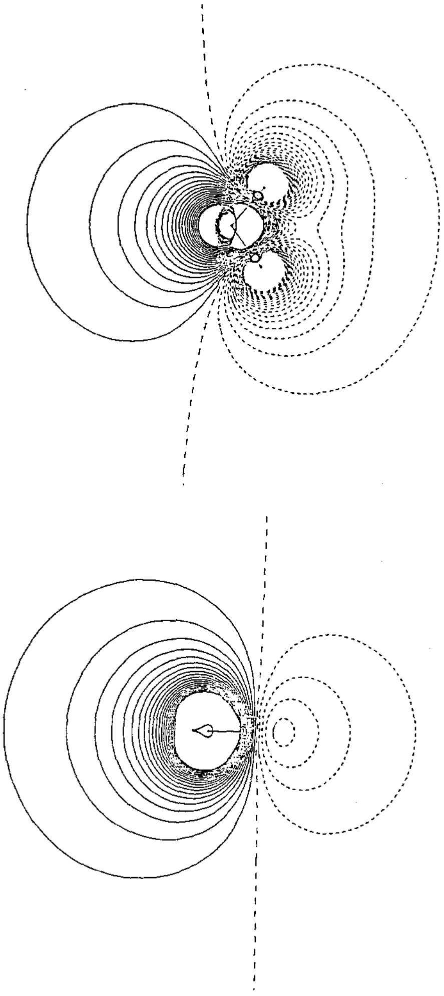


Fig. 5. The MEP for H_2O using the point charge model

distances this model will be superior to any one based on point elements alone. Figs. 10 and 11 show similar results for HF and NH_3.

5. Discussion

The success of the mixed model has several interesting consequences. It suggests an interesting physical picture of the molecule. Some of its electrons are localized into definite points within the molecule to represent inner shells, lone pairs or bonds but some remain in a delocalised cloud which belongs to the molecule rather than to any of its parts. In a larger molecule one of these diffuse functions will be centred near each of the heavier nuclei so that the cloud will cover the molecule.

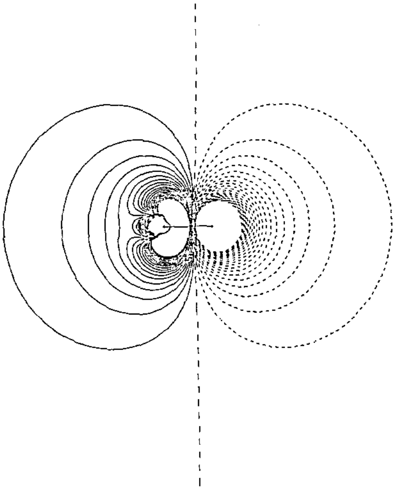


Fig. 6. The MEP for HF using the point charge model

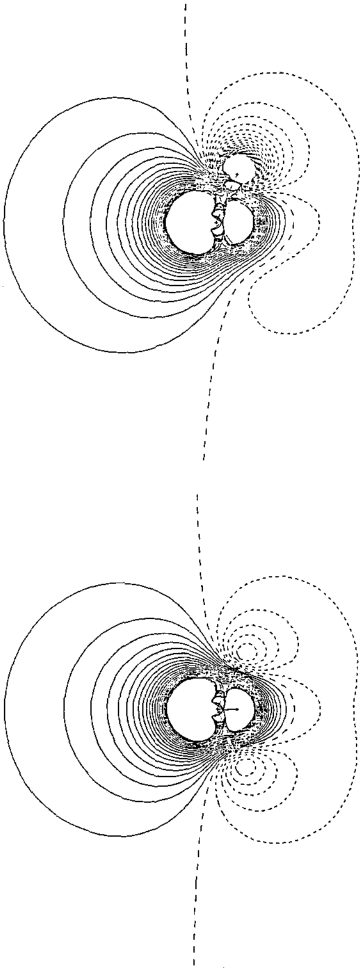


Fig. 7. The MEP for NH_3 using the point charge model

Fig. 9. The MEP for H_2O using the mixed model with one diffuse Gaussian and point charges

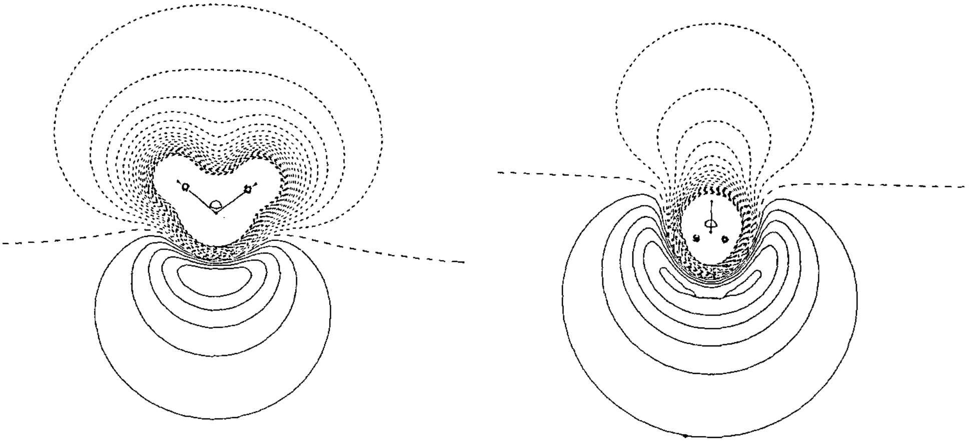
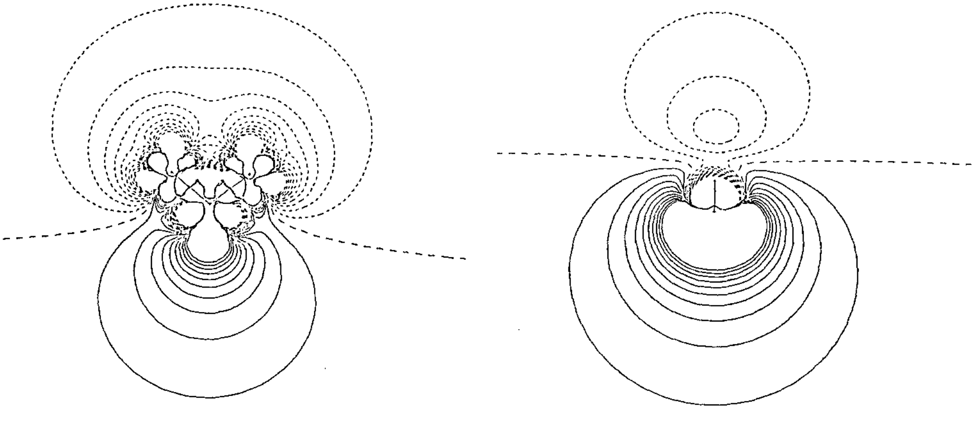


Fig. 8. The MEP for H_2O using the segmented moment model



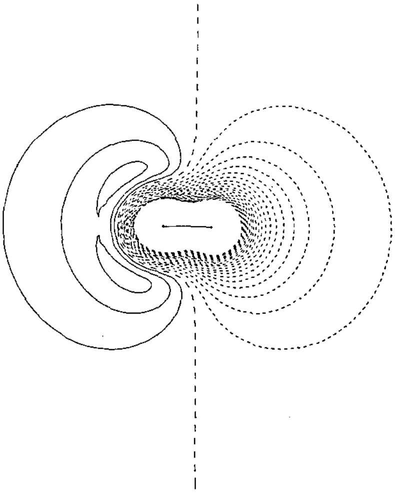


Fig. 10. The MEP for H_2O using the mixed model with one diffuse Gaussian

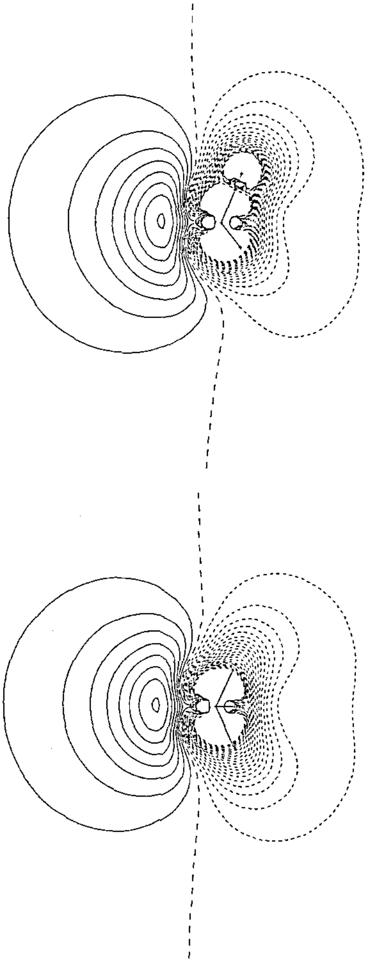


Fig. 11. The MEP for NH_3 using the mixed model with one diffuse Gaussian

This model also makes possible the calculation of intermolecular forces. This will be discussed in a later publication.

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