Theoret. Chim. Acta (Berl.) 39, 7—16 (1975)

First and Second-Order Properties of Charge-Localized and Frost-Localized Orbitals

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Received December 23, 1974/April 1, 1975

Two methods of localization of Frost-model molecular orbitals are considered, both of which are extremely easy to apply, requiring the evaluation of only one-election integrals. The charge-localization criterion can be used with any single-determinant wavefunction, but when applied to the Frost model it yields similar orbitals to those got by orthonormalizing the basis of floating spherical gaussians, while maintaining their localized feature. Properties of charge-localized orbitals are calculated for NH_3, H_2O, CH_4, C_2H_6.

Key words: Charge-localized orbitals – Frost-localized orbitals – Dipole moments – Quadrupole moments – Polarizabilities

1. Introduction

It has now become a standard technique to find Hartree-Fock wave functions for molecules. Sometimes these wave functions are computed to high accuracy using large basis sets but, for some purposes, it may be sufficient to make calculations of a low degree of accuracy. For example, Frost-model calculations [1–4], which employ a minimum basis set of floating spherical gaussians, can only give about 80–90% of the exact Hartree-Fock energy but nevertheless they can provide useful information on relative, if not absolute, values of energies and other observables as well as giving insights into chemical behaviour.

High-accuracy calculations do not always allow for a simple interpretation although ways are known of transforming the computed wave functions into forms which correspond to chemical ideas. One of the most useful such transformations is to a Slater determinant built up of localized orbitals [5–8], these localized orbitals conforming to the chemist's ideas of inner-shells, lone-pairs, covalent bonds. Apart from the qualitative aspects of these localized orbitals there are two quantitative advantages which they have. The first is that they are transferable from molecule to molecule in the sense that, for example, the localized orbital for a CH bond in methane is nearly the same as that for a CH bond in ethane. The second is that they provide a useful starting point when Hartree-Fock perturbation theory is applied to finding first and second-order properties of molecules. Recently, for example, dipole and quadrupole moments of CC and CH bonds have been calculated using energy-localized orbitals found from quite accurate Hartree-Fock wave functions [9] and two of us have used the same localized orbitals to find polarizabilities of CC and CH bonds [10].

In this paper we investigate how well such properties can be calculated using the much less accurate Frost-model wave functions. As a preliminary the wave function has to be transformed into a Slater determinant built up of orthogonal localized orbitals. The key word here is orthogonal; a Frost-model wave function is normally written as a Slater determinant of spherical gaussians which are certainly localized but are not orthogonal and unfortunately this means that standard Hartree-Fock perturbation theory cannot be used. There is, as it happens, no great problem in transforming to an orthogonal localized set to which Hartree-Fock perturbation theory can be applied. In fact we find that two choices of localized orbitals, charge-localized and what we term Frost-localized are particularly easy to obtain and use. From them we obtain first and second-order molecular properties that to some extent are satisfactory but that also have consistent errors which are due to the nature of the Frost model.

2. Charge-Localized Orbitals

All localization criteria are based on the fact that the Hartree-Fock wave function

$$\Psi = |\phi_1\alpha\phi_1\beta\ldots\phi_n\alpha\phi_n\beta|$$

is invariant to a unitary transformation of the orthonormal orbitals $\{\phi_r\}$ [5, 6]. Thus if we define a new set of orbitals $\{\chi_i\}$ by

$$\chi_i = \sum_{s=1}^{n} U_{is}\phi_s$$

where U is unitary, then

$$\Psi = |\chi_1\alpha\chi_1\beta\ldots\chi_n\alpha\chi_n\beta|\,.$$

For the new set $\{\chi_i\}$ to be localized in various regions of space U should be chosen to maximize a sum of the form:

$$\sum_i \iint \chi_i^2(1)\chi_i^2(2)f(r_{12})d\tau_{12}$$

where $f(r_{12})$ is a monotonic function of r_{12}. Different choices of $f(r_{12})$ will lead to different localized orbitals but it is generally thought that these differences will not be too important.

Ruedenberg [7] has mentioned several possible choices of $f(r_{12})$ of which the most well-known one is $f(r_{12}) = r_{12}^{-1}$. This has frequently been used to find localized orbitals and, provided this is done as an additional stage of a Hartree-Fock calculation, there is no problem in applying it. On the other hand, when the process of localization is performed long afterwards on a given set of canonical molecular orbitals, the fact that Coulomb and exchange integrals are needed makes the calculation difficult and time-consuming.

Alternative choices of $f(r_{12})$ which do not have this problem are $f(r_{12}) = r_{12}^2$ and $f(r_{12}) = \delta(r_{12})$ since, for these, the integrals required are one-electron only. The first of these, $f(r_{12}) = r_{12}^2$, is related to the Boys' localization method [6, 11] while the second gives charge-localized orbitals.

The charge density corresponding to Ψ is given by

$$\varrho(1)=2\sum_s|\phi_s(1)|^2=2\sum_i|\chi_i(1)|^2\,.$$

Consequently $|\phi_s(1)|^2$ will be the charge density associated with an original orbital ϕ_s while $|\chi_i(1)|^2$ will be the charge density for the localized orbital χ_i. If the $\{\phi_s\}$ are the canonical molecular orbitals they are usually delocalized throughout the molecule and so the same will be true of the associated charge density. On the other hand, localized orbitals should have localized charge densities. Consequently the charge-overlap

$$\int|\chi_i(1)|^2|\chi_j(1)|^2d\tau$$

between the charge densities of two localized orbitals should be small. This leads to the condition that the unitary transformation $\boldsymbol{U}$ should be chosen so that

$$\sum_{i\neq j}\int|\chi_i(1)|^2|\chi_j(1)|^2d\tau$$

is a minimum. An equivalent alternative form of this condition is that the sum of the self overlaps of the charge densities should be as large as possible i.e.

$$\sum_i\int\{|\chi_i(1)|^2\}^2d\tau$$

is a maximum.

Charge-localized orbitals have been defined implicitly by Edmiston and Ruedenberg [5] and investigated in more detail by von Niessen [12]. In particular the latter author has shown that, for a number of atoms and molecules, charge-localized orbitals are similar to other types of localized orbitals e.g. those obtained by Boys' method. Von Niessen has also pointed out that the integrals needed to find charge-localized orbitals are much simpler and, therefore, easier to calculate than those needed for most of the other localization methods.

3. Application to the Frost Model

The basis for the Frost model [1–4] is a minimal set of floating spherical gaussians. The basis functions are allowed to moves centres and alter exponents until the energy is minimum. It is typical to find a spherical gaussian with a large exponent sited on a heavy nucleus and a gaussian with a small exponent on the axis of a single bond. Thus the basis functions already represent inner-shells and bonds. Lone pairs present some difficulties as functions placed in the lone-pair region are inclined to crash into the heavy nucleus if allowed to float. It is usual in this case to fix the lone-pair gaussian near the nucleus and just let the exponents vary.

Although the basis functions of the Frost model are localized they are not orthogonal, making comparison with other localized molecular orbitals difficult. Such a set can be orthogonalized, for example, by the Gram-Schmidt procedure. Alternatively, if the Frost-model calculation is made by utilizing an optimizing iterative SCF program (such as OPIT [13]) the program will automatically give orthogonal molecular orbitals which are the best approximation to the true canonical molecular orbitals obtainable using the basis set of gaussians. In this case the orthogonal orbitals can then be localized by standard methods.

It is particularly easy to find charge-localized orbitals from Frost-model calculations because the integrals required are trivially easy to compute [12]. Applying the standard iterative procedure of Edmiston and Ruedenberg [5] it is found that the most complicated integral required is

$$\int \omega_1(\alpha, \boldsymbol{R}_1, 1)\omega_2(\beta, \boldsymbol{R}_2, 1)\omega_3(\gamma, \boldsymbol{R}_3, 1)\omega_4(\delta, \boldsymbol{R}_4, 1)d\tau$$

where, for example, ω_1 is a spherical gaussian with exponent α centered at the point $\boldsymbol{R}_1$. The well-known result that the product of two spherical gaussians is itself a spherical gaussian can be used to find the value of the integral which is

$$\sqrt{\frac{\pi^3}{\mu^3}}\exp(\mu\boldsymbol{R}\cdot\boldsymbol{R}-\alpha\boldsymbol{R}_1\cdot\boldsymbol{R}_1-\beta\boldsymbol{R}_2\cdot\boldsymbol{R}_2-\gamma\boldsymbol{R}_3\cdot\boldsymbol{R}_3-\delta\boldsymbol{R}_4\cdot\boldsymbol{R}_4)$$

where

$$\mu=\alpha+\beta+\gamma+\delta \quad \text{and} \quad \mu\boldsymbol{R}=\alpha\boldsymbol{R}_1+\beta\boldsymbol{R}_2+\gamma\boldsymbol{R}_3+\delta\boldsymbol{R}_4\,.$$

The results of applying the iterative procedure to finding the charge-localized orbitals for a number of Frost-model wave functions are given in the next section. What is found is that the charge-localized orthonormal orbitals $\{\chi_i\}$ are localized in the same regions of space as the non-orthogonal floating gaussian orbitals $\{\omega_i\}$. This suggests an alternative and extremely simple method for finding orthogonal localized orbitals for the Frost model. Namely we choose χ_i to be the orthogonal combination of the $\{\omega_j\}$ which is least changed from the gaussian orbital ω_i. This is done by a transformation

$$\chi_i=\textstyle\sum_{j=1}^{n} A_{ij}\omega_j$$

where, in order that the $\{\chi_i\}$ be orthonormal, the matrix A must satisfy

$$\boldsymbol{A}^+\boldsymbol{S}\boldsymbol{A}=\boldsymbol{1}$$

with $\boldsymbol{S}$ the overlap matrix given by,

$$S_{ij}=\int \omega_i\omega_j d\tau\,.$$

The localization criterion is that

$$D=\textstyle\sum_{i=1}^{n}\int |\chi_i-\omega_i|^2 d\tau$$

be a minimum. It has been shown [14] that $A=\boldsymbol{S}^{-\frac{1}{2}}$ is the choice of A which minimizes D (see also Ref. [5]).

These Frost-localized orbitals are clearly very easy to find and, as will be seen, they are very similar to charge-localized orbitals. Their disadvantage is that they are special to the Frost model and have no analogues for more complicated wave functions, but we only use them here to compare with the charge-localized orbitals which are of general applicability.

4. Results

Both methods of localization were applied to Frost-model wave functions of methane, water, ammonia and ethane and from the localized orbitals first and second-order bond properties have been obtained. There are several reasons for the choice of these particular molecules. One is their general importance and the fact that methane and ethane provide the prototype CH bond and CC single bond while water and ammonia enable us to consider lone pairs. Secondly, values of bond dipole moments, quadrupole moments and polarizabilities calculated from quite accurate wave functions for these molecules are available for comparison with our values found from the much less accurate Frost-model wave functions. Finally, since the Frost model seems to work best for hydrocarbons the results for methane and ethane can be used to estimate the degree of accuracy to be expected of calculations of this type in the most favourable case while the unfavourable case is covered by the results for ammonia and water, where the Frost model works somewhat badly.

We find that for the two types of localization the two sets of coefficients in the expansion of the orthonormal molecular orbitals over the basis set spherical gaussians are very alike in all four cases, indicating that the charge-localized orbitals are indeed localized. Due to the similarity of the pairs of results we have only listed both matrices of coefficients for ammonia, which is a typical case (Table 1). The main difference between the two sets of localized orbitals is that $S^{-\frac{1}{2}}$ is symmetrical, and thus that for the Frost-localized orbitals some coefficients not intrinsicly related by molecular symmetry are forced to be equal. The optimized floating-spherical-gaussian bases of methane and ethane are nearly the same, and, as is to be expected, so are the localized orbitals for the CH bond and carbon inner-shell in both molecules. Both sets of charge-localized orbitals are reproduced in Table 2, most of the molecular orbitals being omitted since they are generated

Table 1. Localized orbitals of ammonia

Basis function	Atomic orbital coefficients				
	N i.s.	NH_1	NH_2	NH_3	Nl.p.
(a) Charge-localized					
N	−1.0135	0.0401	0.0401	0.0401	0.0864
NH_1	−0.0100	−1.5370	0.1384	0.1384	0.7571
NH_2	−0.0100	0.1384	−1.5370	0.1384	0.7571
NH_3	−0.0100	0.1384	0.1384	−1.5370	0.7571
Nl.p.	0.1127	0.6038	0.6038	0.6038	−2.5539
(b) Frost-localized					
N	−1.0158	0.0145	0.0145	0.0145	0.0839
NH_1	0.0145	−1.5659	0.1095	0.1095	0.7055
NH_2	0.0145	0.1095	−1.5659	0.1095	0.7055
NH_3	0.0145	0.1095	0.1095	−1.5659	0.7055
Nl.p.	0.0839	0.7055	0.7055	0.7055	−2.4756

Geometry: NH bond length = 1.91 a.u.; HNH angle = 97°.

Floating spherical gaussians: exponents 13.0046, 0.4309, 0.3965; positions 0.0007 off N, towards H; 0.8914 a.u. along NH; 0.2224 off N, away from H.

Table 2. Charge-localized orbitals of methane and ethane

Basis function	methane		ethane		
	C i.s.	CH_1	C i.s.	CH_1	CC
C $i.s._1$	−1.0108	0.0494	−1.0104	0.0490	0.0449
C $i.s._2$			−0.0004	−0.0060	0.0449
CC			0.0278	0.1954	−1.3240
CH_1	0.0254	−1.2057	0.0259	−1.1877	0.1637
CH_2	0.0254	0.1864	0.0259	0.1817	0.1637
CH_3	0.0254	0.1864	0.0259	0.1817	0.1637
CH_4	(0.0254)	(0.1864)	−0.0072	−0.0504	0.1637
CH_5			−0.0072	−0.0074	0.1637
CH_6			−0.0072	−0.0074	0.1637

(a) Methane: geometry: CH length = 2.0665 a.u.; floating spherical gaussians: exponents 9.3072, 0.3562, position in CH bonds = 1.2362 a.u. from C.

(b) Ethane: geometry: CH length = 2.0825 a.u.; CC length = 2.9159; floating spherical gaussians: exponents 9.3006, 0.3531, 0.3549; position in CH bonds = 1.2716 a.u. from C.

by symmetry. The similarity of the CH bond in both environments is underlined by the closeness of the CH values of the electric properties of bonds which we now proceed to consider.

The electric moments for the bonds are defined in the following way:

The charge density of the *i*th bond is

$$\varrho_i(\boldsymbol{r})=\sum_\alpha Z_{\alpha i}\delta(\boldsymbol{R}_\alpha-\boldsymbol{r})-2\omega_i^*(\boldsymbol{r})\omega_i(\boldsymbol{r})$$

where $Z_{\alpha i}$ is the nuclear charge contribution to the *i*th orbital from the αth nucleus. Following England and Gordon [15] and Pritchard and Kern [9], two units of charge are associated with each localized orbital, the charge being evenly divided among the nuclei associated with the orbital.

The bond dipole moment is thus

$$\boldsymbol{\mu}_i=\langle\varrho_i(\boldsymbol{r})\boldsymbol{r}\rangle$$

and the bond quadrupole moment is

$$\boldsymbol{\theta}_i=\langle\varrho_i(r)\tfrac{1}{2}(3\boldsymbol{r}\boldsymbol{r}-r^2\boldsymbol{I})\rangle\,.$$

The last definition depends on choice of origin (unless the dipole moment vanishes); to conform with the work of Pritchard and Kern the origin is taken to be the midpoint of the two nuclear charges associated with the orbital. The principal components of these vector and tensor quantities are listed in Table 3.

The bond contributions to molecular properties cannot be compared directly with experimental data, but a number of conclusions may be drawn by comparison within the theoretical data. One evident feature of the bond results is that the figures for the CH bond in methane and the CH bond in ethane are very nearly identical, which is precisely what is intuitively expected. The dipole moments of the CH, NH, and OH bonds are negative, indicating the electronegativity of the hydrogen nucleus, and appear to be in the correct order, decreasing with increasing heavy nuclear charge. The dipole moments of the lone pairs in ammonia and water are of similar magnitude with the oxygen lone pair rather closer to the nucleus.

Table 3. Electric moments of charge-localized orbitals in the Frost model

Molecule/Orbital		Dipole moments[a,b]		Quadrupole moments[a]			
				This paper		Other calcs.	
		This paper	Other calcs.	∥	⊥	∥	⊥
CH_4	CH	−2.08	−2.02 [19a] −1.86 [17] −2.03 [15]	2.19	−1.09	1.32	−0.66 [19a]
C_2H_6	CH	−2.17	−1.97 [9] −1.84 [17] −1.95 [15] −1.87 [19b]	2.21	−1.11	1.33 1.43	−0.66 [9] −0.72 [19b]
	CC	0	0	5.28	−2.64	4.09 4.45	−2.04 [9] −2.23 [19b]
H_2O	OH	−0.55	−1.03 [19c]	1.84	−0.92[c]	0.91	−0.46 [19c]
	O l.p.	−3.40	−2.88 [19c]	−1.35	0.68[c]	−1.07	0.54 [19c]
NH_3	NH	−1.03	−1.24 [19d]	1.70	−0.85[c]	1.18	−0.59 [19d]
	N l.p.	−3.93	−3.32 [19d]	−2.03	1.01	−1.57	0.79 [19d]

[a] Units: dipole = debye; quadrupole = buckingham.

[b] The positive direction is defined to be from the heavy nucleus outwards so that, for example, $\mu_{CH} = -2.08$ implies C^+H^-.

[c] Average value.

There have been a number of previous calculations of CC and CH bond dipole moments and quadrupole moments. For example, Pritchard and Kern [9] have found bond moments by using the localized orbitals obtained from the Pitzer and Lipscomb [16] wave function for ethane. Rothenberg [17] has calculated bond dipole moments as have England and Gordon [15], the former using *ab initio* wave functions while the latter authors have used semi-empirical ones. These values are listed in Table 3 where they can be compared with the results obtained using the Frost-model wave functions. It is clear from the table that, although the Frost-model bond dipole moments are a little too large, they are, on the whole, in very satisfactory agreement with the more accurate values. The quadrupole moments are less satisfactory being quite appreciably too large in magnitude. It is plausible that the diffuse nature of the floating spherical gaussians is the cause of this error, which can be expected to get worse for higher moments.

It should be pointed out that these CH bond dipole moments are much larger than earlier calculations, for example that of Coulson [18], have suggested. The analysis of Ref. [9] makes it fairly clear that these earlier calculations are in error due to inadequate wave functions but there then remains the problem of reconciling these large bond dipole moments found theoretically with experimental evidence which indicates, although far from decidedly, that the value of the CH dipole should be of the order of 0.4 debyes. A number of suggestions have been made as to how this might be done [17] but the question is far from settled and in the present situation it seems best to use the definition of bond moment given here and used by earlier authors [9, 15] with the understanding that it must be modified in some way before it can be compared with "observed" bond dipoles whatever they may be. As well as results for CC and CH bonds Table 3 gives the moments of OH, NH bonds and oxygen and nitrogen lone pairs. We also give in the table values of the same moments we have calculated using the more accurate Slater basis wave functions [19] localized with the "self-energy" criterion [5].

The results of Table 3 indicate that the only really satisfactory agreement is obtained for the dipole moment of the CH bond, which is about -2. The values for the bonds and lone pairs (axis through centroid) in H_2O and NH_3 show much more departure from the other calculations. This is not surprising because the floating spherical gaussians, which determine the bond dipole moments by their positions along the bonds, do not behave well when forced to simulate lone pairs, which adversely affects the moments of both the bonds and the lone pairs. NH_3 is not so badly affected as H_2O. All the quadrupole moments show only crude agreement with the more accurate calculations, reflecting the diffuse nature of the spherical-gaussian charge distributions.

The calculation of the electric polarizabilities was made using a form of uncoupled Hartree-Fock perturbation theory described elsewhere [10, 20]. Because of the nature of the Frost model in its use of spherical gaussians, the localized orbitals are themselves almost spherically symmetric. As a consequence the components of the polarizability tensor are found to be almost isotropic which, of course, is not actually the case. This is shown in Table 4 where we give polarizability values calculated from accurate wave functions [19] for comparison with the Frost-model ones. It is clear from the table that the main fault with the Frost-model results is that the parallel components of the bond polarizabilities are almost always very much underestimated. The perpendicular components on the other hand are quite satisfactory. The net result of this is that the average bond polarizability for CC and CH bonds is underestimated by about 25%. For the other bonds a similar effect is observed, but the discrepancy is much larger. The polarizability of the lone pairs, on the other hand, appears to be greatly overestimated.

Using the bond moments and polarizabilities it is possible to obtain dipole and quadrupole moments and polarizabilities for the molecules themselves.

Table 4. Bond polarizabilities of charge-localized orbitals in the Frost model

Molecule	Orbital	Polarizabilities[a]			
		This paper		Wave functions of Ref. [19]	
		$\parallel$	$\perp$	$\parallel$	$\perp$
CH_4	CH	4.63	4.99	8.41	4.51
C_2H_6	CH	4.58	4.98	8.68	4.87
	CC	4.07	4.54	7.19	3.81
H_2O	OH	2.10	1.87[b]	7.65	3.56[b]
	O l.p.	2.54	1.75[b]	1.01	1.14[b]
NH_3	NH	3.20	3.27[b]	8.11	4.27[b]
	N l.p.	3.45	3.25	1.74	1.74

[a] Units of 10^{-25} c.c. [b] Average value.

Table 5. Molecular properties from charge-localized orbitals

Molecule	Theoretical	Experimental	Error as % of experimental	Ref. for exp.
(a) Dipole moment				
H_2O	2.54	1.82	40%	a
NH_3	2.34	1.47	59%	a
(b) Quadrupole moment				
C_2H_6	$-1.19(\parallel)$	-0.8 ± 0.1		b
	$0.60(\perp)$	0.4 ± 0.1		
H_2O[c]	$0.54, -0.05(\parallel)$	-0.13 ± 0.03		d
	$3.04, 3.34(\perp$[e]$)$	2.63 ± 0.02		
	$-3.58, -3.29(\perp)$	-2.50 ± 0.02		
NH_3[c]	$-2.91, -3.45(\parallel)$	-2.32 ± 0.07		f
	$1.46, 1.73(\perp)$	1.16 ± 0.04		
(c) Polarizabilities				
CH_4	19.49	25.6	24%	g
C_2H_6	33.46	44.7	25%	h
H_2O	7.92	14.4	45%	j
NH_3	13.07	22.2	41%	h

Units as in Tables 3, 4.

[a] McClellan, A. L.: Tables of experimental dipole moments. San Francisco: Freeman 1963.

[b] Buckingham, A. D., Disch, R. L., Dunmur, D. A.: J. Am. Chem. Soc. **90**, 3104 (1968).

[c] The first column contains values referred to the heavy atom; the second values are referred to the molecular centre of mass.

[d] Rock, S. L., Pearson, E. F., Appleman, E. H., Norris, C. L., Flygare, W. H.: J. Chem. Phys. **59**, 3940 (1973).

[e] Component perpendicular to axis and parallel to HOH plane.

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These figures are given in Table 5 where some comparison with experiment is made. Due to the spherical symmetry of the gaussians the polarizability anisotropy of the molecules will be zero in each case which, of course, is incorrect. The average polarizability, however, is predicted none too badly at least for CH_4 and C_2H_6. For water and ammonia the calculated average polarizability is only about 50% of the experimental value, but this seems as much a special difficulty associated with the lone pairs in these molecules as a fault of the Frost model itself: calculations based on accurate Hartree-Fock wave functions also give poorer results for molecules with lone pairs. This same problem is probably responsible for the unsatisfactory values for the dipole moments of water and ammonia.

5. Conclusion

The charge-localization criterion, as well as being intuitively pleasing, has the advantage over more usual choices of leading to one-electron integrals which can be evaluated simply and rapidly. This is a very desirable property when large molecules are being considered. This localization criterion can be easily extended to wavefunctions built up of Slater-type atomic orbitals.

Although the Frost model is rather crude, a number of results obtained from it may be useful for estimates of the relative magnitudes of values of molecular and bond properties. We have found that the orthonormal localized orbitals of the CH bond in methane and ethane are almost identical, and we would expect this similarity to persist in much larger saturated hydrocarbons. In fact, due to the simplicity of the Frost model and the ease with which the charge- or Frost-localization criteria can be applied, this may be the way to settle the theoretical question of transferability of bond properties between different molecular systems. The degree of variation of the parameters will indicate the degree of non-transferability.

The absolute values of the first and second-order properties themselves are not in terribly good agreement with experiment. However for hydrocarbons we expect that the method used here will give average polarizability values which are fairly consistently about 75% of the true value. For molecules, like water, with lone pairs, the situation is much more difficult but it would seem that the polarizability values are greatly underestimated and the dipole moments over-estimated.

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