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The currant bun model of simple molecules

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The model of a molecule previously introduced by the authors, in which most of the electronic charge is represented by point charges on the nuclei, in the lone pairs and bonds, and the remainder is in a diffuse function which represents the outer electrons, is here extended. Molecules with several heavy atoms require several diffuse functions, one for each heavy atom, in addition to one at the centre of nuclear charge. In an electric field the centre of each diffuse function moves against a harmonic restoring force and this gives rise to the polarizability of the molecule. When two molecules interact the movement of this function produces the dispersion force. The model thus embodies all the long range forces between molecules in a more accurate and simpler way than was possible earlier.

Key words: Point charge models – Polarizability – Dispersion forces

1. Introduction

Lord Kelvin, many years ago, produced an electrostatic model of the atom consisting of a sphere of uniform positive charge in which localized negative charges were placed so as to reach equilibrium. The model was further elaborated [1] to show shell structure by J. J. Thomson following his discovery of the electron. The effect is like the distribution of currants through the texture of a currant bun. This model was decisively rejected when Rutherford proved that the positive charge was not so distributed but strongly localized at the centre. Nevertheless their conviction that electrical forces play a decisive role in atomic structure was important for the development of later theories.

Recent papers from this laboratory [2, 3] have established methods of approximating to the electron density of a molecule using a linear combination of spherical Gaussians at optimized positions within the molecule. By fitting a good calculated density with a large enough set of Gaussian densities, the accuracy of properties calculated from the fitted density can be made high. Some properties, such as the spherical moments of the charge, remain invariant if the model is further simplified by shrinking the Gaussians into delta functions [4]. The resulting point charge models have significance in the calculation of the electrostatic forces between molecules. The shrinking process is justified for more general properties when the exponents are large so that the Gaussian is already well-localized. It is found, however, that many models contain diffuse functions with small exponents and, for these, shrinking is much less appropriate. In a previous paper of the present authors [5] it was shown that by retaining one diffuse function for each heavy atom along with the point charges, the representation of the MEP (molecular electrostatic potential) can be made very accurate both outside the molecule and partially inside.

In this paper this model of a molecule consisting of point charges for the nuclei and for most of the electrons but with some electronic charge remaining in a diffuse cloud will be considered further. Since its representation of the MEP has already been discussed it will not be reconsidered. In Sects. 3, 4 the molecular polarizability will be treated and in 5 the dispersion energy between two molecules. The conclusion is suggested that this model can represent very compactly those parts of the molecule which determine the long-range intermolecular forces.

Although the origin and use of this model differs considerably from that of Kelvin and Thomson yet it gives a picture of the molecule which is largely determined by electrostatics and so has much in common with theirs once the obvious change of sign of the charge cloud is made. There is also a significant connection between this model and the shell models of defects used by Faux and Lidiard [6].

2. The diffuse functions

The approximating of ρ, the electron density of a molecule, by using a linear combination of spherical Gaussian densities has been described fully elsewhere [2]. The approximate form

$$\rho^* = \sum_t q_t G_t(\mathbf{r} - \mathbf{r}_t) \tag{1}$$

where G_t is defined as

$$G_t = (a_t/\pi)^{3/2} \exp\left(-a_t(\mathbf{r} - \mathbf{r}_t)^2\right) \tag{2}$$

has been shown to give a good representation of ρ for a modest number of terms provided that the origins $\mathbf{r}_t$ are well-chosen and the exponents a_t and charges q_t are optimized.

The density G_t is the same as that of the ground state eigenfunction of a spherical oscillator with the exponent a_t related to the mass m_t and frequency ω_t by

$$a_t = m_t \omega_t. \tag{3}$$

For such an oscillator the potential energy has the form

$$V = 1/2 \, m\omega^2 r^2 \tag{4}$$

and the force constant is $k = m\omega^2$.

It was noticed in practice [7, 5] that, when the exponents were optimized, the fitting of Gaussians to the electron density normally produced a few functions for each molecule with rather small exponents. These were located close to the centre of nuclear charge in small molecules. The arbitrary criterion of an exponent less than 1 was taken as the definition of these diffuse functions. This implies a spread of the charge over several nuclei. In practice the exponents are usually significantly different from 1 so that this number in the definition is not critical. The number of diffuse functions increases as the total number of Gaussians increases and the description of each atom improves. It seems significant that at least one for each heavy atom is required to obtain a good density.

In general the most diffuse function is put near the charge centre and has a charge of several electrons. It especially represents the electron density in the outer part of the molecule since the small exponent allows it to extend further than the other, more localized, functions. Since this is the region where penetration effects are first felt its inclusion as a continuous distribution explains why the representation of the MEP is improved so much. The next most diffuse functions tend to be on or near the heavy atoms. They represent the outer charge associated with that atom and give shape to the diffuse cloud. Together, these functions include a major part of the valence electrons.

Typical figures for the exponent and charge of the most diffuse function are given in Table 1 for various molecules. It is located at or near the centre of nuclear charge. For the molecules with two heavy atoms the exponent decreases by approximately a factor of four, showing that the function extends to twice the distance. The table also includes the less-diffuse functions for the larger molecules,

Table 1. Diffuse functions for molecules

Molecule	Exponent	Charge
H_2O	0.4616	3.1376
HF	0.4951	1.9907
NH_3	0.3326	2.5183
C_2H_4	0.1116	1.2402
(on C	0.6344	4.0184)
HCHO	0.1451	0.8820
(on C	0.7314	3.4442)
(on O	0.7174	4.2319)
CH_3F	0.1529	1.1463
(on C	0.6569	3.8828)
CH_3OH	0.1689	1.4762
(on C	0.6755	3.7135)
(O lone pair	0.8243	1.8132)

Table 2. Polarizability of molecules

Molecule	H_2O	HF	NH_3
α_{xx}	2.62900	1.79536	8.86588
α_{yy}	6.73356	1.79536	8.86588
α_{zz}	4.84376	4.12828	5.16318
expt $\bar{\alpha}$	9.72	5.6	14.98

which are located on the heavy nuclei or in the O lone pair and give the diffuse cloud its shape. These are in parentheses.

3. Polarizability of molecules

To calculate the polarizability of a molecule the easiest procedure is to add electric field terms to the Hamiltonian and solve the equations again. This finite field approach [7] investigates very directly the distortion of the electron density due to the field. About 20 small values of the field were taken in turn and the wavefunction calculation repeated. By numerical differentiation of the dipole moment with respect to the field the polarizability is obtained.

This procedure was applied to three molecules and the results are given in Table 2. In these calculations the z axis is the molecular axis and the yz plane contains a H atom. The field is taken in two or three principal directions as necessary to find all the tensor components of the polarizability. It can be seen that the results are fairly satisfactory considering that the basis set was not enlarged to permit the distortion of each basis function caused by the field to be fully described. The experimental polarizabilities [9, 10, 11] are spherical averages and so are about twice the values calculated here.

4. In an electric field

From the electron density in the presence of the field the density-fitting process can be repeated so that the changes in density induced by the field can be described more simply.

In the presence of an electric field E the potential of a spherical oscillator with charge q changes to

$$V = 1/2m\omega^2 r^2 - q(r \cdot E)$$
$$= 1/2m\omega^2(r - q/m\omega^2 E)^2 - q^2/2m\omega^2 E^2. \qquad (5)$$

This implies that the system oscillates with the same frequency about an origin which has moved in the direction of the field by an amount proportional to the field:

$$\text{displacement/field} = q/m\omega^2. \qquad (6)$$

Thus the force qE produced by the external field is balanced by the harmonic restoring force with this displacement. The polarizability of the oscillator is then given by

$$\alpha_{xx} = -d^2(\text{energy})/dE_x^2$$
$$= q^2/m\omega^2 \qquad (7)$$

and is isotropic. When the oscillator is constrained to move along a line which is not in the direction of the field this formula has to be amended. Only the resolved part of the force in the direction of the line will be effective in moving the function. Thus when a spherically symmetric harmonic oscillator is put into an electric field its wavefunction retains the same shape, including its exponent, but changes its origin.

This theory of the spherical oscillator will now be used as an analogy for the Gaussian model of a molecule. Consequently, when fitting the density in the presence of a field, Gaussians with the same charges and exponents as before but re-optimized origins are used. Each Gaussian was allowed to move only in a restricted direction. The lone pair Gaussians, for example, remained in the lone pair direction but could move along it. The inner shell Gaussians are so strongly attracted to the nucleus that they did not move.

From the spherical oscillator, the Gaussian exponent is identified as

$$a_t = m_t\omega_t \qquad (8)$$

where m_t is an effective mass connected with the charge in the Gaussian. From the calculation of the displacements of the Gaussian G_t in the presence of a finite electric field the force constant, $k_t = m_t\omega_t^2$, was found. In practice the displacements were closely linear in the field despite the fact that the original basis set is fixed. The mass and the frequency can be deduced from these. Since this movement of the Gaussian is easier in some directions than others the effective mass will depend on the field direction, i.e. it will be a tensor. The polarizability depends on this mass and on the exponents so it will become a tensor also. It is clear from this that the polarizability is largely determined by those Gaussians which move most in a field. The Gaussians on the nuclei move little or no distance so they contribute little or nothing to the polarizability but those on the lone pairs and in the centre of the molecule are sensitive to the field and contribute most of the effect.

For many molecules the principal directions of the mass tensor are determined by symmetry so that the principal components of the polarizability can be found directly. In such a direction the polarizability is

$$\alpha_{xx} = q_t^2/m_t\omega_t^2$$
$$= q_t^2 m_t/a_t^2. \qquad (9)$$

According to this model the diffuse functions will contribute most significantly to the polarizability since they have the smallest exponents. It happens also that they have the smallest effective masses but the result remains that the polarizability

Table 3. Diffuse function contribution to polarizability

		H_2O	HF	NH_3
Force constant	xx	3.20606	1.75829	0.97036
	yy	2.10225	1.75829	0.97039
	zz	2.58086	0.74385	1.20423
Effective mass	xx	0.06647	0.13940	0.11403
	yy	0.01014	0.13740	0.11403
	zz	0.08257	0.32951	0.09188
Polarizability	xx	3.07056	2.25392	6.53575
	yy	4.68281	2.25392	6.53575
	zz	3.81439	5.32772	5.26664

is almost all due to the diffuse functions. Since these functions represent the outer, less firmly bound electrons this is a natural conclusion. The extent of this is shown in Table 3 which gives the force constant and effective mass for the diffuse function as determined by fitting and, hence, the contribution of this function to the polarizability. By comparing with Table 2 it can be seen that the major component of the polarizability has been found.

5. Dispersion forces

In view of this success in calculating the polarizability from the diffuse function it is natural to ask whether the dispersion forces also can be calculated. The Drude model which invokes the coupling of harmonic oscillators in the two molecules is the simplest starting point. Calculations of this type have been performed by Amos and Yoffe [12] and by Waldman and Gordon [13]. In the simplest form of this model the dipole-dipole dispersion term C_6 is determined by the mean polarizabilities $\bar{\alpha}_1$, $\bar{\alpha}_2$ of the molecules and the frequencies ω_1, ω_2:

$$C_6 = 3/4(\bar{\alpha}_1\omega_1)(\bar{\alpha}_2\omega_2)/(\omega_1 + \omega_2). \tag{10}$$

Higher order dispersion coefficients can also be calculated from this model but this has not been investigated.

Some results for C_6, the isotropic van der Waals term, are shown in Table 4. They are compared with accurate results (quoted from [14]) calculated using good values of the dipole–dipole oscillator strengths. The agreement obtained is

Table 4. The isotropic C_6 coefficient of the dispersion forces between identical molecules calculated using only the diffuse function

	This	Accurate
H_2O	61.67	45.37
HF	19.68	—
NH_3	87.41	89.08

surprisingly good in view of the simplicity of the model and suggests that C_6 is even more sensitive to the outermost electrons than is the polarizability. A similar experience of a low value of the polarizability leading to a good value of C_6 using a model of this type was reported by Mulder et al. [14] and they have analyzed the reasons for it.

6. Discussion

By retaining one diffuse function for each heavy atom but shrinking into point charges the remaining Gaussians, a model of a molecule is obtained which has great similarities with the old currant bun model. For a molecule such as water or ammonia with one heavy atom it has one diffuse function and, hence, a spherical external shape. Inside this function there are point charges, both positive and negative, which, together with it, give a Molecular Electrostatic Potential very close to the true one. When acted on by an external field the charge cloud polarizes by moving its, origin against the harmonic restoring force due to the rest of the system. When attracted by another molecule this polarizable cloud contributes most of the van der Waals force. The angle-dependent part of the intermolecular forces is predominantly the electrostatic force and this is determined by the point charges placed carefully around the molecule. The dispersion and repulsive forces are conveniently centred where the diffuse function is, close to the charge centre of the molecule. When there are several heavy atoms there will be a diffuse function for each of these together with a very diffuse function at the charge centre. This rebaked currant bun model is a very significant improvement on pure point charge models or atomic multipole models. It is more difficult to use than these in such applications as molecular dynamics calculations, because the electric field on each molecule must be calculated iteratively in order to determine how far it will cause the diffuse function to move and so represent the polarized molecule, but the resulting increased accuracy would make its introduction worth the effort in some circumstances.

The shell model of an ion, as used by Faux and Lidiard [6] in their calculations of defects in ionic crystals, divides the ionic charge into two parts, outer and inner, coupled harmonically. Such a model incorporates the polarization effects and the induced dipoles caused by an external field through the movement of the outer shell against the inner core. The present treatment, if applied to ions, would allow a determination of the charge in each region, the force constant and the effective mass by fitting the density from *ab initio* calculation. It would also permit the inner electronic charge to be shrunk to a point charge on the nucleus. This would make the shell model an *ab initio* model instead of a semi-empirical one.

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