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Electric Polarizabilities Using Point Charge Models

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The formula for the electric polarizability of a molecule using a Frost model Lewis basis set, that is one orbital per electron pair, can be extended to include wavefunctions containing additional Gaussians using point charge models. Using these alternative formulae, results for hydrocarbon Lewis sets and molecular fragment wavefunctions are in good agreement with experiment and with the results obtained using the original formula. In addition results for atomically centred wavefunctions for molecules containing lone pairs are also good and show an improvement over the Lewis set results for these species.

Key words: Electric polarizabilities – Point charge models

1. Introduction

A particularly simple expression for α, the electric polarizability of a molecule, may be obtained from its Frost model wavefunction [1] using symmetry adapted perturbation theory [2] or a classical approach [3]. The calculations are restricted to Lewis basis sets, that is one orbital per electron pair, containing *s*- and *p*-type Gaussians [4] though it was shown that the formula could also be used when extra inner shell orbitals are added. The inner shell contributions to the molecular polarizability are small and so effectively the method was to just calculate valence electron terms. Results using the Lewis set wavefunctions were generally very good though somewhat less successful for molecules containing lone pair electrons.

Wavefunctions built from basis sets consisting of a large number of Gaussians are very common [5–8] and, unlike a Lewis set where two electrons may be allocated to each Gaussian, it is not always clear as to the occupancy of each Gaussian without recourse to density and overlap matrices. Moreover, for these large sets it is convenient to centre the orbitals on atoms so that their positions do not have to be

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optimized, relative to atomic centres. It is then the delocalized molecular orbitals, rather than the localized single centred ones in the Lewis set case, that provide a good description of the bonding regions so important in the calculation of a property like the polarizability. For these atomically centred basis sets the formula derived for α using a Lewis basis set must be extended to cope with the increased number of Gaussians.

For small systems using accurate Hartree-Fock wavefunctions there are probably more accurate methods for calculating α [9], but we are interested here in methods that are applicable to larger systems and even macromolecules, calculations on macromolecules wavefunctions containing a large number of Gaussians per basis function may well become prohibitively too large and so in this paper we are only concerned with wavefunctions containing relatively few Gaussians per basis function. An alternative method for macromolecules is the use of fragmenting techniques [10] which have met with much success employing a much smaller basis set. Even so, once again there are additional Gaussians and the Lewis set formula for α must be extended.

Point charge models provide a good description of the electrostatic potential for a molecule and various property results have been in good agreement with experiment [3]. Indeed the Lewis set formula for α can be derived in a straightforward manner from a particularly simple point charge model. The procedure adopted here will be to extend the formula to wavefunctions such as those mentioned above, by considering point charge models that are not restricted to Lewis sets.

2. Point Charge Models

We consider the problem in terms of point charge models, that is using a classical approach. Various point charge models have been suggested, notably those of Hall [11, 12], Shipman [13] and Amos and Yoffe [3]. The Hall point charge model is an approximation to the electron density $\rho(\boldsymbol{r})$ where, summing over the number of orbitals,

$$\rho(\boldsymbol{r}) = 2 \sum_{ij} P_{ij} \phi_i(\boldsymbol{r}) \phi_j(\boldsymbol{r}) \tag{1}$$

where P_{ij} is an element of the density matrix calculated from an SCF wavefunction and $\phi_i(\boldsymbol{r})$ and $\phi_j(\boldsymbol{r})$ are normalized spherical Gaussian orbitals with centres $\boldsymbol{R}_i$, $\boldsymbol{R}_j$ and exponents α_i, α_j respectively. Their product, written $\phi_{ij}(\boldsymbol{r})$, will also be a spherical Gaussian with centre

$$R_{ij} = \frac{\alpha_i \boldsymbol{R}_i + \alpha_j \boldsymbol{R}_j}{\alpha_i + \alpha_j} \tag{2}$$

and exponent $2\alpha_{ij}$ where

$$\alpha_{ij} = (\alpha_i + \alpha_j)/2. \tag{3}$$

Thus ρ is a sum of spherical Gaussians and the point charge model is to replace Eq. (1) by

$$\rho_H^*(\boldsymbol{r}) = 2\sum_{ij} P_{ij}S_{ij}\delta(\boldsymbol{r} - \boldsymbol{R}_{ij}) \tag{4}$$

where S_{ij} is the overlap between ϕ_i and ϕ_j. The model, therefore, places charges $Z_{ij} = 2P_{ij}S_{ij}$ at positions $\boldsymbol{R}_{ij}$ and we associate Gaussian ϕ_{ij} and frequency $\omega_{ij} = 2\alpha_{ij}$ with charge Z_{ij}.

The Shipman point charge model redistributes off centre charges in Hall's model onto Gaussian centres by rewriting the total charge Z as

$$Z = \sum_i q_i \tag{5}$$

with

$$q_i = \sum_j \frac{2\alpha_i Z_{ij}}{(\alpha_i + \alpha_j)}. \tag{6}$$

Then the point charge approximation to Eq. (1) is

$$\rho_S^*(\boldsymbol{r}) = \sum_i q_i\delta(\boldsymbol{r} - \boldsymbol{R}_i) \tag{7}$$

which places charges q_i at positions $\boldsymbol{R}_i$ and we associate Gaussian ϕ_i and frequency $\omega_i = 2\alpha_i$ with charge q_i.

The Amos-Yoffe model was much simpler than the other two but gave similar results for various molecular properties. It is an approximation to the electron density $\bar{\rho}(\boldsymbol{r})$ where

$$\bar{\rho}(\boldsymbol{r}) = 2\sum_i \phi_i(\boldsymbol{r})\phi_i(\boldsymbol{r}) \tag{8}$$

given by

$$\rho_{AY}^*(\boldsymbol{r}) = 2\sum_i \delta(\boldsymbol{r} - \boldsymbol{R}_i) \tag{9}$$

which amounts to simply placing a charge of 2 at each Gaussian centre and we associate Gaussian ϕ_i and frequency $\omega_i = 2\alpha_i$ with the charge 2 placed at $\boldsymbol{R}_i$.

The central properties satisfied by all three models are that the total electronic charge and dipole moment are conserved. Unlike the other two methods, however, the Amos-Yoffe model is restricted to Lewis basis sets and so it only seems natural to turn to the Hall and Shipman models in our search for non-Lewis set formulae.

3. Formulae for α

We follow a similar approach to before [3] and consider the second order property W_2 to be calculated using the general expression

$$W_2 = \frac{1}{2}\int w(\boldsymbol{r})\rho'(\boldsymbol{r})\,d\boldsymbol{r} \tag{10}$$

where $\rho'(\boldsymbol{r})$ represents the first order change in $\rho(\boldsymbol{r})$ due to the perturbation $w(\boldsymbol{r})$. Then the results for the different models correspond to different choices of $\rho'(\boldsymbol{r})$. Before, we considered the classical equations of motion and the Drude theory [14] to find $\rho'(\boldsymbol{r})$, and the simplest extension of this theory is to use point charge models to compute $\rho'(\boldsymbol{r})$ and hence W_2.

We consider the general case of a molecule represented by a set of point charges $\{Z_u\}$, with associated frequencies $\{\omega_u\}$, and the various point charge models will simply be specific choices of $\{Z_u\}$, $\{\omega_u\}$. The point charge density is written

$$\rho^*(\boldsymbol{r}) = \sum_u Z_u \delta(\boldsymbol{r} - \boldsymbol{R}_u) \tag{11}$$

and when the molecule is perturbed by a static electric field $\boldsymbol{E}$ the equation of motion of charge Z_u is

$$\frac{d^2\boldsymbol{r}_u}{dt^2} + \omega_u^2 \boldsymbol{r}_u = \boldsymbol{E} \tag{12}$$

where $\boldsymbol{r}_u = \boldsymbol{r} - \boldsymbol{R}_u$, so that

$$\boldsymbol{r}(Z_u) = \boldsymbol{R}_u + \frac{1}{\omega_u^2}\boldsymbol{E} \tag{13}$$

on setting the amplitude for the harmonic terms equal to zero. The total density will therefore be

$$P(\boldsymbol{r}) = \sum_u Z_u \delta\left(\boldsymbol{r} - \boldsymbol{R}_u - \frac{1}{\omega_u^2}\boldsymbol{E}\right) \tag{14}$$

and

$$\rho'(\boldsymbol{r}) = P(\boldsymbol{r}) - \rho^*(\boldsymbol{r}) = \sum_u Z_u \left\{\delta\left(\boldsymbol{r} - \boldsymbol{R}_u - \frac{1}{\omega_u^2}\boldsymbol{E}\right) - \delta(\boldsymbol{r} - \boldsymbol{R}_u)\right\} \tag{15}$$

Since $w(\boldsymbol{r}) = -\boldsymbol{r}$ and the polarizability α satisfies $W_2 = -\frac{1}{2}\alpha E$ it follows that

$$-\frac{1}{2}\alpha \boldsymbol{E} = -\frac{1}{2}\int \boldsymbol{r}\rho'(\boldsymbol{r})\, d\boldsymbol{r} = -\frac{1}{2}\sum_u Z_u\left(\boldsymbol{R}_u + \frac{1}{\omega_u^2}\boldsymbol{E} - \boldsymbol{R}_u\right) \tag{16}$$

that is

$$\alpha = \sum_u \frac{Z_u}{\omega_u^2}. \tag{17}$$

As before [3] if the electric field is time-dependent it is easy to derive $\alpha(\omega)$, the frequency-dependent polarizability, which is

$$\alpha(\omega) = \sum_u \frac{Z_u}{\omega_u^2 - \omega^2}. \tag{18}$$

The results for the three models are special cases of Eq. (17). For the Hall model using $\rho^*(\boldsymbol{r})$, given by Eq. (4), we have charges $\{Z_{ij}\}$, defined in Sect. 2, and frequencies $\{\omega_{ij}\}$ ($\omega_{ij} = 2\alpha_{ij}$, defined by Eq. (3)) yielding the formula for the polarizability α_{H}

$$\alpha_{\mathrm{H}} = \frac{1}{4}\sum_{ij}\frac{Z_{ij}}{\alpha_{ij}^2}. \tag{19}$$

For the Shipman model we use $\rho_S^*(\boldsymbol{r})$, given by Eq. (7), giving charges of $\{q_i\}$, defined by Eq. (6), with frequencies ω_i ($\omega_i = 2\alpha_i$) yielding the formula for the polarizability α_S

$$\alpha_S = \frac{1}{4}\sum_i \frac{q_i}{\alpha_i^2}. \tag{20}$$

Finally, the original formula is to simply use $\rho_{AY}^*(\boldsymbol{r})$ of Eq. (9), that is charges of 2 with frequencies $\{\omega_i\}$, as for the Shipman model, giving α_{AY}

$$\alpha_{AY} = \frac{1}{2}\sum_i \frac{1}{\alpha_i^2}. \tag{21}$$

For the time dependent case, formulae for the three models are simply obtained from Eq. (18) by substituting in the values for the point charges and their respective frequencies. When $\omega = 0$, Eq. (18) naturally reduces to Eq. (17) as is to be expected.

In quantum mechanical terms the use of the semi-classical density function P is equivalent to assuming the effect of the field is taken into account by a shift in point charge positions and that any redistribution of charges can be neglected.

4. Results for the Electric Polarizability

4.1. Lewis Set Wavefunctions

The formulae of Eqs. (19–21) for α are first tested on Frost model Lewis basis set wavefunctions for hydrocarbons and results are compared with experimental values in Table 1. The wavefunctions and the results using the formula of Eq. (21) for α_{AY} have been given previously [15] but the polarizability values are included once more for comparison with the other results. The wavefunctions for both C_3H_4 and C_4H_6 contain orbitals fixed at the centre of CC bonds whilst C_4H_6 has different parameters for inner and outer CH exponents and orbital positions. The wavefunctions for C_6H_6 either place *p*-type Gaussians in alternate CC bonds (BOND),

Table 1. Electric polarizabilities of some hydrocarbons using Frost model Lewis basis sets[a]

Molecule[b]	α_{AY} (Eq. (21))	α_H (Eq. (19))	α_S (Eq. (20))	Experimental
CH_4	23.36	23.55	23.53	25.6[c]
C_2H_6	41.25	41.60	41.58	44.7[d]
C_2H_4	42.22	42.60	42.55	42.2[d]
C_2H_2	35.15	35.47	35.44	34.9[d]
C_3H_6	56.03	56.99	56.84	56.4[d]
C_3H_4	53.85	54.40	54.33	55[c], 60[e]
C_4H_6	81.72	82.63	82.51	84[e]
C_6H_6 (ATOM)	94.52	95.56	95.44	104[d]
C_6H_6 (BOND)	108.89	109.88	109.78	104[d]

[a] Units of 10^{-25} cc.
[b] For wavefunctions see Ref. [15] and Sect. 4.
[c] Ref. [21].
[d] Ref. [22].
[e] Ref. [23].

that is providing a Kekulé structure, or on alternate CC atoms (ATOM). All wavefunctions were obtained using the OPIT program [16] at Nottingham and employed experimental geometries. Some of the wavefunctions contain p-type Gaussians as well as s-type ones and we may use exactly the same formula as before. This point is discussed in Sect. 5.

As can be seen from the table values for α for the three methods are very similar and are in good agreement with experiment. A general rule from Table 1 for Hydrocarbon Lewis set wavefunctions is $\alpha_{AY} < \alpha_S < \alpha_H$ with α_S and α_H in especially close agreement. The results do indicate that not only can similar results be obtained for properties such as the electrostatic potential [3] using the three models but also for a second order property α.

4.2. Molecular Fragment Wavefunctions, Wavefunctions Containing Additional Inner Shell Gaussians and Wavefunctions Containing S-Type Functions Only

We now consider wavefunctions that use either a Lewis basis set or one containing only a few additional Gaussians. Firstly, the addition of an extra inner shell Gaussian on each carbon atom leads to improved results for both CH_4 and C_2H_6 using the formulae for α_H and α_S. For CH_4 we find $\alpha_H = 23.66$ and $\alpha_S = 23.64$ whilst for C_2H_6 we obtain $\alpha_H = 41.80$ and $\alpha_S = 41.76$ (10^{-25} cc). However, the improvement over Lewis set results is only slight and simply using α_{AY} for these wavefunctions and ignoring inner shell Gaussians provides results of 23.39 and 41.27 for CH_4 and C_2H_6 respectively.

Turning now to fragmenting techniques, for C_2H_6 using the orbital parameters and geometry of Ref. [17] with optimized density matrix elements provided by OPIT we find $\alpha_H = 43.16$ and $\alpha_S = 43.16$ in excellent agreement with the experimental value. For C_2H_4 using orbital and geometry values of Ref. [10] we obtain $\alpha_H = 36.04$ and $\alpha_S = 35.90$ whilst using an experimental geometry we find $\alpha_H = 36.71$ and $\alpha_S = 36.47$, again density matrix elements were found using OPIT. These results may be compared with values given in Table 1 and those given below and clearly the formulae can be used in conjunction with fragmenting techniques.

Using the original formula, α_{AY} values obtained using Frost model Lewis set wavefunctions containing just s-type functions for pi-bonding systems C_2H_2 and C_2H_4 [2, 18] were poorer than those for saturated systems or results obtained using p-type functions [4]. Using the point charge model formulae in conjunction with those wavefunctions and geometries, but with density matrix elements determined by OPIT, we find $\alpha_H = 37.60$ and $\alpha_S = 37.47$ for C_2H_4 and $\alpha_H = 42.01$,

Table 2. Electric polarizabilities of molecules containing lone pairs[a]

Molecule	α_{AY}	α_H	α_S	Experimental[b]
NH_3	18.2	18.9	20.2	22.2
H_2O	9.0	12.9	14.2	14.4

[a] Units of 10^{-25} cc. [b] Ref. [22].

$\alpha_S = 38.65$ for C_2H_2 showing improvement over the α_{AY} result of 36.9 for C_2H_4 but not for C_2H_2 when we find $\alpha_{AY} = 31.6$.

4.3. Atomically Centered Wavefunctions

Of particular interest are species for which Frost model Lewis set wavefunctions give a poor result for α such as molecules containing lone pairs. In Table 2 results are given using α_{AY} for wavefunctions from Ref. [18] for H_2O and NH_3 and this may be compared with values obtained for α_H and α_S for atomically centred wavefunctions. Two *s*-type Gaussians were centered on each hydrogen whilst four *s*-type Gaussians and two *p*-type Gaussians for each direction, making a total of ten Gaussians, were centred on each heavy atom, O and N. Exponents were taken from the unconstrained set given by Pople *et al.* [7] but the contraction coefficients were not used and the density matrix using all the functions was found by OPIT.

As can be seen from the table the use of these atomically centred wavefunctions, of approximately STO-2G complexity, in conjunction with α_H or α_S, gives an improved result over the Lewis set value α_{AY} especially for water.

5. Discussion

The proposed point charge model formulae α_H and α_S provide excellent results for a number of different types of wavefunction. The results for Lewis set wavefunctions for hydrocarbons are in good agreement with experiment and the original formula, α_{AY}, whilst the addition of an extra inner shell orbital provides slightly improved results for CH_4 and C_2H_6. The formulae may also be used in conjunction with molecular fragmenting techniques as well as wavefunctions containing just *s*-type functions, even for pi-bonding systems. Atomically centred wavefunctions of approximately STO-2G complexity provide good results for H_2O and NH_3 using α_H and α_S, showing improvement over the Lewis set value α_{AY}.

The formulae are derived for *s*-type Gaussians but we can in fact use *p*-type Gaussians as well. For in the case of *p*-type Gaussians in conjunction with the Hall model the total charge will once more be conserved but the dipole moment will not. We may use exactly the same point charge model as before or, alternatively, using differential operators it is possible to construct a point charge model for *s*- and *p*-type Gaussians that retains the same point charges as before and also conserves the dipole moment [20]. Either way we may use exactly the same formulae for α_H and α_S for *p*-type Gaussians as well. Indeed it is possible to show quantum mechanically that the formula for α_{AY} applies not only to *s*-type functions but *p*-type Gaussians as well [4] and so it is to be expected that the same should hold for α_H and α_S.

Currently we are considering other properties and interaction coefficients using point charge models.

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