Theor Chim Acta (1986) 69: 63-69

Theoretica Chimica Acta

The approximation of electron densities

C. M. Smith and G. G. Hall

Division of Molecular Engineering, Kyoto University, Kyoto, 606, Japan

(Received June 27/Accepted September 12, 1985)

This paper discusses the approximate representation of the electron density produced by an *ab initio* calculation. A linear combination of Gaussians is fitted to the density by minimizing a functional which is the consequent error in field-energy. The practical implementation of the procedure, following a Gaussian 80 calculation, is described and some of the complications are analysed.

Key words: Electron density — Gaussian 80 — Point charge models

1. Introduction

The electron density, in the form in which it emerges from an *ab initio* calculation, is very difficult to comprehend and interpret. Often the Mulliken populations are also listed as the only aid to interpretation but the use of these has been frequently criticised because of the simple, but arbitrary way in which the overlap density is equally allocated between the atoms. There is a clear need for other quantities which can express features of the density in an unambiguous and useful way.

This paper follows an earlier one [1] in which the electron density was approximated using spherical Gaussians centered on the nuclei. The results showed that such calculations were feasible and that the approximate densities were sufficiently accurate for various purposes. In this paper the limitation to functions centered on the nuclei will be lifted so that more flexible trial functions can be used. The restriction to spherical Gaussians remains but is not of significance since Gaussians on different centers can represent the lack of spherical symmetry just as effectively as using higher angle-dependent Gaussians. From the Gaussian densities, point charge models of molecules can be readily deduced.

In the following paper [2], results are given of calculations on the water molecule using the techniques described here.

The idea of using spherical Gaussians to represent the electron density has been suggested by Rys et al. [3] and by Yanez et al. [4]. They have adopted the criterion of a least-squares fit to the calculated electron density itself but their Gaussians are constrained by the need to fit first the different atoms. This limits the quality of the fit.

There are many methods now in use to calculate point charge models of molecules. Momany [5], Cox and Williams [6] and Ray et al. [7], and others, use a least-squares fitting over a finite grid to fit the molecular electrostatic potential with point charge potentials. Since the point charge potentials diverge, this process is strongly dependent on the choice of grid. Brobjer and Murrell [8] prefer to determine the positions and charges of their point charge models by fitting the molecular multipole moments (experimental, where possible, otherwise calculated). They argue that their several-center models are superior to one-center multipole models. On the other hand, Sokalski and Poirier [9] use the atomic orbitals of each atom's basis set to define local multipole moments and so generate atom-based multipole models. Bonaccorsi et al. [10], Dovesi et al. [11] use localized orbitals to define local densities and their centers of charge to define locations. This results in models having point charges not restricted to the nuclei.

The fitting process described here differs from all of these in that it uses an energy as a fitting criterion. This means that the results will be more suitable for calculating energy-type properties. It also derives point charge models by shrinking Gaussians to delta functions and so avoids the serious problems of divergence which affect all attempts to fit point charges directly to the electron density.

2. The form of the electron density

It is convenient to begin this discussion with an analysis of the electron density as produced in present-day packages. These employ basis sets already determined by previous research as of good quality for the atomic orbital concerned. Each of these is defined using a number of "primitive Gaussians" to represent its radial dependence. The use of Gaussians ensures that all the integrals in the calculation can be evaluated to any desired accuracy. The electron density is a quadratic form in the basis and, hence, in the primitive Gaussians viz.

$$\rho(\boldsymbol{r}) = \sum_{st} p_{st}\varphi_s(\boldsymbol{r})\varphi_t(\boldsymbol{r}), \tag{1}$$

where p_{st} is the element of the density matrix and $\varphi_s(\boldsymbol{r})$ a primitive Gaussian. This structure remains the same whether or not the calculation includes configuration interaction.

If $\varphi_s(\boldsymbol{r})$ is a normalized spherical Gaussian orbital at the point $\boldsymbol{A}_s$:

$$\varphi_s(\boldsymbol{r}) = (2a_s/\pi)^{3/2} \exp\left[-a_s(\boldsymbol{r}-\boldsymbol{A}_s)^2\right] \tag{2}$$

then the product of two orbitals is a spherical Gaussian density at the point

$$\boldsymbol{A}_{st} = (a_s\boldsymbol{A}_s + a_t\boldsymbol{A}_t)/(a_s + a_t). \tag{3}$$

The relation can be written as

$$\varphi_s\varphi_t = S_{st}G_{st} \tag{4}$$

where S_{st} is the overlap integral and G_{st} a normalized spherical Gaussian density with exponent

$$a_{st} = a_s + a_t \tag{5}$$

and center at $\boldsymbol{A}_{st}$

$$G_{st} = (a_{st}/\pi)^{3/2} \exp\left[-a_{st}(\boldsymbol{r} - \boldsymbol{A}_{st})^2\right]. \tag{6}$$

This was first pointed out by Boys [12] and is the basis of his integration techniques for these functions. It is also the basis of the point charge models discussed by Tait and Hall [13]. Boys also showed that the angular factors can be treated simply by differentiating the spherical functions with respect to their positions. The extension of this to point charge models was given by Martin and Hall [14].

Since the product of two primitive Gaussians on the same center is a Gaussian density the exponent of which is the sum of their exponents, n primitive Gaussians on a center will give, in general, $n(n+1)/2$ distinct Gaussian densities there. For the water molecule, using a STO-6G wavefunction, each H will have 21 Gaussian densities and the O has 78 densities. When there are two centers the overlap densities will be at different points along the line joining them so that, for water, there will be 36 densities along HH but 6 of these are at the mid-point; along OH there will be 72 densities. If one orbital is of p type then the products will all be of p type but the centers will be the same. For two p functions the product will include both spherical and d type Gaussians. Thus the density can be re-written as

$$\rho = \sum_{st} p_{st}S_{st}G_{st} \tag{7}$$

where G_{st} may now include some higher Gaussians or groups of spherical Gaussians (lobe functions) to simulate them.

The density is then exactly expressible as a linear sum of Gaussians on many centers along the internuclear axes. Some may have angular factors. This form for the density is not a practical one for present purposes since the number of charges and centers is excessively large. It does show, however, that the fitting process is really an economization of the density. The optimization process picks out the major terms and locates charge where they are. The many small terms are grouped together and represented by diffuse Gaussians. As the process proceeds, with more fitting functions, there will be Gaussians in the original ρ competing for an exact fit and, as the trial function ρ^* comes near to one or other of these, the functional may have a local minimum. This is especially likely to occur during the optimization of a Gaussian in a bond since ρ has so many Gaussian densities there. The process may then show many local minima before the global minimum is found.

3. Optimization

The criterion for the fitting which was previously used was the minimizing of the functional which is the integral of the square of the difference in electric fields and can be written as

$$U=\tfrac{1}{2}\iint [\rho(1)-\rho^*(1)]\frac{1}{r_{12}}[\rho(2)-\rho^*(2)]\,d\tau_1\,d\tau_2 \tag{8}$$

where ρ is the electron density and ρ^* the approximate one. The best fit for a given form of trial density is found by minimizing U with respect to the parameters in ρ^*. Since U is non-negative the size of U is a good measure of the accuracy of the fitting. It is convenient to measure both ρ and ρ^* in electron charges rather than proton charges.

The approximation used here is

$$\rho^*=\sum_t q_t G_t \tag{9}$$

where G_t is a Gaussian density, as (6), but with arbitrary exponent and position, while q_t represents its charge, and the sum is written as a single sum. U is, therefore, a quadratic form in terms of the charges q_t:

$$U=U_0-\sum_t q_t U_t+\tfrac{1}{2}\sum_{st} q_s U_{st} q_t, \tag{10}$$

where

$$U_0=\tfrac{1}{2}\iint \rho(1)\rho(2)/r_{12}\,d\tau_1\,d\tau_2 \tag{11}$$

$$U_t=\iint G_t(1)\rho(2)/r_{12}\,d\tau_1\,d\tau_2 \tag{12}$$

$$U_{st}=\iint G_s(1)G_t(2)/r_{12}\,d\tau_1\,d\tau_2. \tag{13}$$

There are two stages in the optimization. The charges q_t are found first. The functional U is replaced by W

$$W=U+\lambda\left(Q-\sum_t q_t\right) \tag{14}$$

so that the total charge Q can be constrained to equal the total number of electrons

$$Q=\sum_t q_t \tag{15}$$

The optimal charges satisfy

$$\partial W/\partial q_t=-U_t+\sum_s q_s U_{st}-\lambda=0 \tag{16}$$

so that

$$q_s=\sum_t N_{st}(U_t+\lambda) \tag{17}$$

where

$$\sum_{s} N_{us} U_{st} = \delta_{ut} \tag{18}$$

and λ is fixed by the constraint (15)

$$\lambda = \left(Q - \sum_{st} N_{st} U_t \right) \Big/ \sum_{st} N_{st}. \tag{19}$$

Since the equations (18) are linear their solution is normally unique and results in a numerical value of W. The second stage in the optimization is the variation of the exponents and positions of the Gaussians. This is a non-linear process and much more laborious. In this program a quasi-Newton routine was used. It was obtained as a standard package from the Kyoto University subprogram library. The variables optimized were functions of the exponents and positions rather than these variables themselves. This enabled the parameters of Gaussians on different centers to be kept the same. Each time the minimization routine changed the values of the exponents or the positions a new set of optimized charges was calculated.

There are many ways to constrain a function to move along a line between two centers. Two of these were used here viz.

a) $\boldsymbol{L} = (x\boldsymbol{A} + \boldsymbol{B})/(x+1)$ (20)

b) $\boldsymbol{L} = x\boldsymbol{A} + (1-x)\boldsymbol{B}.$ (21)

Frequently a) gave better results than b) although it allows $\boldsymbol{L}$ to approach $\boldsymbol{A}$ only by giving large values to x.

The exponents of the Gaussians must all remain positive and those on the same center must be unequal (otherwise U becomes singular). To enforce the first of these constraints the value of W was made large and positive if the sub-program called for a negative exponent. For the second, W was similarly enlarged when e, where

$$e = \sum_{sut} \left(U_{st} N_{tu} + N_{st} U_{tu} \right) - 2Q, \tag{22}$$

became greater than 10^{-9}.

4. Integral evaluation

In the Gaussian 80 program [15], the molecular orbitals are expressed as a sum over s, p, d and f type atomic orbitals, the radial parts of which are linear combinations of primitive Gaussians, on the nuclear centers. All of the integral evaluations, which are required to find U, can be performed by the same integral subroutines which are used to evaluate the two-electron part of the Fock matrix because ρ^* is a linear sum of s-type Gaussians. Extra routines to assemble these integrals to find the Coulomb energy were written. This involved multiplying integrals by the correct pair of elements of the density matrix and adding.

Similarly, routines were written to find U_t and U_{st} using the same integral routines. The Gaussians densities in ρ^*, Eq. (9), were written as the product of two square roots because the Gaussian 80 integral routines expect to treat integrals having four orbitals. U_t is a sum of products of an integral, involving ρ and G_t, and an element of the density matrix, while U_{st} is an integral involving only G_s and G_t. In this way a routine can be written to find U for any positive set of exponents and any change of position of the functions in ρ^*.

5. Calculation strategy

The input for the initial values of the non-linear parameters and for the control of the program was given in the form of free format code-words. This made it possible to run several types of fitting of the same original density in one program run. If desired, some of the parameters obtained in one fitting can be the initial values for the next calculation. Thus, from an initial very constrained calculation, fittings with fewer constraints can be obtained in stages so that the non-linear optimization process remains stable. The calculations on water, for example, which are reported in the following paper [2] started by fixing all the Gaussians on the nuclei and then allowed an O function to move from the nucleus in two directions to become the lone pair functions. Later one of each of the hydrogen functions was allowed to move along its OH bond to represent the bond density. This procedure seems to give stable results.

When the number of non-linear parameters becomes large the functional W begins to become flat and to show local minima in the manner discussed above. Attempts were made to deal with this by rescaling the variables so that W became less flat but no uniform procedure was found to be generally successful.

6. Negative charges

In some fittings some of the charges were found to be negative (corresponding to a positive contribution to the electron density). There seemed to be three situations which produced this.

a) In some early test runs using a STO-3G wavefunction it was found, when ρ^* contained more than 3 O Gaussians, that pairs of functions with almost the same exponent but opposite charges were obtained. This is similar to the effect of a differentiation of the Gaussian with respect to the exponent and such functions could be helpful in describing the L shell. Since this occurred only for simple wavefunctions it suggests that the fitting has gone beyond what such a simple wavefunction justifies.

b) During the STO-6G calculations, when there were three Gaussians on O and two functions for the lone pairs, the minimized exponent for the lone pair function was about 1.4, while the smallest of those for the O was 0.2. If, however, the calculation is started off with the lone pair exponent less than those for O then a local minimum is found and the most diffuse O function has a negative coefficient. In this calculation the optimization finds it difficult to enter a region in which the exponents swap sizes. The negative coefficient shows the program trying to correct for the overdiffuse lone pair by removing charge from the O. This observation reinforces the strategic comments above about allowing the optimization to proceed in stages with the exponents changing modestly at each stage. The reluctance of the program to change the order of exponents may have something to do with the conditioning of the matrix U_{st} but this has not been analysed.

c) In the more accurate calculations with many Gaussians it is sometimes found that one function may change sign. It is often unstable and changes sign several times during the calculations. This is not very significant. It represents a small adjustment in the density in one region to compensate for too much density put there by another function. This can occur just as, in the exact expansion, a term with negative overlap charge can occur.

7. Conclusion

A program has been implemented for the fitting of the electron density by a linear combination of Gaussians at arbitrary centers. The difficulties in the programming and in the control of the computing have been discussed. The success of the result depends on having an optimization routine which can control nonlinear optimization involving a shallow minimum and, possibly, several local minima. No artificial constraints on the functions are needed to make the process converge but some of the functions produced are diffuse and cannot be interpreted as localized to one atom.

Acknowledgment. The authors wish to acknowledge their thanks to the Japanese Ministry of Education for the award of a scholarship (to CMS).

References

1. Hall, G. G., Smith, C. M.: Int. J. Quant. Chem. **25**, 881 (1984)
2. Hall, G. G., Smith, C. M.: Theor. Chim. Acta **69**, 71 (1986)
3. Rys, J., King, H. F., Coppens, P.: Chem. Phys. Lett. **41**, 617 (1976)
4. Yanez, M., Stewart, R. F., Pople, J. A.: Acta Crystall. **A34**, 641 (1978)
5. Momany, F. A.: J. Phys. Chem. **82**, 592 (1978)
6. Cox, S. R., Williams, D. E.: J. Comp. Chem. **2**, 304 (1981)
7. Ray, N. K., Shibata, M., Bolis, G., Rein, R.: Int. J. Quant. Chem. **27**, 427 (1985)
8. Brobjer, J. T., Murrell, J. N.: J. Chem. Faraday Trans. 2 **78**, 1853 (1982)
9. Sokalski, W. A., Poirier, R. A.: Chem. Phys. Lett. **98**, 86 (1983)
10. Bonaccorsi, R., Scrocco, E., Tomasi, J.: J. Am. Chem. Soc. **98**, 4049 (1976)
11. Dovesi, R., Pisani, C., Ricca, F., Roetti, C.: J. Chem. Soc. Faraday Trans. 2 **70**, 1381 (1974)
12. Boys, S. F.: Proc. Roy. Soc. **A200**, 542 (1950)
13. Tait, A. D., Hall, G. G.: Theoret. Chim. Acta (Berl.), **31**, 311 (1973)
14. Martin, D., Hall, G. G.: Theoret. Chim. Acta (Berl.), **59**, 281 (1981)
15. Brinkley, J. S., Whiteside, R. A., Krishnan, R., Seeger, R., DeFrees, D. J., Schlegel, H. B., Topiol, S., Kahn, L. R., Pople, J. A.: Q.C.P.E. **13**, 406 (1981)