NOTIZEN

Some Remarks on the Gaussian Basis Functions

Application to Methylammonium

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The present work is an attempt to find a way for obtaining both relatively good total molecular energies and calculated molecular geometries, by using a relatively small basis set of Gaussian functions. It was found that if such functions are located in the middle of the bonds too, this goal can be achieved.

The choice of a basis set constitutes a problem when using Gaussian functions in a quantum chemical calculation. The threefold freehand, i. e. the number of functions, their exponents and location make this problem more complicated. For this reason there exist many ways of choosing such a basis set [1–4]. The general method is based on parameter optimization. This is currently being done for the atomic case. When dealing with molecules, it has been suggested that the number of functions be increased instead of making a new optimization, which is a very lengthy process. All these methods are based on energy minimization. The total energy of the system constitutes the criterion for judging the goodness of the chosen basis set.

Some works [5, 6] have dealt with the influence of the chosen basis set on other molecular features than energy. It was found that the best basis set for the total energy is not always the best one for other physical and chemical properties.

In the present work we have tried to find some guide lines of how to choose a basis set in a molecular calculation which yields a relatively good total energy but also a good calculated molecular geometry of the system.

The molecular geometry is generally considered as a derived propertey [7], but there are cases where the geometry of the system plays a certain role in the calculations. For example, it is known that the chemical reactions in the solid state (i. e., the reaction paths) are structure (geometry) dependent [8]. There are cases where the geometry is not known experimentally, and theoretical calculations are used to attempt to determine the geometry as well as the conditions in which the compound can be found experimentally [9]. For such cases, it is important to obtain an accurate calculated molecular geometry. Moreover, the molecular geometry can be determined experimentally with sufficient accuracy so that it can be used also as a criterion for judging the chosen basis set.

Calculations and Results

The calculations were carried out for Methylammonium ion — $(H_3N-CH_3)^+$ — the staggered conformation. A program based on the SCF-MO-LC(LCGO)-method, written by W. Meyer and P. Pulay of this Institute was used. We began with a basis set consisting of 40 "pure" Gaussian functions making 34 groups as shown in Table 1.

Table 1.

Atom	Type of function	No. of functions	No. of groups
each H	3 (1s)	18	18
N and C,	5 (1s)	10	10
respec-	2 (p_x)	4	2
tively	2 (p_y)	4	2
	2 (p_z)	4	2
		40	34

All exponential parameters (η values) were taken as the optimized values given by PREUSS [2]. The following geometrical parameters were kept fixed during the calculations:

The HNH and HCH angles (α angles), all equal to 109°.
The HN bond length equal to 1.04 Å and the HC bond length equal to 1.09 Å.

The only geometrical parameter allowed to vary was the C—N interatomic distance (R).

Some trial calculations were carried out with a fixed R value and varying the angle α and the hydrogen-heavy atom distances. It was found that the former values for these parameters were the best ones according to the total energy.

The total molecular energy as a function of R showed a minimum at $R=1.63$ Å. This value is too far from

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the experimental one [10]. We tried to improve our results by increasing the basis set. This was done in two ways:

a) By adding Gaussian functions in the middle of the C–N bond.
b) By taking a larger basis set on each heavy atom.

Case a)

Adding one Gaussian with $\eta = 1.562$ a. u. we obtained a lowering of the total energy but no shift in the position of the minimum. However, we observed a trend toward a greater lowering of the energy for smaller values of R (the right direction according to our point of view). By adding a second function at the same location with $\eta = 2.0$ a. u. we obtained, together with a lowering of the energy, a shift of the minimum to $R = 1.58$ Å. A third function with $\eta = 0.5$ a. u. did not change the position of the minimum and the energy decrease was very small. The final results are given in Table 2.

Case b)

In this case, we took for the (1s) orbitals on the heavy atoms, 7(1s) functions from the Huzinaga 9(1s) basis set [4]. The p functions and those on the hydrogen were left as in Case a). According to the total molecular energy these functions are better. We obtained a lowering of the energy by about 0.05% compared to Case a). In regard to the geometry the situation was not the same. For this case the minimum is located at $R = 1.62$ Å (Table 2).

Discussion

To obtain a shift of the energy minimum to smaller values of R means in fact to be able to increase in some way the attractive term (i. e., to extend the preponderance of the attractive part toward smaller R values) and (or) to decrease the repulsive term. The Gaussian functions we have located in the middle of the C–N bond tend to do this. They increase the nucleus-electron attraction by the fact that these electrons are now shared by the two nuclei. They also decrease the nucleus-nucleus repulsion by constituting a screen.

If all this is true, then functions though located at the middle of the C–N bond but which are more expanded in space (i. e., with small η values), have to shift the minimum toward larger values of R. In order to check this, we took only two functions in the middle of the bond (the shift in Case a) was observed with the first two functions). Two kinds of calculations were done:

Case c)

For this case we took as exponential parameters of the two functions:

$$\eta_1 = 0.3 \text{ a. u.}$$
$$\eta_2 = 0.7 \text{ a. u.}$$

These values correspond to a range of the Gaussians:

$$\varrho_1 = 0.953 \text{ Å}$$
$$\varrho_2 = 0.653 \text{ Å} \qquad \text{where} \quad \eta = 1/\varrho^2.$$

The results, Table 2, indicate a shift of the minimum to $R = 1.64$ Å. The total energy is now lower than in Case a), which means that these η values are better according to energy but not to molecular geometry.

Case d)

In this case we took more diffuse functions, expanded even beyond the two nuclei. The exponential parameters were:

Table 2.

R (Å)	Total Energy (a. u.)						
	Case a)	Case b)	Case c)	Case d)	Case e)	Case f)	Case g)
1.53	−94.15550						
1.545	−94.15610	−94.19792					
1.55	−94.15622		−94.15625				
1.56	−94.15646	−94.19933			−94.28261		
1.58	−94.15667	−94.20067	−94.15776			−94.29845	
1.59	−94.15666						
1.60	−94.15657		−94.15836	−94.15083			
1.608		−94.20157			−94.28800	−94.29870	
1.62		−94.20164				−94.29864	
1.63	−94.15590	−94.20155	−94.15875	−94.15351	−94.28953	−94.29853	−94.29318
1.64			−94.15876				
1.66		−94.20061	−94.15860	−94.15530	−94.29070	−94.29782	−94.29526
1.68					−94.29099		
1.69				−94.15632	−94.29099	−94.29656	−94.29661
1.72				−94.15662	−94.29049		−94.29721
1.73							−94.29727
1.75				−94.15633			−94.29720
1.78				−94.15547			

[10] L. E. SUTTON, Tables of Interatomic Distances, Spec. Public. 18, The Chemical-Society, London 1965.

$\eta_1 = 0.05$ a. u.
$\eta_2 = 0.10$ a. u. which correspond to:
$\varrho_1 = 1.672$ Å
$\varrho_2 = 2.365$ Å.

The results, Table 2, indicate now a shift of the minimum to $R = 1.72$ Å, as expected. The total energy has also increased.

One can argue that these results are not conclusive enough because we have used a too small basis set and in this case the addition of a new function can result in a large change in energy and geometry. But this is not the case. We have repeated the calculations with the full Huzinaga 9(1s) basis set (Case e). The results, Table 2, indicate an important lowering of the total energy, but the minimum is located now at $R = 1.685$ Å, a value far from the experimental one. In this case, if one tries to add functions at the middle of the C–N bond, as we did, one finds the same screening effect. So, in Case f), putting a function in the middle of the bond with exponential parameter $\eta = 0.7$ a. u., we obtained a lowering of the total energy but also a shift of the minimum to $R = 1.608$ Å, which is an improvement according to geometry (Table 2). If we put now in the middle of the bond a more expanded function (Case g), with exponential parameter $\eta = 0.2$ a. u., the increase in energy is small, of the order of 0.01%, but the minimum is now shifted to $R = 1.73$ Å, as expected (Table 2).

From this, one can conclude that in order to obtain a relatively good calculated geometry, when dealing with Gaussian functions, it is desirable to locate functions in the middle of the bond too, and with such an exponent that they are not too expanded in space.

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EPR-Untersuchung am Tetracyanochinodimethan-Anion in flüssigen Kristallen

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Die beobachtete Verschiebung der Hfs-Konstanten Δa beim Übergang von isotroper zu nematischer Phase läßt sich bekanntlich deuten [1] bei Kenntnis der Ordnungsmatrix Θ_{ij} und des Hfs-Tensors $A_{ij} = A_{ij}' + a_{\mathrm{iso}}\,\delta_{ij}$:

$$\Delta a = \tfrac{2}{3} \sum_{i,j} \Theta_{ij}\, A_{ij}'. \qquad (1)$$

Für axialsymmetrische Tensoren vereinfacht sich Gl. (1) zu

$$\Delta a = \Theta_{33}\, A_{33}'. \qquad (2)$$

Die Berechnung von Δa setzt also neben der Kenntnis des Ordnungsparameters Θ_{33} die Kenntnis der Hfs-Tensorkomponente A_{33}' im moleküleigenen Koordinatensystem voraus. A_{33}' kann entweder berechnet oder – besser – aus Festkörper-EPR-Spektren gewonnen werden. Die Berechnung von A_{33}' nach MCCONNELL und STRATHDEE [2] unter Verwendung von Slater-Orbitalen führt für C^{13}-Kerne in Aromaten mit $Z_{\mathrm{eff}}^{\mathrm{C}} = 3{,}18$ zu recht befriedigenden Ergebnissen [1, 3, 4], jedoch versagt diese Methode beim Tetracyanoäthylen(TCNE)-Anion für Δa(C) und Δa(N) [5, 6] und führt zu anomal großen Ordnungsparametern [7] $\Theta_{33} \approx -0{,}5$. Benutzt man dagegen die in glasartig erstarrter Matrix *gemessene* Hfs-Tensorkomponente A_{33}'(N) $= +3{,}87$ Oe [9], so erhält man in p-Azoxyanisol (PAA) ($\vartheta = 120$ °C) $\Theta_{33} = -0{,}23$, was mit dem aus der g-Faktorverschiebung ermittelten Wert [6] verträglich ist. Im flüssigen Kristall Licristal IV (Firma Merck, Darmstadt), der seine nematische Phase im Bereich 16 °C $\leqq \vartheta \leqq$ 76 °C hat, folgt aus dem bei $\vartheta = 17$ °C gemessenen Δa und der gemessenen Komponente A_{33}'(N) ein $\Theta_{33} = -0{,}31$. Die isotropen Aufspaltungskonstanten sind in beiden Lösungsmitteln gleich.

Von dem Anionradikal des Tetracyanochinodimethans (TCNQ) (Abb. 1) läßt sich A_{33}'(N) leider nicht aus dem Glasmatrix-Spektrum bestimmen, da sich das EPR-Spektrum wegen der vergleichbar großen Protonen- und Stickstoff-Hfs-Kopplungen nicht auflösen läßt. Zur Auswertung von Δa ist man also auf eine theoretisch gewonnene Tensorkomponente angewiesen. Wir woll-

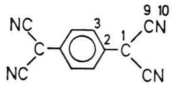

Abb. 1. Tetracyanochinodimethan (TCNQ).

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