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Minimal Basis Set *ab initio* LCGO Calculations

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ab initio calculations using a minimal basis set of Gauss functions have been carried out on the molecules CH_4, C_2H_2, C_2H_4, N_2, HCN and CH_3NH_2 in order to test the usefulness of the basis set in predicting properties such as charge distributions and dipole moments in large molecules.

Introduction

As interest in *ab initio* calculations grows to include the investigation of the electronic structures of increasingly larger molecules, it becomes necessary to find more efficient Gaussian-type orbital (GTO) basis sets in order for the calculation to be practicable in terms of the amount of computer time necessary. Preuß has introduced and extensively studied the use of pure Gaussian functions as basis sets [1–4] and has developed a basis set of 5 GTO's for the description of the core configuration $(1s)^2\,(2s)^2$ for the second-row elements [4]. Hartmann [5] has subsequently used these in an investigation of the geometry of the methylammonium ion.

Pople and coworkers [6–10] have reported extensive studies on Gaussian expansions of Slater-type orbitals (STO) and on energy-minimized, minmal GTO basis sets. Another approach which has been used in order to obtain greatest accuracy with a minimum number of functions is to add Gaussian lobes in the bond regions [3, 5, 11, 12].

In the present investigation on some simple molecules, each hydrogen atom is represented by one Gaussian function [13] and each carbon and nitrogen atom by three Gaussian functions [14] for the configuration $(1s)^2\,(2s)^2$ and two Gaussian functions for each of the $2p_x$, $2p_y$, and $2p_z$ atomic orbitals. The p-type functions have been optimized for the carbon atom and for the nitrogen cation and anion, respectively. Values for the exponents η in the Gaussian functions

$$\varphi_\lambda(\boldsymbol{r}_\lambda, \eta_\lambda) = \left(\frac{2\,\eta_\lambda}{\pi}\right)^{3/4} \exp\{-\eta_\lambda(\boldsymbol{r}-\boldsymbol{r}_\lambda)^2\}$$

are given in Table 1. All calculations reported here have been carried out using the closed-shell MOLPRO system [15].

Table 1. Exponents η for energy-optimized Gaussian functions for H, C, and N.

	s-type		p-type	E_{total}
H	0.283 [13]			
C^{2+}	47.9 [14]	C	0.2920	− 36.14991
	6.90			
	0.39			
N^{3+}	68.5	N^+	0.6275	− 51.69437
	9.90	N^-	0.3085	− 51.55100
	0.59			

Results and Discussion

The basis functions described above have been used to calculate the total energies, dipole moments, and charge distributions for CH_4, C_2H_2, C_2H_4, N_2, NH_3, HCN and CH_3NH_2. In addition, the exponents of the p-type GTO's have been varied in each molecule in order to determine which values give minimum energies for the various types of bonding. It has been found that the p-type functions optimized to give a minimum energy for the atoms do

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Table 2. CH_4: gross atomic charges, charge densities and bond orders, and total energies.

C η_{2p}	n_C	n_H	ϱ_C	ϱ_H	ϱ_{CH}	ϱ_{HiHj}	E_{TOT}(a.u.)
0.2920	6.706	0.823	4.8418	0.4480	0.4165	– 0.0137	– 38.24294
0.49	5.635	1.091	3.9098	0.8135	0.3782	– 0.0334	– 38.5113
0.52	5.517	1.121	3.9764	0.8606	1.0932	– 0.1776	– 38.52655
0.55	5.409	1.148	3.9062	0.9048	1.0954	– 0.1911	– 38.53801
0.60	5.249	1.188	3.6529	0.9724	0.3455	– 0.0434	– 38.55018
0.65	5.110	1.223	3.5692	1.0333	0.3314	– 0.0474	– 38.55535
0.70	4.887	1.253	3.4994	1.0885	0.3181	– 0.0511	– 38.55501
0.75	4.878	1.281	3.4402	1.1386	0.3056	– 0.0545	– 38.55027
0.80	4.780	1.305	3.5455	1.1843	1.0801	– 0.2823	– 38.54202
0.85	4.692	1.327	3.5007	1.2263	1.0729	– 0.2971	– 38.53094

Table 3. NH_3: gross atomic charges, charge densities and bond orders, dipole moments, and total energies.

N η_{2p}	n_N	n_H	ϱ_N	ϱ_H	ϱ_{NH}	ϱ_{HiHj}	Dipole Moment (D)	E_{TOT}(a.u.)
0.4680	7.2158	0.928	5.9923	0.6335	0.3633	– 0.0345	1.2032	– 53.54658
0.3085	7.7640	0.7453	6.5005	0.3897	0.3794	– 0.0120	1.2073	– 53.18537
0.6275	6.7113	1.0965	5.6747	0.8991	0.3027	– 0.0528	0.7387	– 53.64808
0.30	7.7789	0.7404	6.5171	0.3835	0.3791	– 0.0111	1.1503	– 53.15296
0.35	7.6486	0.7838	6.3785	0.4372	0.3802	– 0.0170	1.3472	– 53.31988
0.40	7.4678	0.8440	6.2046	0.5155	0.3770	– 0.0243	1.3400	– 53.43905
0.45	7.2811	0.9063	6.0441	0.6021	0.3678	– 0.0318	1.2470	– 53.52311
0.50	7.1050	0.9655	5.9089	0.6895	0.3537	– 0.0388	1.1179	– 53.58095
0.55	6.9392	1.0203	5.7995	0.7746	0.3358	– 0.0450	0.9736	– 53.61880
0.60	6.7886	1.0705	5.7133	0.8563	0.3151	– 0.0504	0.8230	– 53.64115
0.65	6.6507	1.1164	5.6474	0.9333	0.2921	– 0.0545	0.6692	– 53.65133
0.70	6.5241	1.1586	5.5993	1.0065	0.2672	– 0.0575	0.5128	– 53.65189
0.75	6.4072	1.1976	5.5665	1.0758	0.2408	– 0.0593	0.3530	– 53.64483
0.80	6.2986	1.2338	5.5473	1.1416	0.2128	– 0.0603	0.1884	– 53.63176
0.85	6.1972	1.2676	5.5399	1.2044	0.1835	– 0.2287	0.0186	– 53.61397

not yield a minimum energy for the molecules; similar results have been reported by HEHRE et al.[6]. On the other hand, the dipole moments and charge distributions are generally more adequately described with the best-atom functions.

Typical results for these molecules may be illustrated by those for CH_4 and NH_3, which are summarized in Tables 2 and 3, respectively. Here are given, as a function of the Gaussian exponent η_{2p}, the total energies; charge densities and bond orders $\varrho(\lambda, \mu)$,

$$\varrho(\lambda, \mu) = \sum_{r_\lambda} \sum_{s_\mu} P_{r_\lambda s_\mu} S_{r_\lambda s_\mu}$$

where μ, λ are atoms, r, s are GTO's, and P is given by

$$P_{r_\lambda s_\mu} = \sum_{i}^{\text{occ.mo}} 2\, c_{r_\lambda}\, c_{s_\mu}$$

where the c's are the coefficients of the GTO's in the occupied molecular orbitals; the gross atomic charges n_λ,

$$n_\lambda = \sum_{\lambda} \varrho(\lambda, \lambda) + \tfrac{1}{2} \sum_{\mu \neq \lambda} \varrho(\mu, \lambda)$$

and, in the case of NH_3, the dipole moments. The best-atom η's are included; in the case of N, where this value could not be calculated for the neutral atom, the values for N^+, N^-, and the average value of these two have been used. Figures 1 and 2 show the variation in gross atomic charges n_λ for C in CH_4 and for N in NH_3, respectively, with η. Figure 3 shows the variation in the dipole moment of NH_3 with η.

PALKE and LIPSCOMB[16], using STO *ab initio* calculations, have reported the electron density at the carbon in CH_4 to be 6.534 e^-; here we have obtained a value of 6.706 e^-, which is appreciably higher. NH_3 presents a better example since this molecule has a dipole moment, and a comparison of calculated and experimental values affords a better test of the method being investigated here. PALKE and LIPSCOMB[16] obtain a value of 1.72 D while the experimental value is 1.47 D; we obtain here a value of 1.20 D using the average value, which is about as much too low as Palke and Lipscomb's

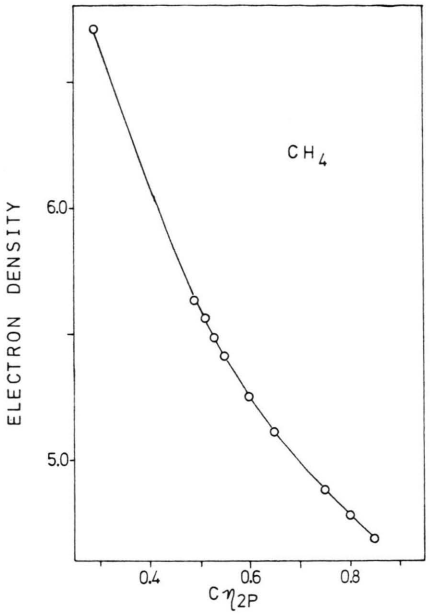

Fig. 1. Variation of electron density η of carbon in CH_4 as a function of the Gaussian exponent η_{2p}.

value is too high. The electron density on N in NH_3 is calculated by Palke and Lipscomb to be 7.467 e^-, while we obtain 7.216 e^-.

Table 4 summarizes the results for CH_4, NH_3, C_2H_2, C_2H_4 and N_2. Included for comparison are the results of Palke and Lipscomb [16] and those of Hehre et al., who use basis sets of intermediate size.

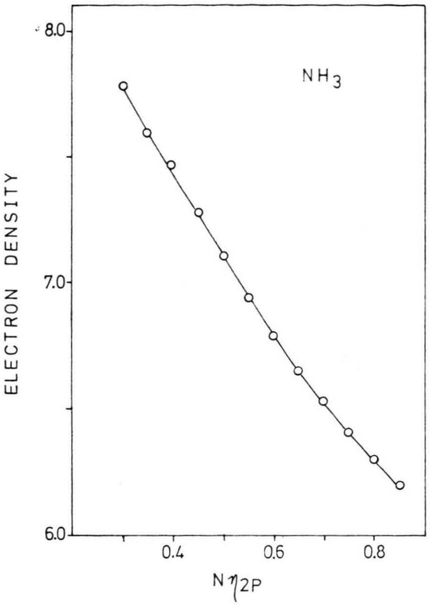

Fig. 2. Variation of the electron density η of nitrogen in NH_3 as a function of the Gaussian exponent η_{2p}.

In some cases the results obtained here show better agreement with the more exact calculations than do those of Hehre et al. and in other cases the agreement is poorer. In all cases our results give best agreement with the more exact calculations when the atom-optimized functions are used!

For the molecules HCN and CH_3NH_2, the presence of both carbon and nitrogen atoms and the

Table 4. Summary of results for C_nH_m and N_nH_m compounds.

Molecule		η_{2p}	E_{TOT}	n_λ	n_H	Dipole Moment (D)
CH_4	best-atom	0.292	− 38.2429	6.706	0.823	
	best-molecule	0.675	− 38.5554	5.060	1.260	
	STO-3G [6]		− 39.7153	6.524	0.869	
	STO [16]		− 40.1141	6.534	0.867	
C_2H_4	best-atom	0.292	− 74.4907	6.397	0.802	
	best-molecule	0.512	− 74.8827	5.700	1.075	
	STO-3G [6]		− 77.0506	6.276	0.862	
	STO [16]		− 77.8343	6.278	0.860	
C_2H_2	best-atom	0.292	− 73.4634	6.357	0.643	
	best-molecule	0.460	− 73.7397	6.001	0.999	
	STO-3G		− 75.8415	6.187	0.813	
	STO [16]		− 76.6185	6.188	0.812	
N_2	best-atom	0.468	−104.1320	7.000		
	best-molecule	0.60	−104.2740	7.000		
NH_3	best-atom	0.468	− 53.5466	7.216	0.928	1.203
		0.3085	− 53.1854	7.7640	0.745	1.207
	best-molecule	0.675	− 53.6530	6.590	1.138	0.585
	STO-3G [6]		− 55.4536	7.450	0.850	1.66
	STO [16]		− 56.0050	7.467	0.845	1.72

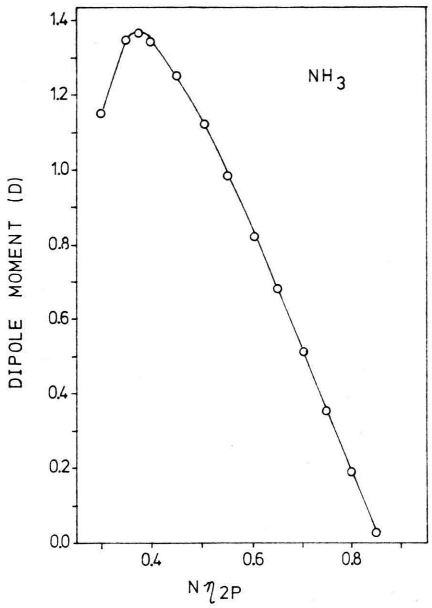

Fig. 3. Variation of the dipole moment of NH_3 as a function of the Gaussian exponent η_{2p}.

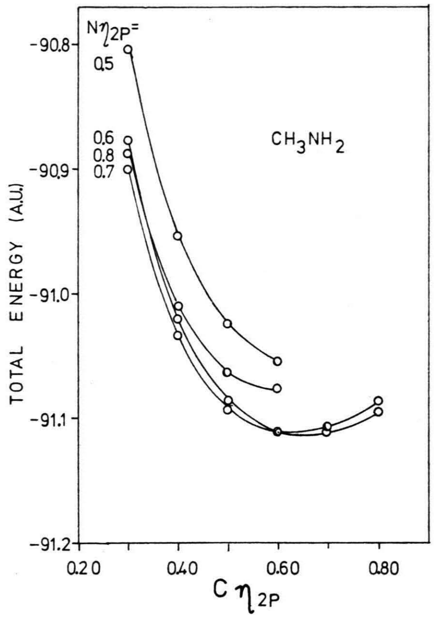

Fig. 5. Variation of the total energy (in a. u.) of CH_3NH_2 as a function of the two Gaussian exponents η_{2p} for C and N.

availability of experimental dipole moments afford a still better test of the method. Figures 4 and 5 show the variation in total energy as a function of the carbon and nitrogen η_{2p} values for HCN and CH_3NH_2, respectively. Figures 6 and 7 show the variation in the dipole moments as a function of the exponents.

In both of these molecules, as in the case of those previously discussed, the lowest energies occur for η_{2p} much larger than in the atoms. But here the me-

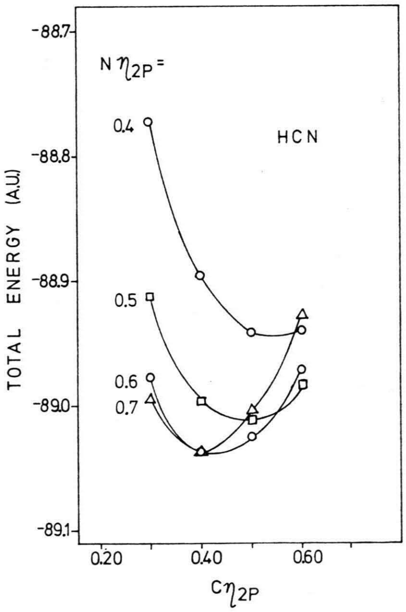

Fig. 4. Variation of the total energy (in a. u.) of HCN as a function of the two Gaussian exponents η_{2p} for C and N.

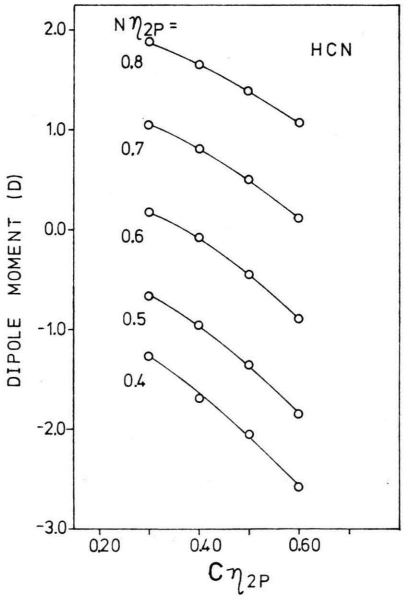

Fig. 6. Variation in the dipole moment of HCN as a function of the two Gaussian exponents η_{2p} for C and N.

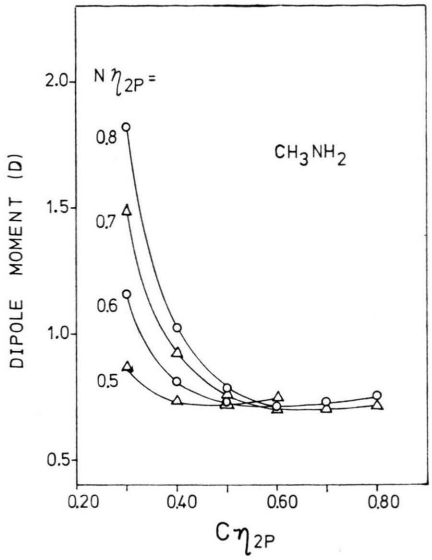

Fig. 7. Variation of the dipole mmoent of CH_3NH_2 as a function of the two Gaussian exponents η_{2p} of C and N.

thod fails to give a reasonable dipole moment with the best atom exponents, the value for HCN being actually negative, about $-1.$ D as compared to 2.95 D experimentally[17]; that for CH_3NH_2 is also too small, bring $0.7-0.8$ D as compared to 1.29 D experimentally[17]. Gross atomic charges for HCN and CH_3NH_2 are given in Table 5, with the values from other *ab initio* calculations using larger basis sets included for comparison.

One disturbing feature of the results for HCN and CH_3NH_2 is that the predicted gross atomic charges become worse as the dipole moment improves. For example, if we choose C $\eta_{2p} = 0.30$, very near the best-atom value of 0.292, the dipole moment in HCN improves as N η_{2p} increases, but the N atoms is in all cases positively charged and becomes increasingly so as N η_{2p} increases, as shown in Table 6. The results for CH_3NH_2, also included in the Table, are similar.

The difficulty in determining a good exponent for the 2p GTO's in C and N is probably due to the failure of the s-type functions used to give an adequate description of the atomic cores. When these functions are used in calculations on molecules, the p-type GTO's require a larger exponent and hence become less diffuse in space in order to better describe the C or N atom in the molecule, with the result that bonding between C or N and other atoms such as H is not well characterized. Evidence for this can be seen in the results of the Mulilken po-

Table 5. HCN and CH_3NH_2: gross atomic populations and dipole moments.

HCN:	N η_{3p}	C η_{2p}	n_N	n_C	n_H	Dipole		Moment (D)
This Work:	0.3085	0.2920	6.8827	6.2716	0.8457	-1.1374		
	0.4680	0.2920	6.7463	6.3866	0.8671	-0.8864		
McLean[18]			7.082	6.156	0.761			
Expt[17]						2.95		
CH_3NH_2[19]:	N η_{2p}	C η_{2p}	n_N	n_C	$n_{H1,H2}$	$n_{H3,H4}$	n_{H5}	Dipole Moment (D)
This Work:	0.3085	0.2920	7.9850	6.3704	0.5864	0.8091	0.8536	0.6949
	0.4680	0.2920	7.3646	6.3797	0.7962	0.8656	0.9320	0.8253
Pedersen and Morokuma[20]			7.6406	6.3948	0.7424	0.8118	0.8561	
Expt[17]								1.29

Table 6. Variation in gross atomic charges n in HCN and CH_3NH_2 as a function of N η_{2p} with C η_{2p} held constant at 0.30.

	HCN				CH_3NH_2[19]					
N η_{2p}	n_N	n_C	n_H	Dipole Moment (D)	n_N	n_C	$n_{H1,H2}$	$n_{H3,H4}$	n_{H5}	Dipole Moment (D)
0.40	6.8417	6.2996	0.8587	-1.269						
0.50	6.6978	6.4358	0.8663	-0.666	7.2385	6.3775	0.8381	0.8798	0.9481	0.872
0.60	6.5174	6.6348	0.8679	0.184	6.8872	6.4674	0.9445	0.8903	0.9756	1.159
0.70	6.3354	6.7988	0.8658	1.054	6.5967	6.6550	1.0302	0.8948	0.9983	1.487
0.80	6.1654	6.9730	0.8616	11.876						

pulation analysis for CH_4 and for NH_3 in Tables 2 and 3: as the exponent for the p function becomes larger, leading to a more stable molecular energy, too much charge is transferred from C or N to the H atoms. Similar effects are observed in the cases of HCN and CH_3NH_2, given in Table 6.

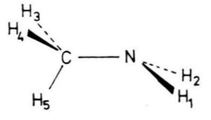

Fig. 8. Numbering of atoms in CH_3NH_2.

Johansen[21] has suggested that the bonding properties of molecules calculated using minimal GTO basis sets may be improved if more of the Gaussian functions are assigned to the description of the valence electrons and fewer to that of the core electrons. The use of this technique would undoubtedly improve the present results.

Hehre and coworkers[6] have found that, although least-energy minimized GTO's give a lower energy for molecules than do the GTO expansions of STO's, the latter usually require fewer functions in order to yield optimum values of charge distributions and dipole moments. They have also found that their STO-NG basis sets are usually applicable to a wider variety of molecules with less required re-scaling of parameters.

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