Electronegativities and Gaussian Orbital Exponents

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(Z. Naturforsch. **28 a**, 1828–1831 [1973]; received 13 August 1973)

A method for selecting orbital exponents for Gaussian type functions (α_g's) may be based on a connection between these exponents and Pauling electronegativities (ε's). An analogous relationship between α_g's and ε's would be expected: GTO exponents derived by different authors give α_g/ε^2's which are approximately constants. A number of GTO sets recommended by several authors have been revised.

The choice of exponents for basis functions is always a problem in molecular quantum mechanics. This is particularly true for Gaussian type functions, where no guide like the Slater rule for STO's is available. A number of methods for overcoming this difficulties have been elaborated [1–5], which can be used to solve problems also for chemically interesting molecules.

A method for selecting orbital exponents for Gaussian type functions (α_g's) may be based on a connection between these exponents and Pauling electrognegativities (ε's). This has the added advantage of giving chemical meaning to the exponent values.

As can be seen from Table 1, the ratio of the Slater exponents and the Pauling electronegativities is constant in the second row of the periodic table. For the sake of simplicity we restrict ourselves to these atoms, for which STO exponents can be derived from electronegativities by multiplying the latter by 0.65 [6].

Since STO's and GTO's differ in that STO's contain terms in r when GTO's contain terms in r^2, an analogous relationship between α_g's and ε's would be expected to take the form $\alpha_g/\varepsilon^2 = \text{constant}$. In the following we wish to show that GTO exponents derived by different authors give α_g/ε^2's which are approximately constants. A number om GTO sets recommended by several authors have been revised.

1. Orbital Exponents Derived by Preuss [1]

In Tables 2 and 3 α_g's determined by Preuss have been brought into relation with ε's. As can be seen the exponents for configurations $(1s)^2$ and $(1s)^2(2s)^2$ when divided by ε's give approximately constant values for atoms in the second periodic row. The tables also show that deviations from the average are within few per cent.

	Li	Be	B	C	N	O	F	Average
I_a	0.65	0.975	1.30	1.625	1.95	2.275	2.6	
I_b	1.00	1.50	2.00	2.50	3.00	3.50	4.00	
I_c	0.65	0.65	0.65	0.65	0.65	0.65	0.65	0.65

Table 1. I_a Slater orbital exponents, I_b Pauling electronegativities, I_c Ratio of I_a and I_b.

	B	C	N	O	F	Ne
1.	2.6263	3.9285	5.4975	7.3343	9.4410	11.8185
2.	0.6545	0.6286	0.6108	0.598	0.6052	0.6014
3.	104.1%	100%	102.9%	104.9%	103.9%	104.5%
1.	10.9025	16.3080	22.8204	30.4465	39.1918	49.0612
2.	2.725	2.608	2.536	2.486	2.512	2.534
3.	104.3%	100%	102.8%	104.9%	103.8%	102.9%
1.	53.5951	80.0034	111.952	149.364	192.266	10240.683
2.	13.399	12.720	12.179	12.324	12.324	12.462
3.	105.9%	100%	102.2%	104.4%	103.2%	102.1%
1.	329.562	492.961	689.818	920.341	1184.0	240
2.	82.390	78.814	76.646	75.129	75.942	76.602
3.	104.2%	100%	102.9%	104.9%	103.8%	103.0%

Table 2. Values of α_g/ε^2's calculated from orbital exponents of Ref. [1]; conf. $(1_s)^2$.

	B	C	N	O	F	Ne
1.	2.9508	4.41234	6.1536	8.17443	10.4744	13.0545
2.	0.7377	0.7060	0.7060	0.6673	0.6713	0.6743
3.	6.327	1.758	1.758	3.820	3.243	2.811%
1.	12.2495	18.3166	25.5453	33.9339	43.4816	54.1880
2.	3.0620	2.9307	2.8384	2.7701	2.7883	2.7990
3.	6.887	2.304	0.918	3.302	2.66	2.293%
1.	60.0931	89.8574	125.319	166.472	213.311	265.834
2.	15.0233	14.3772	13.9243	13.5896	13.6716	13.7310
3.	6.905	2.307	0.917	3.368	2.770	2.290%
1.	370.279	553.679	772.187	1025.76	1314.37	1638.0
2.	92.568	88.5886	85.1986	83.7355	84.2410	84.6074
3.	6.903	2.308	2.069	2.854	2.713	2.174%

1. $\alpha_{g,i}$ s 2. $\alpha_{g,i}/\varepsilon^2$'s 3.% deviation from average values

Table 3. Values of α_g/ε^2's calculated from orbital exponents of Ref. [1]; conf.: $(1s)^2(2s)^2$.

2. Orbital Exponents Used by Csizmadia and Coworkers

Orbital exponents derived by Csizmadia and coworkers have also been investigated, in order to show their connection with electronegativities. In Tables 4 and 5 calculational results are reported established for s and p type sets. α_g's divided by the correspondent ε's give very good constants.

Csizmadia and coworkers obtained their GTF's by scaling sets optimized for neon and nitrogen respectively. Their formulae (65) and (66) in Ref. [2] show the relationships they used to obtain the scaling factors; Eq. (65) defines factors for the s type, Eq. (66) those for the p type exponents. By the use of the electronegativities both equations can be replaced by only one based on the proportionality:

$$\alpha_{g,i}: \alpha_{g,j} = \varepsilon_j^2 : \varepsilon_i^2 .$$

3. Calculations with Orbital Exponents Used by Palmer and Gaskell

Palmer and Gaskell used contracted sets of exponents derived originally by Roos and Siegbahn [7].

	B	C	N	O	F	Ne
1.	0.101	0.154	0.217	0.291	0.376	0.471
2.	0.0252	0.0246	0.0241	0.0238	0.0235	0.02326
1.	0.402	0.608	0.857	1.15	1.48	1.86
2.	0.1005	0.0973	0.095	0.0938	0.0925	0.0919
1.	1.58	2.39	3.37	4.51	5.83	7.31
2.	0.395	0.382	0.370	0.368	0.364	0.361
1.	6.23	9.42	13.3	17.8	23.0	28.8
2.	1.56	1.51	1.48	1.45	1.44	1.42
1.	24.6	37.3	52.5	70.4	90.9	114.0
2.	6.15	5.9	5.83	5.75	5.68	5.63
1.	96.6	146	206	276	356	447
2.	24.15	23.36	22.89	22.53	22.25	22.07
1.	380	575	811	1090	1400	1760
2.	95.0	92.0	90.1	89.0	87.5	86.9

1. $\alpha_{g,i}$'s 2. $\alpha_{g,i}/\varepsilon^2$'s

Table 4. Values of α_g/ε^2's calculated from orbital exponents of Ref. [2]; 7 s sets.

Table 5. Values of $\alpha_g/\varepsilon^{2'}$ calculated from p-orbital exponents of Csizmadia and cws.

		B	C	N	O	F	Ne
1p	1.	0.244	0.382	0.550	0.749	0.978	1.24
	2.	0.061	0.061	0.061	0.061	0.061	0.061
2p	1.	0.161	0.252	0.363	0.494	0.646	0.817
	2.	0.040	0.040	0.040	0.040	0.040	0.040
	1.	0.948	1.48	1.13	2.90	3.79	4.80
	2.	0.237	0.237	0.237	0.237	0.237	0.237
3p	1.	0.114	0.178	0.257	0.350	0.457	0.578
	2.	0.028	0.028	0.029	0.029	0.029	0.029
	1.	0.591	0.923	1.33	1.81	2.36	2.99
	2.	0.148	0.148	0.148	0.148	0.148	0.148
	1.	3.06	4.78	6.89	9.38	12.2	15.5
	2.	0.765	0.765	0.766	0.766	0.762	0.766

1. $\alpha_{g,i}$; 2. $\alpha_{g,i}/\varepsilon^{2'}$

Their numerical values have been reported in Table 6, where the connection with electronegativities has also been shown. The authors in Ref. [3] give exponents only for the H, C, N, and O atoms. Using the constant α_g/ε^2 values derived from these atoms further basis sets have been obtained for the F atom by extrapolation. Some calculational results of molecules containing fluorine have been performed using the Meyer-Pulay program Molpro,

Table 6 a. Values of α_g/ε^2's calculated from orbital exponents of Ref. [3]; conf $(ls)^2$.

	C	N	O	F (extrapol)
1 a	14.12	2038.4	2714.9	3473.42
2 a	226	226.5	221.6	
3 a	101.9%	102.2%	100%	
1 b	206.9	301.7	415.7	529.392
2 b	33.1	33.5	33.9	
3 b	102.5%	101.2%	100%	
1 c	45.850	66.463	91.981	117.14
2 c	7.34	7.38	7.51	
3 c	102.3%	101.7%	100%	
1 d	12.389	17.808	24.452	31.1426
2 d	1.98	1.98	1.99	
3 d	100.7	100.9	100%	
1 e	3.7234	5.3045	7.2229	9.1992
2 e	0.596	0.589	0.590	
3 e	99%	100%	100%	

Tab. 6 b. Values of α_g/ε^2 calculated from orbital exponents of Ref. [3]; conf $(1_s)^2(2\,s)^2$.

	C	N	O	F (extrapol)
1 a	0.5242	0.7650	1.0631	1.3548
2 a	0.0839	0.0850	0.0868	
3 a	96.7%	97.9%	100%	
1 b	0.1635	0.2344	0.3227	0.41034
2 b	0.262	0.0260	0.0263	
3 b	100.4%	101.1%	100%	

1. $\alpha_{g,i}$ 2. $\alpha_{g,i}/\varepsilon_i^2$ 3. $(\alpha_{gi} \times 100)/g(0)$

Table 7. Total energies calculated by basis sets extrapolated by authors using e.n. dependence.

		1	2	3	4
1.	HF	99.991	99.853	99.79	
2.	F_2	98.714	98.412		98.11
3.	FCN		191.4239		
4.	N_2O		183.1804		
5.	O_2F		246.913		

1. Ext. STO [8], 2. This work, 3. Ref. [9], 4. Ref. [10]. 2 and 3 are calculated by 73 and 73/3+1 basis sets respectively.

and are listed in Table 7. The last column of Table 6 contains the extrapolated orbital exponents of the F atom.

4. Orbital Exponents Derived by Huzinaga

In Table 8 some calculational results have been presented on α_g/ε^2 values obtained using basis sets derived by Huzinaga. As a simple example the p-orbital exponents of his Gaussian set $10\text{-}(1s)_g$, $6\text{-}(2p)_g$ has been used. In our Table 8 only the 2p part is presented.

Table 8. Values of α_g/ε^2's calculated from the orbital exponent set $10-(1\,s)_g$, $6-(2\,p)_g$ of Huzinga; numbers reported belong to the p-orbital part.

B	C	N	O	F	Ne
15.4594	25.3655	35.9115	49.8279	65.9993	84.8396
3.864	4.05	3.99	4.06	4.11	4.13
3.4835	5.7764	8.4804	11.4896	15.2187	19.7075
0.88	0.93	0.94	0.94	0.95	0.96
1.0658	1.7873	2.7056	3.6092	4.7882	6.2219
0.252	0.286	0.300	0.294	0.298	0.303
0.39278	0.6577	0.9921	1.3205	1.7319	2.2106
0.100	0.106	0.110	0.108	0.109	0.108
0.1503	0.2480	0.3727	0.4821	0.6206	0.7853
0.0376	0.0397	0.0414	0.0394	0.0388	0.0384
0.0572	0.0911	0.1346	0.1641	0.2070	0.2567
0.0143	0.0146	0.0149	0.0135	0.0126	0.0122

1. row: orbital exponents,
2. row: o. exponents divided by sq. of electronegativities.

Huzinagas α_g values have been generated by expansion of the STO functions in terms of the Gaussian exponents. Some of his sets are reported in Reference [4].

5. Minimal Basis Sets Used by Mely and Pullman

Gaussian basis sets obtained by optimization of the total energies of H_2, O_2, N_2, and C_2 molecules have been used to calculate the energies and other properties of heterocyclic molecules by Mely and Pullman [5]. Their Gaussian type functions can be used after drastic contraction as minimal basis sets,

Table 9. Final exponents in the GTO bases used by Pullman and Mely.

	C (25)	N	O
1.	56.2694	79.2170	102.268
2.	9.003	8.801	8.675
3.	1.0229	1.0000	0.9857
1.	8.7923	12.379	16.605
2.	1.391	1.375	1.356
3.	1.0232	1.0000	0.9861
1.	1.6909	2.3800	3.1930
2.	0.27054	0.2644	0.26065
3.	1.0232	1.0000	1.0145
1.	0.2254	0.3170	0.4257
2.	0.03606	0.03522	0.03475
3.	1.0238	1.000	0.9866
1.	0.7393	1.0610	1.44700
2.	0.1183	0.1179	0.1181
3.	1.0034	1.0000	1.0017
1.	0.17259	0.2490	0.3392
2.	0.02761	0.02766	0.02769
3.	0.09965	1.0000	1.0019

1. orbitalexponents; 2. orbitalexp.'s/ε^2; 3. % deviation.

and it is thus possible to perform calculations for larger and more chemically interesting molecules. α_g and α_g/ε^2 values are presented in Table 9. The deviation of the latter from an average is almost negligible.

6. Hartree-Fock Limits and Electronegativities

A close connection exists between the total energies and the Pauling electronegativities in a number of atoms and molecules. In Table 10 we present

Table 10. Connection between HF limits and ε^2's.

atom	HF-limits	HF $1/\varepsilon^2$	ε_{calc}	$\varepsilon_{Pauling}$	% deviation
Be	14.57302	6.4768	1.535	1.5	2.3
B	24.52905	6.1323	1.9918	2.0	0.4
C	37.6886	6.0	2.4689	2.5	1.1
N	54.4009	6.0445	2.9662	3.0	1.1
O	74.80936	6.1069	3.4784	3.5	0.6
F	99.40924	6.2131	4.009	4.0	0.02
Ne	128.5470	6.3480	4.5559	4.5	1.2
average		6.1931			

Hartree-Fock limits and values obtained by dividing the H – F limits by the second power of electronegativities. As can be seen these latter values deviate only by a few per cent from an average.

Hartree-Fock limits divided by this average lead to second power of the electronegativities to a very good approximation.

The main result of our work was that we could point out that HF-limits and Gaussian orbital exponents have dependence on electronegativities. In some cases however, mainly where authors generated their basis sets without any scaling a successively growing tendency in deviations can be noticed. In a following paper we wish to show that these discrepancies can be eliminated by using a factor corresponding to the number of electrons of the individual atoms [10].

In Table 10 electronegativities are calculated only on the basis of the Be-Ne HF-limits. Calculations have been performed also inclusive the characteristics of the Li atom. Results of these calculations are reported in Table 11. As can be seen only the

Table 11. Calculation of Hartree-Fock electronegativities inclusive Li

atom	HF-$1/\varepsilon^2$	ε_{calc}	$\varepsilon_{Pauling}$	deviation %
Li	7.43227	1.082	1.0	8.2
Be	6.47689	1.515	1.5	1.0
B	6.13226	1.967	2.0	1.6
C	6.03017	2.436	2.5	2.6
N	6.04454	2.927	3.0	2.4
O	6.10688	3.433	3.5	2.0
F	6.21308	3.956	4.0	1.1
Ne	6.43800	4.5	4.5	0
average	6.348			

Table 12. Values of α_g/ε_H^2's calculated from the orbital exponent set $10-(1s)g$, $6-(2p)g$ of Huzinaga; numbers reported belong to the (1 s) orbital part. ε_H^2's are taken on the basis of Table 11.

1.	1.906	6.2529	13.4578	23.3705
2.	1.569	1.6161	1.5703	1.4924
1.	14.320	55.834	120.899	209.192
2.	14.320	14.431	14.107	13.358
1.	60.072	202.205	439.998	756.670
2.	51.299	52.261	51.365	48.318
1.	267.096	916.065	1998.96	3431.25
2.	228.092	236.764	233.25	219.11
1.	0.71719	2.3118	4.9930	8.6237
2.	0.61307	0.5975	0.5826	0.5507
1.	0.2034	0.6824	1.5687	2.6916
2.	0.1728	0.1723	0.1830	0.1719
1.	0.0772	0.2604	0.5800	1.0088
2.	0.0659	0.0673	0.0677	0.0644
1.	5.4030	17.8587	38.4711	66.7261
2.	4.6130	4.6157	4.4890	4.2609
1.	1782.90	6249.60	13515.30	23342.20
2.	1522.50	1615.2	1577.0	1490.6
1.	0.02854	0.0894	0.1923	0.3312
2.	0.02437	0.02311	0.02244	0.02146

1.: α_g's.
2.: α_g/ε_H^2's; ε_H's are electronegativities calculated from the HF-limits.

electronegativity of Li deviates more considerably from the corresponding Pauling value. Table 12 shows α_g/ε_H^2 values, using α_g's of Huzinaga.

ε_H's are electronegativities calculated from HF-limits as reported in Table 11. For demonstrating the connection between HF-limits and electronegativities, Huzinaga's $10\text{-}(1s)_g\ 6\text{-}(2p)_g$ orbital exponent set was used. As can be seen in Table 12, the α_g/ε_H^2's deviate from their mean values only by few per cent.

[1] H. Preuss, Z. Naturforsch. **20 a**, 1290 [1965].
[2] I. G. Csizmadia, M. C. Harrison, J. W. Moskowitz, and B. T. Sutcliffe, Theoret. Chim. Acta (Berl.) **13**, 378 [1969].
[3] M. H. Palmer and A. I. Gaskell, Theoret. Chim. Acta (Berl.) **23**, 2352 [1971].
[4] S. Huzinaga, J. Chem. Phys. **42**, 1293 [1965].
[5] B. Mely and A. Pullman, Theoret. Chim. Acta (Berl.) **13**, 378 [1969].
[6] S. Szöke, Acta Chim. Acad. Sci. Hung. **68**, 349 [1971].
[7] B. Roos and P. Siegbahn, Proceedings of Seminar in Quantum Chem., Straßburg 1969.
[8] R. K. Nesbeth, J. Chem. Phys. **36**, 1528 [1962].
[9] P. Pulay, Dissertation 1971.
[10] H. Preuss and S. Szöke, to be published in this periodical.