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Polarization Functions for Gaussian Basis Sets for the First Row Atoms

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Exponent optimization was performed for a single set of *d*-type Gaussians on the first row atoms C, N, and O in fifteen small molecules. The hydrogen *p*-exponents were kept at the fixed value of 1.0. For the underlying valence shell basis sets, Dunning's double zeta basis sets were used. Standard exponents of polarization functions are suggested for the most common valence states of the C, N, and O atoms.

Key words: Polarization functions, exponent optimization of ~

1. Introduction

Our project on the *ab initio* calculations of equilibrium constants of chemical reactions brought us to look for a basis set of the "double zeta plus polarization" quality. The nature of the project demanded such a basis set which would be versatile enough and which need not be modified in the next several years. For the *sp* basis of the first row atoms and *s* basis for hydrogen we adopted the Dunning's double zeta basis sets [1]. As regards the polarization functions, the situation in the literature was less favourable. Typically, the reported exponent optimizations were performed for one particular molecule. Among more general studies we cite the paper of Roos and Siegbahn [2] who performed the *d*-exponent optimization for H_2O and H_2S with the Gaussian double zeta basis sets. The *d*-exponents for the other first and second row atoms were inferred from the optimum oxygen and sulfur exponents by means of the trends of calculated charge densities in *p* and *d* atomic orbitals. A set of *d*-functions reported by Ahlrichs and collaborators [3] was obtained by minimizing the IEPA energy. Use of these exponents in the SCF calculations would not be rationalized, though their values are probably not far from the optimum exponents for the SCF energy. A study of Hariharan and Pople

[4] was oriented on the effect of polarization functions on the heats of reactions. The SCF calculations were performed with the 6–31 G basis set augmented with a single set of *d*-Gaussians. From the results for CH_4, NH_3, H_2O, HF, N_2, and C_2H_2 the authors concluded that the optimum value of *d*-exponent does not depend strongly on chemical environment and suggested $\alpha_d = 0.8$ as the standard value for all the atoms C, N, O, and F. This conclusion is consistent with the commonly accepted opinion which may be best expressed by the words of Schaefer [5]: "... calculated total energies are not too sensitive to small variations in exponents and one can usually make reasonable choices based on optimized small molecule calculations. For hydrogen, a reasonable value of the Slater exponent $\zeta(2p)$ is 2.0, while a reasonable value of the Gaussian exponent $\alpha(2p)$ is 1.0. For first-row atoms reasonable values are $\zeta(3d) = 2.0$ and $\alpha(3d) = 0.8$, although for beryllium a Slater function as small as 1.5 might be somewhat more appropriate while for neon $\zeta(3d)$ as large as 3.0 might prove more effective".

With regard to the calculations with the "chemical" accuracy, the situation seemed to us not to be entirely satisfactory and we attempted for a more rationalized choice of polarization functions. The paper of Hariharan and Pople [4] only demonstrates that considerably better agreement is obtained for the calculated energies of reactions with experiment if the double zeta basis set is augmented by polarization functions with standard exponents ($\alpha_d = 0.8$ for the atoms C, N, O and $\alpha_p = 1.1$ for hydrogen). Since the dependence of energy on the *d*-exponent is most typically very flat [6] it appears that the choice of polarization functions is not critical in calculations of energies of reactions. As a matter of fact this assumption has not been numerically tested and a certain effect of chemical environment cannot *a priori* be disregarded. This is topical particularly for reactions involving charged species (and open shell systems) for which it is possible to anticipate that their optimum exponents are markedly different from the optimum exponents for neutral molecules. To explore this effect we considered it expedient to perform α_d optimization for several small molecules and ions that may be taken as representants of the most common valence states of atoms C, N, and O. It is hoped that the exponents of polarization functions thoroughly determined in this way will be also useful for other applications of *ab initio* calculations than for the energy predictions in problems of chemical reactivity.

2. Calculations

Fifteen small molecules and ions were treated. The geometries assumed are listed in Table 1. In all cases the calculations were standard SCF closed shell and RHF open shell calculations performed by the program POLYATOM/2. For the atoms C, N, and O we selected the Dunning's $(9s5p)/[4s2p]$ Gaussian basis sets [1], for hydrogen the Dunning's $(4s)/[2s]$ basis set [1]. The hydrogen Gaussian exponents were multiplied by a scale factor of $(1.2)^2 = 1.44$. On each hydrogen a single set of *p*-type Gaussians (p_x, p_y, p_z) was added. It is believed that the hydrogen *p*-exponent is less sensitive on the molecular structure than the *d*-exponents of heavy atoms. Accordingly, a standard value of $\alpha_p = 1.0$ was used throughout. Our *d*-sets consisted

Table 1. Geometries used and total energies[a]

		Energy		
Molecule	Geometry	DZ	DZ+P[b]	Difference in kJ/mol
CH_4	experimental[c] (T_d) r(CH) = 2.0665	−40.185335	−40.207390	57.91
CH_3^+	assumed (D_{3h}) r(CH) = 2.039	−39.220317	−39.242298	57.71
$CH_3^{\cdot}$	experimental[d] (D_{3h}) r(CH) = 2.039	−39.549532	−39.567929	48.30
H_2CO	experimental[e] r(CO) = 2.2825; r(CH) = 2.109; $\sphericalangle$HCH = 116.5°	−113.829345	−113.894537	171.16
C_2H_2	experimental[c] r(CC) = 2.27149 r(CH) = 2.00315	−76.799167	−76.832595	87.77
CO	experimental[c] r(CO) = 2.132	−112.685041	−112.760195[f]	197.32
N_2	experimental[c] r(NN) = 2.068	−108.878177	−108.959825	214.37
NH_2^-	optimum for the DZ basis set r(NH) = 1.958; $\sphericalangle$HNH = 104.0°	−55.482969	−55.509974	70.90
$NH_2^{\cdot}$	experimental[d] r(NH) = 1.9351; $\sphericalangle$HNH = 103.4°	−55.543823	−55.573489	77.89
NH_3^+	6–31G* optimum[g] (D_{3h}) r(NH) = 1.9124	−55.868110	−55.891818	62.25
NH_3	experimental[h] r(NH) = 1.9117; $\sphericalangle$HNH = 106.7°	−56.175992	−56.209327	87.52
NH_4^+	6–31G* optimum[g] (T_d) r(NH) = 1.91618	−56.528278	−56.557034	75.50
OH^-	optimum for the DZ basis set; r(OH) = 1.84473	−75.351207	−75.372827	56.76
H_2O	experimental[d] r(OH) = 1.8111; $\sphericalangle$HOH = 104.45°	−76.009256	−76.046472	97.71
H_3O^+	optimum for the [7s4p1d/4s1p] basis set[j], r(OH) = 1.814; $\sphericalangle$HOH = 113.5°	−76.293074	−76.330202	97.48

[a] If not otherwise noted all entries are in atomic units. Since these are non-SI units we give to lengths and energies the meaning of dimensionless quantities r/a_0 and E/e_0, respectively where $a_0 = 0.52917 \times 10^{-10}$ m and $e_0 = 2625.5$ kJ/mol.

[b] Valence state d-exponents from Table 2 used.

[c] Interatomic distances, ed. by Sutton, L. E.; London: The Chemical Society 1958.

[d] Herzberg, G.: Molecular spectra and molecular structure. III. Electronic spectra and electronic structure of polyatomic molecules. New York: Nostrand Reinhold Comp. 1966.

[e] Oka, T.: J. Phys. Soc. Japan **15**, 2274 (1960).

[f] Optimum exponents used: α_d(C) = 0.705; α_d(O) = 1.11.

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of six primitive Gaussians (x^2, y^2, z^2, xy, yz, xz). Their exponents were optimized with a grid of 0.15 (or lower) and the optimum values were interpolated by a quadratic fit. We have retained all six d-functions. The diffuse s-function ($x^2+y^2+z^2$) was not eliminated, because its effect on the molecular energy is believed to be unimportant.

3. Results and Discussion

Originally, we wanted to select standard *d*-exponents for the atoms C, N, and O that would be an average of optimum values for the molecules treated. However, this turned out to be difficult. As shown in Fig. 1 for nitrogen compounds, the dependence of α_d on the structure is not negligible if a "chemical" accuracy (say 4 kJ mol^{-1}) is to be reached for the calculated energies of reaction. For example if $\alpha_d = 0.8$ is used for NH_3^+ instead of the optimum value of 1.25, the respective difference in total energies amounts to almost 2 kJ mol^{-1} and if $\alpha_d = 0.8$ is used for N_2 instead of the optimum value of 0.93, the difference is 3.5 kJ mol^{-1}. Instead of standard exponents for atoms we suggest therefore the use of standard exponents for particular valence states of atoms (subsequently referred to as valence state exponents). The optimum and valence state α_d values for the molecules treated are presented in Table 2. The entries of Table 2 and Fig. 1 conform to the anticipated trends in exponents: compared to neutral closed shell molecules the positively charged species have higher exponents and the negatively charged species and neutral open shell systems have lower exponents. The range of α_d is as large as 0.5–0.7. The well of the energy dependence is flatter, the larger the number is of hydrogen atoms in the molecule. This is comprehensible because the larger the number of hydrogen atoms, the larger the basis set. Another explanation for the decreasing dependence of the energy on α_d with increasing numbers of hydrogens is simply that polarization effects are less important in bonds to hydrogen than in other bonds. Among the nitrogen molecules treated, the steepest energy dependence on α_d was found with N_2 (Fig. 1). The entries of Table 2 permit to estimate optimum exponents for molecules that are not treated in this paper. From the trends in the series H_3O^+–H_2O–OH^-, NH_4^+–NH_3–NH_3^+–NH_2^-–NH_2 and CH_4–CH_3^+–CH_3 we attempted to derive some general rules. These may be formulated as follows:

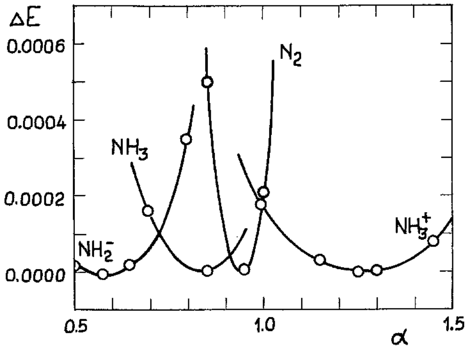
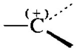
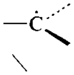
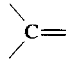
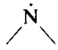
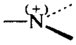
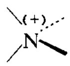
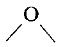


Fig. 1. Dependence of the molecular energy on the exponent of polarization function on the nitrogen atom. The energies are relative to the bottoms of the curves. For meaning of the energy scale see footnote [a] in Table 1

proton addition – increase the exponent by 0.35;
H atom addition – use the same exponent;
electron addition to the singly occupied orbital – lower the exponent by 0.30.

We now compare our results with the results of other authors. As stated by Hariharan and Pople [4] the optimum value of α_d does not depend strongly on the

Table 2. Exponents for *d*-type functions

Valence state of atom	Suggested valence state exponent	Molecule treated and its optimum exponent	
	0.80	CH_4	0.78
	0.70	CH_3^+	0.72
	0.85	$CH_3^{\cdot}$	0.84
	0.70	H_2CO	0.70
—C≡	0.85	C_2H_2 (CO)	0.86 $(0.70)^a$
N≡	0.95	N_2	0.93
	0.55	NH_2^-	0.57
	0.70	$NH_2^{\cdot}$	0.71
	1.25	NH_3^+	1.25
	0.85	NH_3	0.83
	1.20	NH_4^+	1.20
$^{(-)}$O—	0.55	OH^-	0.57
O=	1.05	H_2CO (CO)	1.04 $(1.11)^a$
	0.95	H_2O	0.92
	1.20	H_3O^+	1.22

[a] CO does not conform perfectly to any among the assumed valence states. Its optimum α_d were therefore disregarded in selecting valence state exponents.

underlying *sp* basis provided extended basis sets are used. Dunning [6] performed the *d*-exponent optimization for H_2O with the [4*s*3*p*1*d*/2*s*1*p*] basis set and for N_2 with the [4*s*3*p*1*d*] basis set. His optimum values are 0.88 and 0.98 respectively, compared to our exponents of 0.925 and 0.93. With respect to the exponents of Hariharan and Pople [4], our exponents are consistently higher. Obviously this is due to the fact that the *d*-exponent optimization in Ref. [4] was performed with a basis set without the *p*-type functions on hydrogen. The obtained *d*-functions are therefore more diffuse to account for a residual A–H bond polarization not provided by the hydrogen basis set. With N_2 the two α_d are almost identical, which confirms our opinion. Dunning performed [6] also the α_d-optimization for water without hydrogen *p*-functions. His optimum α_d of 0.75 is practically identical with the optimum α_d of 0.74 reported in Ref. [4].

Table 3. Energies of reactions ΔE (kJ/mol) and the effect of *d*-exponent optimization

	ΔE[a]			
Reaction	valence state α_d	$\alpha_d=0.8$	$\Delta\Delta E$[b]	$\exp(\lvert\Delta\Delta E\rvert/RT)$[c]
$NH_3^+ + NH_3 \rightleftharpoons NH_4^+ + NH_2$	-77.1	-77.1	0.0	1.0
$NH_3^+ + H_2O \rightleftharpoons H_3O^+ + NH_2$	$+90.8$	$+90.7$	$+0.1$	1.0
$NH_3 + H_3O^+ \rightleftharpoons NH_4^+ + H_2O$	-168.0	-167.8	-0.2	1.1
$NH_2 + H \rightleftharpoons NH_3$	-362.8	-363.1	$+0.3$	1.1
$NH_3^+ + H \rightleftharpoons NH_4^+$	-440.0	-440.3	$+0.3$	1.1
$C_2H_2 + 3H_2 \rightleftharpoons 2CH_4$	-495.2	-495.5	$+0.3$	1.1
$OH^- + NH_3 \rightleftharpoons H_2O + NH_2^-$	$+67.5$	$+66.8$	$+0.7$	1.3
$NH_2^- + H^+ \rightleftharpoons NH_3$	-1836.1	-1837.0	$+0.9$	1.4
$NH_2 + H^+ \rightleftharpoons NH_3^+$	-835.8	-834.4	-1.4	1.8
$NH_3 + H^+ \rightleftharpoons NH_4^+$	-912.9	-911.5	-1.4	1.8
$OH^- + H^+ \rightleftharpoons H_2O$	-1768.6	-1770.2	$+1.6$	1.9
$H_2CO + 2H_2 \rightleftharpoons CH_4 + H_2O$	-254.5	-256.8	$+2.3$	2.5
$H_3O^+ + OH^- \rightleftharpoons 2H_2O$	-1023.7	-1026.5	$+2.8$	3.1
$N_2 + 2H_2 \rightleftharpoons 2NH_2$	$+197.5$	$+194.7$	$+2.8$	3.1
$OH^- + NH_4^+ \rightleftharpoons H_2O + NH_3$	-855.8	-858.7	$+2.9$	3.2
$OH^- + NH_3^+ \rightleftharpoons H_2O + NH_2$	-932.9	-935.9	$+3.0$	3.4
$N_2 + 3H_2 \rightleftharpoons 2NH_3$	-171.3	-174.7	$+3.4$	3.9
$CO + CH_4 \rightleftharpoons C_2H_2 + H_2O$	$+232.4$	$+228.5$	$+3.9$	4.8
$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	-262.8	-266.9	$+4.1$	5.2

[a] The total energies for H_2 and H are -1.131197 and -0.497637 respectively.

[b] This is the difference between the entries in the first two columns.

[c] This factor means the ratio of the theoretical equilibrium constants given by the two basis sets for $T=298°K$.

To test the effect of *d*-exponents on the energies of reaction we assumed reactions whose components are molecules from the set treated in Tables 1 and 2. The reactions are ordered in Table 3 according to the ascending difference between the energies of reaction calculated with the valence state *d*-exponents from Table 2 and standard $\alpha_d=0.8$. It is seen from Table 3 that for most reactions the effect of *d*-exponent optimization is small. For some reactions however this effect is significant. Typical examples are the reactions involving species such as N_2 or CO, for which the total energy strongly depends on α_d (see Fig. 1). Furthermore it should be recalled that for the equilibrium constant of a chemical process

$$\mu_1 A_1 + \mu_2 A_2 + \cdots + \mu_m A_m \rightleftharpoons \nu_1 B_1 + \nu_2 B_2 + \cdots + \nu_n B_n \tag{1}$$

it holds

$$K_p = \frac{\prod_{j=1}^{n} (Q_j^0/N_A)^{\nu_j}}{\prod_{j=1}^{m} (Q_j^0/N_A)^{\mu_j}} \exp(-\Delta H_0^0/RT) \tag{2}$$

where Q_j^0 are partition functions, N_A Avogadro's number and ΔH_0^0 heat of reaction at absolute zero. If the d-exponent optimization brings about the change $\Delta\Delta E$ in the energy of reaction then the calculated equilibrium constant is affected by the factor of $\exp(\Delta\Delta E/RT)$. The entries in the last column of Table 3 suggest that this effect is chemically significant with several lowest reactions.

In Table 3 we did not compare the calculated energies of reaction with the experimental heats of reaction. This would be of little use, since for some among the molecules treated the heats of formation at absolute zero are not known and for most molecules involved the corrections for zero-point energies and correlation effects are uncertain. Nevertheless we note here briefly on results obtained for several selected reactions for which the available experimental data permitted to make a meaningful comparison. A very good agreement with experiment was obtained for reactions involving neutral and positively charged species [7]. A completely different situation was found for reactions with negatively charged species (OH^- and NH_2^-), although this can hardly be anticipated from the entries of Table 3. For example, if the corrections are made for the zero-point [8] and correlation [9] energies for the reaction $OH^- + H^+ \rightleftharpoons H_2O$, our basis set with the valence state α_d gives a heat of reaction which is in error by 85.8 kJ/mol. Thus it appears that if a level of the chemical accuracy is to be achieved for reactions with negatively charged species without enlarging the size of the basis set, some care must also be paid to the optimization of the p-set and valence shell s-functions. Lischka

Table 4. One-electron properties of N_2 with standard and valence state exponents of d-functions[a]

Property		$\alpha_d = 0.8$	$\alpha_d = 0.95$
$\langle 1/r_{N_1} \rangle^b$	electronic	-21.6419	-21.6443
	total	-18.2570	-18.2594
$E_z(N_1)^c$		-0.0677	-0.0576
$F_z(N_1)^d$		-0.4739	-0.4032
$\Theta_{zz}{}^e$		-1.0835	-1.1730
$\langle z^2 \rangle^f$	electronic	-23.6245	-23.7004
	total	-8.6563	-8.7322
$\langle x^2 \rangle^{f,g}$		-7.5728	-7.5593
$\langle r^2 \rangle^f$	electronic	-38.7701	-38.8190
	total	-23.8019	-23.8508

[a] All quantities are in atomic units. For the conversion factors to the more common units, as well as for definitions of the properties, see Ref. [11]. If not explicitly stated, only total values (electronic + nuclear contributions) are given.

[b] Potential.

[c] Electric field.

[d] Force on the nuclei.

[e] Quadrupole moment (relative to the center of mass).

[f] Second moments (relative to the center of mass).

[g] This property has only an electronic contribution.

[9] arrived at the same conclusion. Dunning and Hay [10] suggested the use of atomic p-sets augmented with an additional function optimized for the atomic negative ion.

Finally we present results on some one-electron properties given by the standard and valence state exponents. Unlike the total energy, some one-electron properties may be expected to be more sensitive to small changes in α_d. To estimate this effect we selected the N_2 and NH_2^- molecules. For the former we found the steepest dependence of energy on α_d and the latter represents the case where the standard and valence state exponents are markedly different. With N_2 (Table 4) the use of the standard α_d instead of the valence state α_d brings about the 10 % deterioration in forces on the nuclei and the 8 % lowering of the quadrupole moment. The other one-electron properties were affected very little. These are, however, known to be a rather insensitive test of the accuracy of the wave function. Also with NH_2^- (Table 5) the largest effect was found with the forces on nuclei. Surprisingly, the force on nitrogen is 8 % higher for the valence state α_d than it is for the standard α_d. This may be due to the geometry assumed. Since the experimental geometry for NH_2^- is not available, we used the geometry optimum for the double zeta basis set. Although this

Table 5. One-electron properties of NH_2^- with standard and valence state exponents of d-functions[a]

Property		$\alpha_d = 0.8$	$\alpha_d = 0.55$
$\langle 1/r_{H_1} \rangle$[b]	electronic	-5.3275	-5.3263
	total	-1.4284	-1.4271
$\langle 1/r_N \rangle$[b]	electronic	-19.7783	-19.7745
	total	-18.7569	-18.7530
$E_z(H_1)$[c,d]		-0.0022	-0.0014
$E_y(H_1)$[c,d]		$+0.0052$	$+0.0057$
$E_z(N)$[c]		-0.0812	-0.0886
$F_z(N)$[d]		-0.5684	-0.6202
$\langle x^2 \rangle$[e,f]		-8.2827	-8.3250
$\langle y^2 \rangle$[e]	electronic	-10.8703	-10.8692
	total	-6.1091	-6.1080
$\langle z^2 \rangle$[e]	electronic	-9.7230	-9.7043
	total	-7.3389	-7.3203
$\langle r^2 \rangle$[e]	electronic	-28.8760	-28.8985
	total	-21.7307	-21.7532

[a] All quantities are in atomic units. For the conversion factors to the more common units, as well as for definitions of the properties, see Ref. [11]. If not explicitly stated, only total values (electronic + nuclear contribution) are given.

[b] Potential.

[c] Electric field.

[d] Force on the nuclei.

[e] Second moments (relative to the center of mass).

[f] This property has only an electronic contribution.

geometry is close to the optimum geometry obtained by Heaton and Cowdry [12] for a double zeta and polarization basis set, a small deviation from the optimum geometry might be a reason for the change in the computed force. With the other one-electron properties of NH_2^- the differences are very small.

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