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Density matrix averaged atomic natural orbital (ANO) basis sets for correlated molecular wave functions

I. First row atoms

Per-Olof Widmark[1], **Per-Åke Malmqvist**[2], **and Björn O. Roos**[2]

[1] IBM Sweden, P.O.B. 4104, S-203 12 Malmö, Sweden

[2] Department of Theoretical Chemistry, Chemical Centre, P.O.B. 124, S-221 00 Lund, Sweden

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Summary. Generally contracted basis sets for first row atoms have been constructed using the Atomic Natural Orbital (ANO) approach, with modifications for allowing symmetry breaking and state averaging. The ANOs are constructed by averaging over several atomic states, positive and negative ions, and atoms in an external electric field. The contracted basis sets give virtually identical results as the corresponding uncontracted sets for the atomic properties, which they have been designed to reproduce. The design objective has been to describe the ionization potential, the electron affinity, and the polarizability as accurately as possible. The result is a set of well-balanced basis sets for molecular calculations. The starting primitive sets are *8s4p3d* for hydrogen, *9s4p3d* for helium, and *14s9p4d3f* for the heavier first row atoms.

Key words: Atomic natural orbitals – Basis sets – General contraction

1. Introduction

Atomic basis sets for correlated molecular wave functions have in recent years attracted considerable interest, influenced by the realization that traditional Gaussian basis sets with segmented contraction and usually one or two polarization functions are not sufficient for accurately describing dynamic correlations. For example, a recent study of CCl and ClF clearly indicates the importance of a good description of the *3d* orbital of chlorine in order to obtain quantitative results for the binding energy [1]. A systematic study of the basis set dependence of the electron affinity of oxygen shows that a very large primitive basis set is needed to approach the converged result [2]. These and other similar results yield basis sets that are prohibitively large for molecular calculations, and a method for contracting them, with as small effect on the quality as possible, is clearly needed. The general contraction scheme based on atomic natural orbitals (ANOs), which has been suggested by Almlöf and Taylor [3], shows great promise in this respect. A necessary ingredient, which has made it possible to use generally contracted basis sets, is the appearance of efficient computer programs for the calculation of the two-electron integrals [4, 5].

The aim of contracting an atomic basis set is to reduce the one-particle space while reproducing the atomic properties obtained with the primitive set as accurately as possible. The basis sets are normally to be used in molecular calculations. Important atomic properties for an accurate description of a chemical bond are the ionization potential, the electron affinity, and the polarizability. The basis sets presented in this contribution have been prepared to yield only small contraction losses for these properties.

The introduction of the ANOs [3, 6] was a major step towards saturated basis sets for molecular calculations. The original idea was to perform a correlated calculation on the atomic ground state using the primitive set of Gaussian type functions, and to use the most highly occupied natural orbitals in the contracted basis set. The natural orbitals with occupation numbers below a given threshold were discarded, leading to a substantial reduction in the size of the one-particle basis, with only a small contraction error for the atomic state. Such a contraction scheme has the benefit of retaining as much of the atomic correlation energy as possible with a given number of basis functions. A further benefit lies in the simplification obtained in the analysis of the molecular orbitals, since there is a one-to-one correspondence between the basis functions and the atomic orbitals. One drawback with this scheme is the bias obtained in the basis set towards the atomic ground state. As a consequence the spectroscopic properties converge rather slowly with the number of basis functions. This is exemplified for the oxygen atom in Table 4.

The modification of the original ANO scheme presented in this work allows the determination of ANOs which describe the atom, the positive and negative ions, and also the atomic polarization in a balanced way. This is achieved by performing calculations on a number of atomic states, also including calculations where the atom has been placed in a homogeneous electric field. The wave function used is an expansion in all single and double replacement states based on a Hartree–Fock reference state. The contracted basis set is obtained from the natural orbitals corresponding to the *average* density matrix from all these wave functions. The most important electronic structures that have been included in this averaging procedure are for the first row atoms (B – F): the atomic ground state, the ground states of the positive and negative ions, and the atomic ground state perturbed by an external electric field. In some cases atomic excited states have also been included. The atoms H, He, Li, Be, and Ne had to be treated in a special way, as will be described in more detail below.

Almlöf et al. have in a recent paper [6] studied the ANO contraction error for the total energy, the correlation energy and the dipole moment of the HBr molecule. Their approach differs from the present one in the treatment of the diffuse part of the basis set. Instead of using the ANO scheme for all orbitals they suggest that the outermost functions should be left uncontracted in order to allow for a more flexible description of the outer region. We do not believe that such an approach is necessary in the present scheme where the polarizability is explicitly included in the basis set optimization. It is also claimed that the orbitals used to describe angular correlation also account for polarization effects. The present study shows, however, that the orbitals obtained by polarizing the atom are more diffuse than those describing angular correlation. A more extended set of correlating orbitals is therefore necessary in order to include effective polarization functions in the same set.

ANO for the halogens F, Cl, and Br, obtained using the average natural orbitals of the neutral atom and the negative ion SDCI wave functions, were recently derived by Langhoff et al. and were used in multi-reference CI calculations on the aluminium monohalides [7].

2. The averaging procedure

The present ANO sets are designed to be general purpose basis sets for molecular calculations. Important atomic properties, which should be well reproduced by a basis for molecular calculations, are the ionization potential, the electron affinity, and the polarizability. The contracted basis sets are constructed to reproduce the uncontracted basis set results for these properties as accurately as possible, by averaging the density matrices for the neutral atom, the positive and negative ions and the atom perturbed by a homogeneous electric field. Further, the low spin state with the same electronic structure as the ground state of the neutral atom was also included in the averaging whenever it existed.

The average over several states is performed on the one-electron density matrices for the different states, and the final ANO orbital set is obtained by deleting those natural orbitals of the averaged density matrix that have the smallest occupation numbers.

The term "ANO basis set", and the reason for using it, has nothing to do with the selection and the optimization of the uncontracted basis set, but is relevant only to the subsequent contraction. When a general, or Raffenetti [5], type contraction scheme is used, a new basis set is formed as a non-singular linear transformation of the uncontracted AOs. If the new basis set is as large as the original one, nothing is gained, but on the other hand there is no contraction error. Discarding one or more of the new basis functions leads in general to a contraction error when the new basis functions are used in a molecular orbital calculation. The reason for using an ANO type basis set is that this minimizes the contraction error in the following sense. Consider a diagonal element of an average density matrix and assume an orthonormal basis. Recalculating the wave functions without the corresponding basis function leads to a contraction error. The diagonal element under consideration will be zero if and only if this error is zero. Furthermore, it is a non-negative and continuous function of the contraction error. Therefore the diagonal element of the density matrix is a valid measure of the resulting error. Its minimization results in the criterion that the least harmful effect is obtained by diagonalizing the matrix and deleting the ANO with the smallest occupation number. The same applies to sums of diagonal elements when more basis functions are excluded.

The calculations are not performed in spherical symmetry and different components of the same atomic shell are therefore not necessarily equivalent. Furthermore, symmetry breaking, which mixes different shells, always occurs when the atom is placed in an external electric field. Therefore, an anisotropic basis set would be produced by a straightforward averaging of the different density matrices. Isotropy can, however, be restored by simply performing an average over all possible orientations in space of the atom, which can be shown to remove the shell mixing blocks of the density matrix without destroying the desired properties of the natural orbitals. This spherical averaging is easily shown to be equivalent to simply averaging the different components of a given shell and zeroing out the off diagonal blocks of the density matrix. To under-stand the averaging procedure we treat a single orbital and work in a basis of complex spherical harmonics, $Y_{lm}(\theta, \varphi)$. The atomic orbital can then in the general case be written as

$$f(r, \theta, \varphi) = \sum_{n,l,m} c_{nlm} x_{nl}(r) Y_{lm}(\theta, \varphi), \tag{1}$$

which yields the following density matrix elements,

$$P_{nlm,n'l'm'} = c^*_{nlm} c_{n'l'm'}. \tag{2}$$

Following the notation of Silver [8], a rotation of the orbital in space is performed with the following result,

$$\begin{aligned} f_{\alpha\beta\gamma} &= \hat{D}(\alpha, \beta, \gamma) f = \sum_{n,l,m} c_{nlm} x_{nl}(r) \hat{D}(\alpha, \beta, \gamma) Y_{lm}(\theta, \varphi) \\ &= \sum_{n,l,m} c_{nlm} x_{nl}(r) \sum_{m''} D^{(1)}_{m''m}(\alpha, \beta, \gamma) Y_{lm''}(\theta, \varphi), \end{aligned} \tag{3}$$

where $D^{(1)}_{m''m}(\alpha, \beta, \gamma)$ is the Wigner rotation matrix for the Euler angles α, β, and γ. The density matrix elements produced by this rotated orbital can be written as

$$P_{nlm,n'l'm'}(\alpha, \beta, \gamma) = c^*_{nlm}(\alpha, \beta, \gamma) c_{n'l'm'}(\alpha, \beta, \gamma), \tag{4}$$

where

$$c_{nlm}(\alpha, \beta, \gamma) = \sum_{m''} c_{nlm''} D^{(1)}_{mm''}(\alpha, \beta, \gamma). \tag{5}$$

The rotated density matrix can be averaged over all possible orientations by evaluating the integral over the Euler angles

$$\begin{aligned} \int P_{nlm,n'l'm'}\, d\alpha \sin\beta\, d\beta\, d\gamma &= \sum_{m'',m'''} c^*_{nlm''} c_{n'l'm'''} \\ &\quad \times \int D^{(1)*}_{mm''}(\alpha, \beta, \gamma) D^{(1)}_{m'm'''}(\alpha, \beta, \gamma)\, d\alpha \sin\beta\, d\beta\, d\gamma \\ &= \frac{8\pi^2}{2l+1} \delta_{ll'} \delta_{mm'} \sum_{m''} P_{nlm''n'l'm''}. \end{aligned} \tag{6}$$

Thus the averaging produces a density matrix which is block diagonal in blocks defined by l and m. The blocks defined by l, m and l, m' are also identical and are obtained as the average over all m values for a given l,

$$\tilde{P}_{nlm,n'lm} = \frac{l}{2l+1} \sum_{m'} P_{nlm',n'lm'}. \tag{7}$$

The above derivation is valid for every orbital density and thus also for the full density matrix.

So far we have worked with complex spherical harmonics, but most integral programs use a real representation of the angular momentum functions. The density submatrix over m for a given l, n, and n' is a unit matrix multiplied with a scale factor, and a unitary transformation will leave it unchanged. Working with Cartesian basis functions, the density matrix can either be transformed into a real spherical harmonics basis before averaging, or the following explicit averaging formula can be used,

$$
\begin{aligned}
P(p) &= \tfrac{1}{3}P(x) + \tfrac{1}{3}P(y) + \tfrac{1}{3}P(z),\\
P(d) &= \tfrac{1}{5}P(xy) + \tfrac{1}{5}P(xz) + \tfrac{1}{5}P(yz) + \tfrac{2}{5}P(xx) + \tfrac{2}{5}P(yy) + \tfrac{2}{5}P(zz),\\
P(f) &= \tfrac{1}{7}P(xyz) + \tfrac{6}{7}P(xxx) + \tfrac{6}{7}P(yyy) + \tfrac{6}{7}P(zzz)\\
&\quad + \tfrac{2}{7}P(xxy) + \tfrac{2}{7}P(xxz) + \tfrac{2}{7}P(xyy) + \tfrac{2}{7}P(xzz) + \tfrac{2}{7}P(yyz) + \tfrac{2}{7}P(yzz), \qquad (8)
\end{aligned}
$$

with corresponding, but more involved expressions for the higher angular momentum.

This state averaged and symmetry broken way of determining the density matrices has the benefit of yielding basis sets of a given quality with fewer contracted functions than that of the original scheme [3], which is based on a single symmetry restricted case. There is a general trend that functions belonging to the same main shell, e.g. $4s$–$4f$, tend to have similar occupation numbers, as noted previously by others [3, 9], and it therefore seems to be a good strategy to truncate the natural orbital space approximately at a shell boundary. This strategy has been followed except for the larger $6s5p3d2f$ basis set, and the fact that no angular momentum functions higher than f-type have been used; such functions are certainly needed in very accurate work, but it was not felt necessary to include them in a general purpose basis set.

Hydrogen and lithium, being effective one-electron systems, had to be treated in a different way to yield meaningful natural orbitals. The contraction coefficients for hydrogen were obtained by averaging over the atomic ground state with and without an external electric field, the hydrogen molecule, and the anion (the last two at the SDCI level). For lithium the average was performed over the cation, the neutral atom with and without electric field (at the SCF level), and the lithium molecule at the SDCI level. The average for neon was performed on the neutral atom with and without electric field (SDCI).

The electric field strength used in the averaging calculations was 0.01 a.u. for the lighter atoms and 0.05 a.u. for O, F, and Ne. These rather large field strengths were chosen in order to achieve an approximately equal weight of the density contribution from polarization and correlation, respectively.

3. The primitive basis set

The starting primitive Gaussian basis sets were taken from the compilation of van Duijneveldt [10]. The sets chosen were the $7s$ set for hydrogen, the $8s$ set for helium, and the $13s8p$ set for the heavier atoms. For lithium and beryllium $8p$ functions were optimized with respect to the SCF energy for the lowest excited state with the $2p$ orbital occupied. The exponents (ζ_i, $i = 1, n$) were not individually optimized, but a modified even tempered form [11] was used with three variational parameters (c_{-1}, c_0, and c_1):

$$\ln(\zeta_k) = c_{-1}/k + c_0 + c_1 k; \quad k = 1, \ldots, n; \quad \zeta_1 > \zeta_2 > \cdots > \zeta_n, \qquad (9)$$

which yields energies close to that obtained with individually optimized exponents. The starting primitive sets were augmented with higher angular momentum functions optimized in an even tempered form with respect to the SDCI energy of the ground state of the atom, where hydrogen and lithium had to be treated in a special way (*vide infra*). This primitive set was further augmented with a diffuse function for each of the *s*, *p*, *d*, and *f* sets for the heavy atoms, and the *s*, *p*, and *d* sets for hydrogen and helium. The resulting primitive basis sets had the size 14*s*9*p*4*d*3*f* for the heavier atoms, 8*s*4*p*3*d* for hydrogen and 9*s*4*p*3*d* for helium.

Hydrogen and lithium had to be treated in a special way. The *p*- and *d*-type functions for hydrogen were optimized with respect to the SDCI energy for H_2, while for lithium they were optimized with respect to the SDCI energy for Li_2. Both H_2 and Li_2 were at their equilibrium geometry.

4. Test calculations

The basis sets presented here have been designed to be good general purpose basis sets for molecular calculations with primitive sets that are not prohibitively large for sizeable molecules. Some of the flexibility in the basis sets is inevitably lost when they are contracted, and truncation errors occur. Tables 1–3 show how the electron affinity, the ionization potential, and the polarizability are affected by truncation at different levels. All properties are calculated at the SDCI level except for the one-electron cases, which are described by an open shell SCF wave function. As can be seen from the tables, the effect of contraction is very small in most cases, indicating that the truncation error will also be small in molecular calculations. The average of the polarizability tensor was computed using the finite field approach with an external field of 0.02 a.u. This field is much too large to yield accurate values for the lighter elements, particularly lithium. Therefore a series of finite field calculations were performed for this atom with the 6*s*5*p*3*d*2*f* basis set. Extrapolation to zero field gives a polarizability of 169.8 a.u. This value is still about 6 a.u. larger than experiment, but this discrepancy is mainly due to the neglect of 1*s* correlation. Numerical Hartree–Fock

Table 1. The electron affinities (in eV) of the ground state atoms H – F computed using an SDCI wave function

Basis	H	He
primitive	0.723	<0
4*s*3*p*2*d*	0.720	<0
3*s*2*p*1*d*	0.707	<0
3*s*2*p*	0.693	—
2*s*1*p*	0.322	<0
exp[a]	0.754	<0

Basis	Li	Be	B	C	N	O	F
primitive	0.617	<0	0.154	1.133	<0	1.025	2.976
6*s*5*p*3*d*2*f*	0.617	<0	0.153	1.131	<0	1.018	2.972
5*s*4*p*3*d*2*f*	0.616	<0	0.151	1.131	<0	1.016	2.975
4*s*3*p*2*d*1*f*	0.568	<0	0.143	1.125	<0	0.982	2.951
exp[a]	0.618	<0	0.277	1.263	<0	1.461	3.399

[a] Experimental results from [14]

Table 2. The ionization potentials (in eV) of the ground state atoms H – Ne computed using an SDCI wave function

Basis	H	He
primitive	13.606	24.556
4s3p2d	13.605	24.550
3s2p1d	13.605	24.525
2s1p	13.542	24.502
exp[a]	13.606	24.580

Basis	Li	Be	B	C	N	O	F	Ne
primitive	5.342	9.292	8.179	11.158	14.451	13.327	17.133	21.296
6s5p3d2f	5.342	9.295	8.173	11.153	14.448	13.313	17.123	21.319
5s4p3d2f	5.342	9.296	8.169	11.155	14.456	13.316	17.123	21.363
4s3p2d1f	5.340	9.297	8.113	11.124	14.444	13.257	17.069	21.455
exp[a]	5.390	9.320	8.296	11.264	14.534	13.614	17.42	21.56

[a] Experimental results from [15], except for hydrogen, where the infinite mass eigenvalue is used

Table 3. The average polarizability (in au) of the ground state atoms H – Ne computed using an SDCI wave function

Basis	H	He
primitive	4.47	1.37
4s3p2d	4.43	1.38
3s2p1d	4.28	1.27
3s2p	4.28	—
2s1p	1.77	0.71
exp[a]	4.50	1.38

Basis	Li	Be	B	C	N	O	F	Ne
primitive	172.5	38.98	21.01	11.72	7.21	5.05	3.50	2.50
6s5p3d2f	172.4	38.92	21.06	11.74	7.22	5.04	3.40	2.34
5s4p3d2f	172.4	38.91	21.00	12.09	7.22	5.05	3.46	2.40
4s3p2d1f	173.4	38.31	20.89	11.79	7.18	4.92	3.09	1.73
exp[a]	164	37.8	20.4	11.9	7.42	5.41	3.76	2.66

[a] Recommended values from [16]

calculations yield a polarizability of 170.1 a.u. [12], which is very close to the present result.

The experimental electron affinities are very hard to reproduce for the heavier atoms, since inclusion of higher excitations and the use of saturated basis sets are necessary. Feller and Davidson [2] have recently investigated the basis set and correlation level dependence of the electron affinity for oxygen. They obtained a value of 1.034 eV at the SDCI level with a large basis set (*23s12p10d6f3g*). This result can be assumed to be very close to the basis set limit. The result was obtained with a wave function which included 1*s* correlation. The effect of correlating the 1*s* electron was estimated to be −0.025 eV, which places the valence SDCI value at 1.059 eV, to be compared to the value 1.025 obtained with the primitive basis set used here. We also performed CPF calculations and obtained an electron affinity of 1.21 eV using the 6*s*5*p*3*d*2*f* basis set, which is 0.25 eV lower than the experimental value, but must be considered as very satisfactory.

The ionization potentials are, as can be expected, more stable with respect to basis set truncation. The deviations between the SDCI results and experimental values are most probably due to missing higher order excitations in the wave functions.

In Table 4 we compare the truncation errors obtained with the present average density matrix technique and the original single state optimization scheme suggested by Almlöf and Taylor [3]. These results show clearly that for the properties used in the averaging, much smaller errors due to basis set contraction are obtained with the present scheme.

The truncation error for the total SCF and SDCI energies of the hydrogen molecule (r(HH) = 1.4 a.u.) is shown in Table 5. The SCF energies are almost unaffected by the contraction, while the correlation energy gradually decreases with the contraction, leading to a total contraction energy loss of 0.1 eV for the 3*s*2*p*1*d* set. The truncation error for the nitrogen molecule at a bond distance of 2.1 a.u. is shown in Table 6. The binding energy is computed as the molecular energy minus twice the atomic energy. This introduces a size consistency error at the SDCI level; however the object here is not to compute an accurate binding energy for N_2, but to establish the truncation errors obtained with the present basis sets. As expected the errors are small on the SCF level and slightly larger for the correlation energy. A comparison with results obtained using ground

Table 4. Comparison of truncation errors for the oxygen atom, obtained with the present average density matrix method and ground state optimized ANOs

	Averaged ANOs		Ground state ANOs	
	SCF	SDCI	SCF	SDCI
Polarizability (a.u.)				
primitive	5.032	5.578	5.032	5.578
6*s*5*p*3*d*2*f*	5.035	5.591	3.916	4.160
5*s*4*p*3*d*2*f*	5.041	5.616	3.812	4.016
4*s*3*p*2*d*1*f*	4.975	5.577	3.037	3.052
Electron affinity (eV)				
primitive	<0	1.025	<0	1.025
6*s*5*p*3*d*2*f*	<0	1.018	<0	0.888
5*s*4*p*3*d*2*f*	<0	1.016	<0	0.761
4*s*3*p*2*d*1*f*	<0	0.983	<0	0.395
Ionization potential (eV)				
primitive	11.968	13.327	11.968	13.327
6*s*5*p*3*d*2*f*	11.969	13.313	11.968	13.322
5*s*4*p*3*d*2*f*	11.980	13.316	11.969	13.320
4*s*3*p*2*d*1*f*	11.999	13.257	12.011	13.316

Table 5. Effects of the basis set contraction on the total SCF and SDCI energies for the hydrogen molecule, at equilibrium geometry (in a.u.)

Basis set	SCF	SDCI	*E* (corr.)	%
primitive	−1.133570	−1.173712	0.040212	100.0
4*s*3*p*2*d*	−1.133553	−1.173504	0.039512	98.3
3*s*2*p*1*d*	−1.133479	−1.172575	0.039096	97.2
3*s*2*p*	−1.133418	−1.170720	0.037302	92.8
2*s*1*p*	−1.132793	−1.165245	0.032452	80.7

Table 6. Effects of basis set contraction on the binding energy for the N_2 molecule[a]. Comparison between density averaged and ground state optimized ANOs (energies in eV)

Averaged ANOs	SCF	SDCI
6*s*5*p*3*d*2*f*	5.082	8.378
5*s*4*p*3*d*2*f*	5.064	8.361
4*s*3*p*2*d*1*f*	5.000	8.213
Ground state ANOs		
6*s*5*p*3*d*2*f*	5.086	8.401
5*s*4*p*3*d*2*f*	5.077	8.388
4*s*3*p*2*d*1*f*	5.029	8.245

[a] The calculations were made at $r(\mathrm{NN}) = 2.1$ a.u., and the binding energy was obtained as $2E(\mathrm{N}) - E(\mathrm{N}_2)$.

state optimized ANOs is also made in this same table. We notice that the results obtained with the two different kinds of basis sets are virtually identical. Obviously the detailed way in which the basis set is contracted is not important for the binding energy in this non-polar molecule.

The situation is different for the more polar system HF. CPF [13] calculations were performed at three distances around the minimum geometry (using a separation of 0.1 a.u.). The results are given in Table 7. Obviously the computed spectroscopic constants are not very accurate, due to the large grid and small number of points used, but that is not very important since our aim here is only to compare the effect of contraction and the use of average density ANOs in contrast to single state optimized ANOs. We notice that the latter give a slightly lower total energy, as might be expected. The computed binding energy is, however, larger and more stable with the density averaged basis set, and the dipole moment (and its derivative) converges faster towards the value obtained with the primitive set.

It is well known that ANO basis sets give only small errors due to basis set superposition (BSSE) [3]. In order to investigate the BSSE for the present orbitals we have made calculations on the fluorine atom with a set of fluorine ghost orbitals located at a distance of 2.68 a.u. from the atom (corresponding to the equilibrium bond distance in F_2). The computed SDCI superposition errors

Table 7. A CPF study of the effects of basis set contraction on the properties of the HF molecule. Comparison between density averaged and ground state optimized ANOs

Basis	r_e (Å)	$E + 100$ a.u.	D_e (eV)	ω_e (cm^{-1})	μ (a.u.)	$d\mu/dr$ (a.u.)
Primitive	.922	−.364189	5.94	4165	.701	.304
averaged ANOs						
6s5p3d2f	.923	−.359378	5.89	4178	.709	.302
5s4p3d2f	.923	−.357093	5.89	4174	.713	.303
4s3p2d1f	.924	−.341116	5.89	4190	.734	.309
Ground state ANOs						
6s5p3d2f	.922	−.360546	5.87	4166	.726	.314
5s4p3d2f	.923	−.359581	5.87	4169	.726	.310
4s3p2d1f	.923	−.348379	5.83	4176	.733	.301
exp	.917[a]	—	6.12[a]	4138[a]	.707[b]	—

[a] From [17]
[b] From [18]

for the *6s5p3d2f*, *5s4p3d2f*, and *4s3p2d1f* basis sets were 11.8, 18.7 and 49.7 meV, respectively—a very satisfactory result.

5. Conclusions

The basis sets given in the appendix of the present contribution have been obtained by an averaging procedure, which includes electronic states of the atom that are important in chemical bond formation. Thus, the orbitals have been constructed such that they simultaneously give accurate values for the ionization potential, the electron affinity, and the polarizability of the atom. Results for these properties that are stable with respect to basis set truncation have also been obtained. It is clear from the test calculations on small molecules that the truncation errors are also small for the molecular properties. Like other ANO basis sets, the present set has the additional virtue of yielding very small basis set superposition energies, which is important, especially when they are used to calculate intermolecular forces. Similarly optimized ANOs for second and third row atoms will be presented in forthcoming issues of this journal.

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Appendix

The contracted ANO basis function for the atom H – Ne are given in this appendix. For every atom the largest contracted basis set given is $6s5p3d2f$ for the atoms Li – Ne and $4s3p2d$ for H and He. These basis sets can be further contracted by just deleting functions from the right. The weakly occupied ANOs contain a mixture of correlation and polarization effects. Thus, when only one orbital is used, a compromise between polarization and correlation is obtained. The major contribution to both these features is obtained with two virtual orbitals, corresponding to the basis set $4s3p2d$ for the atoms Li – Ne. Larger basis sets will include more of the finer details in polarization and correlation. Basis sets of the quality $5s4p3d2f$ will give results close to the basis set limit. Notice that the $1s$ orbital in Li – Ne is described by only one ANO. Thus these basis sets cannot be used to correlate the $1s$ shell.

The basis set for hydrogen should preferably not be smaller than $3s1p$. Already this choice gives results not too far from the basis set limit (cf. Tables 1–3, 5). Notice also the small difference between this basis set and $3s2p1d$. An analysis of the occupation numbers of the average density matrix suggests that the third s-type function should be added before the first p-type function.

The basis sets can be obtained from the authors, either on a diskette, or through electronic mail.

Hydrogen atom

Exponents	1s	2s	3s	4s
188.61445	.00096385	-.0013119	.00242240	-.0115701
28.276596	.00749196	-.0103451	.02033817	-.0837154
6.4248300	.03759541	-.0504953	.08963935	-.4451663
1.8150410	.14339498	-.2073855	.44229071	-1.146271
.59106300	.34863630	-.4350885	.57571439	2.5031871
.21214900	.43829736	-.0247297	-.9802890	-1.582849
.07989100	.16510661	.32252599	-.6721538	.03096569
.02796200	.02102287	.70727538	1.1417685	.30862864

Exponents	2p	3p	4p
2.3050000	.11279019	-.2108688	.75995011
.80675000	.41850753	-.5943796	.16461590
.28236200	.47000773	.08968888	-1.371014
.09882700	.18262603	.86116340	1.0593155

Exponents	3d	4d
1.8190000	.27051341	-.7938035
.72760000	.55101250	-.0914252
.29104000	.33108664	.86200334

Helium atom

Exponents	1s	2s	3s	4s
1149.2705	.00035774	-.0005306	.00070544	-.0004722
172.04457	.00277289	-.0040330	.00705199	-.0104722
39.080465	.01429838	-.0225804	.03126037	-.0194099
11.036173	.05586749	-.1026255	.32197965	-.7127356
3.5641520	.16336284	-.4577114	1.0047488	-.0101329
1.2404430	.33133146	-.6059653	-1.290804	1.9343339
.44731600	.41429728	.57131336	-.4725896	-2.541659
.16420600	.18903228	.54758341	.95308829	.89814053
.05747200	.00515606	.01165900	.05061692	.54395940

Exponents	2p	3p	4p
4.5500000	.08926060	-.1867350	.85489228
1.5925000	.38050238	-.5117345	.10926707
.55737500	.44912372	-.1981506	-1.263812
.19508100	.27765440	.99587976	.90243325

Exponents	3d	4d
3.4000000	.28055213	-.9514716
1.3600000	.56558317	.18505878
.54400000	.30332967	.69874000

Lithium atom

Exponents	1s	2s	3s	4s	5s	6s
9497.9344	.00007470	-.0000110	.00000638	-.0000401	.00015532	-.0000908
1416.8112	.00058364	-.0000857	.00004887	-.0003102	.00121291	-.0008080
321.45994	.00306095	-.0004507	.00026583	-.0016465	.00634647	-.0034499
91.124163	.01260109	-.0018630	.00106853	-.0066395	.02593172	-.0182885
29.999891	.04234724	-.0063575	.00397706	-.0226602	.08532950	-.0396592
11.017631	.11475802	-.0177673	.01120297	-.0582447	.21962465	-.1664225
4.3728010	.23936592	-.0397968	.03121889	-.1222607	.40388973	-.0437952
1.8312560	.35759179	-.0701282	.06165080	-.1352471	.36488271	-.5854796
.80226100	.30337582	-.1029469	.15065016	-.0542651	-.5509683	1.9863927
.36264800	.08637933	-.0937078	.18747829	.08320127	-1.387610	-1.189023
.11399500	.00264390	.22012877	-1.094107	1.7479350	1.9839088	-2.535491
.05123700	.00121696	.59337736	-.2924223	-1.646307	-.7590298	5.7082509
.02246800	.00056197	.29452752	.84809436	-.7408542	-.6844426	-4.866391
.00786000	.00001973	.02495030	.44800085	1.3038650	.64145200	1.7783142

Exponents	2p	3p	4p	5p	6p
13.119504	.00144897	-.0023268	.00948249	-.0105332	.01182621
3.0774242	.00799578	-.0112242	.06320779	-.0734282	.10322211
1.0988005	.02134846	-.0344626	.17514656	-.2410174	.88284569
.43577840	.05011954	-.0338775	.57689385	-.8859633	-.4845183
.18024320	.19547388	-.4544520	.55635164	1.6251780	-1.224391
.07613330	.41911190	-.4963084	-1.291082	-.3335684	2.5068516
.03254650	.34816472	.48858791	.20705209	-1.250485	-2.256798
.01401820	.15059753	.56023390	.42867281	.94681211	.70847643
.00490640	.01570330	.07028069	.00433116	.20398213	.40248134

Exponents	3d	4d	5d
.45000000	.02237294	-.0304618	.17667927
.15750000	.37508794	-.5734588	.99447178
.05512500	.46891728	-.2741871	-1.552621
.01929380	.36536291	.95628826	.87869005

Exponents	4f	5f
.24000000	.38777831	-.3795652
.09600000	.40160976	-.6103086
.03840000	.44614994	1.0900688

Beryllium atom

Exponents	1s	2s	3s	4s	5s	6s
22628.599	.00005331	-.0000102	.00001238	-.0000163	.00002035	-.0000176
3372.3181	.00041812	-.0000804	.00009764	-.0001087	.00013929	-.0002212
760.35040	.00222604	-.0004281	.00051672	-.0007272	.00089927	-.0005446
211.74048	.00956276	-.0018487	.00225262	-.0023214	.00303917	-.0059611
67.223468	.03481791	-.0068008	.00822815	-.0124024	.01555533	-.0064601
23.372177	.10594611	-.0213719	.02644133	-.0250911	.03697737	-.0903658
8.7213730	.24566318	-.0530352	.06578965	-.1164622	.15845461	-.0284501
3.4680910	.38607362	-.1004577	.13010642	-.0631167	.08359833	-.6344349
1.4521440	.31037318	-.1375139	.19754924	-.6700337	.95775189	.36704639
.60861500	.06389402	-.0650704	.07492653	1.2263580	-3.527723	2.4990795
.25768600	-.0015314	.32457317	-1.388722	1.0746878	3.7533891	-5.257408
.10417600	.00118247	.61816433	.15458295	-2.962455	-1.194024	6.0739469
.04242700	-.0002521	.20476749	1.0260181	1.5600035	-1.247780	-4.688419
.01484900	.00007381	.00430350	.02577768	.28184411	1.3591094	1.9636275

Exponents	2p	3p	4p	5p	6p
33.710184	.00103783	-.0012142	.00258725	-.0022873	.00676966
8.0576495	.00660868	-.0056126	.02089535	-.0516249	.04194085
2.8364714	.02155898	-.0254797	.05737162	-.0217907	.21838026
1.0999657	.06087782	-.0114415	.26426850	-1.011218	1.1628586
.44339640	.20355732	-.5138507	1.0647600	.73527735	-2.555678
.18222640	.45796695	-.4908092	-1.436307	.91566937	2.6923753
.07572410	.36859063	.72214518	-.0547326	-1.931695	-1.672575
.03168540	.06306415	.43076218	.77703464	1.1633019	.12607530
.01108990	.00210971	.00225563	-.0320504	.20468349	.67295606

Exponents	3d	4d	5d
1.4000000	.00667733	-.0103868	.18372869
.49000000	.24681337	.89258071	.84246998
.17150000	.65744628	-.1507099	-1.494497
.06002500	.25351913	-.6812165	1.1174804

Exponents	4f	5f
.50000000	.32812970	-1.103944
.20000000	.65980420	.65022981
.08000000	.16284725	.35201447

Boron atom

Exponents	1s	2s	3s	4s	5s	6s
33360.217	.00005830	-.0000121	.00001207	-.0000180	.00002150	-.0000297
4972.0952	.00045649	-.0000950	.00009451	-.0001292	.00013762	-.0002597
1125.6417	.00240885	-.0005028	.00049965	-.0007771	.00096494	-.0011674
316.49136	.01016307	-.0021264	.00211919	-.0027820	.00280308	-.0062184
102.00726	.03609547	-.0076744	.00765190	-.0125600	.01654501	-.0182846
36.295873	.10598103	-.0232179	.02340454	-.0301270	.03061558	-.0888952
13.971410	.23956537	-.0569468	.05811557	-.1113291	.16803218	-.1661954
5.7411560	.37377265	-.1062577	.11167395	-.1047497	.02641519	-.3864725
2.4942680	.30814648	-.1457694	.17056231	-.4598841	.82053218	-.3403721
1.1142020	.07769277	-.0430285	.01726759	.67401792	-2.154533	3.3558475
.42154900	.00147971	.37194411	-.9989044	1.5042519	1.0217582	-5.718972
.16963300	.00049907	.56520899	-.2265722	-2.476043	1.7061016	6.0018231
.06853500	-.0000262	.19212692	1.0294550	.57766702	-3.083764	-4.013168
.02398700	.00002361	.02191276	.22137860	.74299933	1.8083378	1.4190724

Exponents	2p	3p	4p	5p	6p
55.000000	.00101856	-.0007776	.00075901	-.0032210	.00638030
13.366101	.00739575	-.0057768	.00591508	-.0325794	.03979359
4.1353940	.03225139	-.0226134	.01360093	-.1313091	.32302223
1.4812560	.09834638	-.0696834	.03206285	-.6809573	.89709816
.60213600	.23180240	-.2551146	.62952613	-.3491983	-1.699850
.25563600	.34124357	-.3607786	.17326486	1.3937462	.57073026
.11115100	.29329828	.06123947	-.8917853	-.3529796	1.3173404
.04764800	.16959513	.29599379	-.3535550	-.7747354	-1.864229
.01667700	.15075694	.66292780	.84690415	.57687382	.89953374

Exponents	3d	4d	5d
1.2000000	.08034579	-.1224628	.51304622
.42000000	.42193576	-.5604733	.50979375
.14700000	.46391674	-.0894260	-1.318999
.05145000	.28557335	.90159381	.86638551

Exponents	4f	5f
.85000000	.18252189	-.4773313
.34000000	.39464534	-.6578114
.13600000	.61043750	.95136724

Carbon atom

Exponents	1s	2s	3s	4s	5s	6s
50557.501	.00005527	-.0000120	.00001185	-.0000156	.00001740	-.0000264
7524.7856	.00043433	-.0000940	.00009271	-.0001140	.00012323	-.0002304
1694.3276	.00231588	-.0005028	.00049893	-.0006731	.00076340	-.0010505
472.82279	.00987292	-.0021476	.00211800	-.0025323	.00270031	-.0055835
151.71075	.03521949	-.0077942	.00777839	-.0109003	.01267800	-.0161830
53.918746	.10419375	-.0237634	.02363282	-.0277807	.03028665	-.0750168
20.659311	.24127411	-.0600235	.06163057	-.0958713	.12014642	-.1431410
8.3839760	.38401741	-.1153985	.11896802	-.1247806	.12427731	-.4657256
3.5770150	.30823714	-.1539009	.18806208	-.3932460	.55304311	-.2830282
1.5471180	.06830554	-.0145946	-.0540304	.67960039	-1.660497	3.6186451
.61301300	.00077821	.38958492	-.9814137	1.1978690	.21977066	-6.077981
.24606800	.00099049	.53972907	-.1096758	-1.897952	2.6568329	5.9472498
.09908700	-.0000893	.18840601	.88473559	-.0044614	-3.596556	-3.682612
.03468000	.00004714	.02585753	.29649833	1.0142148	1.8521129	1.1778905

Exponents	2p	3p	4p	5p	6p
83.333155	.00122406	-.0011444	.00146694	-.0037213	.00715443
19.557611	.00943894	-.0089796	.01445532	-.0379844	.03646278
6.0803650	.04177441	-.0378456	.04663731	-.1698042	.40106973
2.1793170	.13183304	-.1292708	.23665375	-.8114152	.70600551
.86515000	.27891188	-.3784022	.60887342	.24217302	-2.003223
.36194400	.36686633	-.2692137	-.3917793	1.3030673	1.6549840
.15474000	.27905913	.29175424	-.8700229	-1.200142	.06014000
.06542900	.13804807	.54366980	.42005046	-.0905452	-1.254857
.02290000	.03419495	.26283081	.57994967	.56980090	.93443306

Exponents	3d	4d	5d
1.9000000	.09873123	-.1455013	.56376833
.66500000	.45296608	-.5076809	.43125921
.23275000	.43624570	-.1015630	-1.277998
.08146300	.27192502	.92519220	.83542052

Exponents	4f	5f
1.2500000	.31136503	-.5041380
.50000000	.51596730	-.4373719
.20000000	.37742313	1.0147246

Nitrogen atom

Exponents	1s	2s	3s	4s	5s	6s
74761.715	.00005021	-.0000112	.00000972	-.0000121	.00001870	-.0000247
11123.654	.00039457	-.0000878	.00007649	-.0000903	.00012934	-.0002152
2512.6857	.00208853	-.0004667	.00040479	-.0005179	.00082182	-.0009762
703.77729	.00890794	-.0019931	.00173983	-.0020046	.00277581	-.0051642
225.47879	.03208845	-.0073033	.00634559	-.0083600	.01376942	-.0151043
79.615810	.09744736	-.0228259	.02014048	-.0227440	.03116421	-.0698700
30.237283	.23178948	-.0592207	.05240308	-.0744866	.13563675	-.1409305
12.263622	.37769114	-.1156121	.10665174	-.1108600	.13557620	-.4816840
5.2650860	.31879166	-.1565083	.15833879	-.2983389	.66633412	-.3990689
2.3334710	.08237821	-.0231058	-.0050051	.32128217	-1.624942	3.6895463
.90185600	.00279048	.37564757	-.8418720	1.1710298	-.3859865	-5.885458
.35833600	.00024647	.54576534	-.1590563	-.8649562	3.2306654	5.5787940
.14109300	-.0000289	.21035430	.59120260	-1.223793	-3.517450	-3.351193
.04938300	.00000968	.01278945	.57660532	1.4445805	1.5200656	1.0457791

Exponents	2p	3p	4p	5p	6p
126.66657	.00114231	-.0009565	.00142011	-.0027058	.00470949
29.837389	.00895909	-.0075763	.01254386	-.0302621	.03861619
9.3940380	.04053750	-.0336947	.05099132	-.1190992	.26167989
3.4051040	.12949014	-.1133437	.20571183	-.6278549	.90516411
1.3500000	.27678081	-.3055498	.54520414	-.2116148	-1.623290
.55769600	.36888892	-.2733953	-.1522542	1.4074630	.49583691
.23244900	.29346193	.20192518	-.8377166	-.6666649	1.2390022
.09426400	.12846833	.49253441	.04965949	-.6807072	-1.780651
.03299200	.03905858	.40980124	.74594407	.74984862	.94918349

Exponents	3d	4d	5d
2.7500000	.12053068	-.1733321	.61298904
.96250000	.50760685	-.4739903	.31696608
.33687500	.44539556	.03678810	-1.216663
.11790600	.15876917	.89316126	.87035573

Exponents	4f	5f
1.8000000	.33068755	-.7670701
.72000000	.55560706	-.0111511
.28800000	.30748869	.80193318

Oxygen atom

Exponents	1s	2s	3s	4s	5s	6s
105374.95	.00004590	-.0000105	.00000896	-.0000109	.00001811	-.0000224
15679.240	.00036065	-.0000825	.00007048	-.0000822	.00012131	-.0001947
3534.5447	.00191977	-.0004412	.00037567	-.0004675	.00080932	-.0008912
987.36516	.00820666	-.0018864	.00161462	-.0018465	.00257695	-.0046992
315.97875	.02972570	-.0069540	.00593400	-.0075585	.01377944	-.0138134
111.65428	.09045579	-.0217208	.01878662	-.0210868	.02811115	-.0628944
42.699451	.21740537	-.0568513	.04946829	-.0667511	.13747540	-.1285556
17.395596	.36876567	-.1139635	.10303987	-.1093673	.12206903	-.4617198
7.4383090	.33727977	-.1620201	.16205865	-.2731431	.73734928	-.4946086
3.2228620	.09675046	-.0333800	.00093665	.20971367	-1.705751	3.7909700
1.2538770	.00256736	.36550685	-.8224251	1.2034807	-.3504060	-5.906611
.49515500	.00137461	.55200311	-.1017902	-.6774694	3.1429946	5.4974482
.19166500	-.0001410	.22363927	.42539393	-1.429884	-3.347481	-3.298510
.06708300	.00006829	.00657453	.68770275	1.4891068	1.4012375	1.0457181

Exponents	2p	3p	4p	5p	6p
200.00000	.00089331	-.0008384	.00126180	-.0019528	.00307588
46.533367	.00736901	-.0068491	.01116281	-.0243404	.03750571
14.621809	.03493921	-.0328505	.05183165	-.0944754	.18584407
5.3130640	.11529855	-.1100060	.19788446	-.5489856	1.0270651
2.1025250	.25832314	-.3135263	.57076519	-.3495476	-1.567541
.85022300	.36962312	-.3196011	-.1789291	1.4659089	.38159176
.33759700	.32387894	.22172426	-.8982077	-.7571894	1.1466648
.12889200	.14679893	.56226160	.26666430	-.5905673	-1.662704
.04511200	.03361269	.30132513	.62589942	.79593212	.97284427

Exponents	3d	4d	5d
3.7500000	.12849338	-.2182055	.62420931
1.3125000	.52118843	-.4817695	.24030630
.45937500	.43457843	.13575954	-1.183642
.16078100	.14574094	.82977340	.92087218

Exponents	4f	5f
2.3500000	.36341106	-.8835406
.94000000	.56215546	.22624078
.37600000	.26352789	.67223250

Fluorine atom

Exponents	1s	2s	3s	4s	5s	6s
103109.46	.00006366	-.0000148	.00001511	-.0000154	.00002451	-.0000282
15281.007	.00050280	-.0001172	.00011869	-.0001160	.00016934	-.0002659
3441.5392	.00266772	-.0006239	.00063631	-.0006596	.00108913	-.0010810
967.09483	.01120034	-.0026280	.00265994	-.0025500	.00356213	-.0065142
314.03534	.03909798	-.0093503	.00960683	-.0102361	.01777027	-.0149993
113.44230	.11226574	-.0278490	.02843363	-.0267629	.03582817	-.0852224
44.644727	.24720417	-.0676880	.07198306	-.0829345	.16274938	-.1018524
18.942874	.36803449	-.1230542	.13103926	-.1141649	.12263698	-.6493063
8.5327430	.29086165	-.1522180	.20316169	-.3160866	.80374174	.03279916
3.9194010	.07810237	-.0075794	-.0915990	.44872390	-2.231614	3.3332897
1.5681570	.00354034	.37593135	-1.007025	1.1605351	.63328329	-5.838753
.62329000	.00091567	.54384824	.01746266	-1.369570	2.2900002	5.7221505
.24086100	.00007651	.21277464	.74900266	-.6041401	-3.123159	-3.626951
.08430100	.00002052	.00664218	.34476916	1.2967102	1.5381196	1.2345411

Exponents	2p	3p	4p	5p	6p
245.33029	.00098798	-.0009793	.00140028	-.0021447	.00405121
56.919005	.00829107	-.0083410	.01356231	-.0279769	.03277105
17.604568	.04073905	-.0407457	.06060520	-.1126856	.25347429
6.2749950	.13533040	-.1455266	.26782202	-.6847635	.94411468
2.4470300	.28096366	-.3556275	.58183694	.02453601	-1.880888
.99506000	.35883509	-.2537163	-.4280396	1.3824370	1.1269082
.40397300	.30381116	.28087005	-.7991571	-1.144517	.45705245
.15481000	.13893786	.56520351	.46852138	-.2020471	-1.365746
.05418400	.02581864	.23237085	.48624407	.68548718	.97459622

Exponents	3d	4d	5d
5.0000000	.13035593	-.2833655	.64835313
1.7500000	.52550546	-.5329589	.08528133
.61250000	.44216398	.33934736	-1.076245
.21437500	.12327467	.67721894	1.0003287

Exponents	4f	5f
3.2000000	.35649821	-.8994161
1.2800000	.58411540	.26248017
.51200000	.24042220	.65173543

Neon atom

Exponents	1s	2s	3s	4s	5s	6s
166165.08	.00004720	-.0000111	.00001383	-.0000134	.00001875	-.0000176
23107.524	.00040067	-.0000942	.00011547	-.0001015	.00013776	-.0002200
5060.1539	.00219321	-.0005180	.00064915	-.0006547	.00092611	-.0006395
1384.6123	.00958756	-.0022665	.00276318	-.0023205	.00310603	-.0061424
436.51258	.03507343	-.0084593	.01073356	-.0113825	.01639808	-.0077547
153.47148	.10465170	-.0260486	.03183250	-.0253425	.03407524	-.0922738
59.389087	.23771234	-.0653597	.08719603	-.1058383	.16092114	-.0201429
24.861967	.36960611	-.1222657	.15298113	-.0983722	.13776014	-.8470076
11.015704	.30616089	-.1585710	.28479790	-.5230270	.88474081	.68366327
4.9651750	.08419854	-.0060287	-.1929549	1.1226234	-2.832242	2.1521765
1.9365030	.00370345	.38289567	-1.322588	.49014011	2.1910109	-4.935538
.76572800	.00096535	.53886493	.49012790	-1.737905	.44521021	5.6607145
.29553800	.00005404	.21144871	.75461754	.39778722	-2.207583	-4.079378
.10343800	.00002679	.00280490	.06136710	.89004131	1.5272555	1.5437551

Exponents	2p	3p	4p	5p	6p
234.94500	.00158261	-.0022102	.00339886	-.0075907	.01763038
55.077385	.01257669	-.0185114	.03630469	-.0418546	.01841979
17.389549	.05698653	-.0815212	.14392888	-.4327586	1.1400838
6.3895370	.16812301	-.2923570	.73364643	-.7725174	-1.419730
2.5420820	.30738595	-.5403060	-.1076693	2.1038154	.27750201
1.0337640	.35831115	.09151549	-1.214315	-1.597286	1.3170494
.41878800	.27869376	.60908795	.64108328	-.0026161	-2.136422
.16462700	.09521109	.24352740	.35686171	.63860642	1.4278881
.05761900	.00210199	.00713030	.01895012	-.0022546	-.0967242

Exponents	3d	4d	5d
6.4200000	.13708557	-.4204726	.74155798
2.2470000	.54470998	-.5592957	-.3478303
.78645000	.44972742	.70000990	-.6598257
.27525750	.06537094	.33900230	1.0210673

Exponents	4f	5f
4.1900000	.34597039	-.9362870
1.6760000	.61486823	.33666424
.67040000	.20832288	.60353969

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