Contracted polarization functions for the atoms helium through neon

Takeshi Noro[1], Masahiro Sekiya[1], Toshikatsu Koga[2]

[1] Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060, Japan
[2] Department of Applied Chemistry, Muroran Institute of Technology, Muroran 050, Japan

Abstract. Contracted Gaussian-type function sets are proposed for polarization functions of the atoms helium through neon, with the exception of lithium. A segmented contraction scheme is used for its compactness and computational efficiency. The contraction coefficients and orbital exponents are fully optimized to minimize the difference from accurate atomic natural orbitals. The present polarization functions yield more than 99% of atomic correlation energies predicted by accurate natural orbitals of the same size.

Key words: Polarization functions – Correlating functions – Contracted Gaussian-type functions – First-row atoms

1 Introduction

In post-Hartree-Fock (HF) studies of atoms, the basis functions with a higher azimuthal quantum number than that of the highest occupied sub-shell play a significant role in describing the electron correlation effects. These basis functions are also important for the dynamical correlation in post-HF wave functions of molecules. On the other hand, these functions describe the distortion or polarization of atomic orbitals in the molecular environment within HF and multi-configurational self-consistent field (MCSCF) approximations. Thus the additional basis functions may be called either *correlating* functions or *polarization* functions. Though the latter name appears to be more common in the quantum chemistry community, in this study we use the two names interchangeably since we shall determine and discuss them based on the analysis of the electron correlation in atoms.

 Usually, polarization functions are constructed by using an empirical rule [1] or by an explicit optimization with respect to the total energy in molecular HF calcu-

lations. However, the natural orbitals are known [2, 3] to give the fastest convergence in the configuration interaction (CI) expansion of two-electron wave functions and in practice they also result in a good energy convergence for many-electron systems. Almlöf et al. [4] provided Gaussian-type function (GTF) basis sets in a general contraction scheme named ANO, where the contraction coefficients are defined by the atomic natural orbitals obtained from a CI calculation in atomic systems. For polarization functions, they used an even-tempered set as an original basis set. The ANO gave excellent descriptions in post-HF calculations of molecules. However, a general contraction basis set is computationally expensive. Dunning [5] proposed compact sets of primitive GTFs which efficiently describe correlation effects. Even-tempered series were used for the exponents of polarization functions, and the tempering parameters were optimized to minimize the CI energy of atomic systems. His basis set shows better descriptions of dynamical correlations than commonly used polarization functions, but it is still poorer compared to the ANO. The differences from the ANO are larger for smaller sets with lower azimuthul quantum numbers such as $1d$ and $2d1f$. Pettersson and Siegbahn [6] used segmented d and f polarization functions for the chlorine atom and demonstrated its effectiveness on the description of the binding in molecules containing chlorine atoms.

 In the present paper, we study the use of contracted GTFs (cGTFs) for polarization functions. For the sake of computational convenience, the segmented contraction scheme is used. Compared to the general contraction, the segmented contraction has an advantage in the integral generation in that it requires few additional computations. However, it often loses significant amounts of energy relative to the uncontracted sets. We thus optimize both contraction coefficients and orbital exponents to decrease the error of contraction by fitting our cGTFs to accurate atomic natural orbitals which have been generated by atomic CI calculations.

 The next section summarizes the theoretical ground of our approach, and Sect. 3 gives the computational

Correspondence to: T. Noro

details. The results and molecular applications are presented and discussed in Sect. 4. Hartree atomic units are used throughout this paper.

2 Theoretical ground

2.1 Natural spin-orbitals

When an N-electron wave function is expressed by a linear combination of normalized Slater determinants constructed from a common basis of orthonormal spin orbitals $\{\phi_i(\vec{r}, \sigma)\}$, the associated one-electron density function is given by

$$\rho(\vec{r}, \sigma) = \sum_{i,j} P_{ij} \phi_i^*(\vec{r}, \sigma) \phi_j(\vec{r}, \sigma) \tag{1}$$

If the Hermitian density matrix $\{P_{ij}\}$ is diagonalized by a suitable linear transformation of the spin orbitals, the density function can be reduced to a diagonal form

$$\rho(\vec{r}, \sigma) = \sum_k n_k |\lambda_k(\vec{r}, \sigma)|^2 \ , \tag{2}$$

in which $\{\lambda_k\}$ are natural spin orbitals and $\{n_k\}$ are occupation numbers of them,

$$0 \le n_k \le 1, \ \sum_k n_k = N \ . \tag{3}$$

Usually, n_k is close to unity for $k \le N$, and is small for $k \ge N + 1$.

As seen in the HF approximation, the electron density of a single-determinant N-electron wave function already has the form of Eq. (2),

$$\rho(\vec{r}, \sigma) = \sum_{i=1}^N |\phi_i(\vec{r}, \sigma)| \ , \tag{4}$$

where all the occupied spin orbitals have unit occupation number. Comparison of Eqs. (2) and (4) shows that in the electron density representation, the essential part of the electron correlation is embodied by a subset of the natural spin orbitals $\{\lambda_k\}$ with $k \ge N + 1$. This further suggests that good correlating basis functions must be able to well describe the $\{\lambda_k\}$ with $k \ge N + 1$, unless the corresponding occupation numbers are negligibly small.

In fact, it was proved that the natural orbitals give the fastest convergence in two-electron systems [2]. In the singlet case, for example, the *best* approximation of rank r of the exact wave function Ψ is represented by the natural expansion,

$$\Psi_r(\vec{r}_1, \vec{r}_2) = \sum_{k=1}^r c_k \lambda_k(\vec{r}_1) \lambda_k(\vec{r}_2) \Big/ \left(\sum_{k=1}^r n_k \right)^{\frac{1}{2}} \ . \tag{5}$$

It is generally believed that the natural orbitals are also the most suitable orbitals for describing electron correlation in many-electron systems. Thus, *good* correlating basis functions are required to well describe the important natural spin orbitals $\{\lambda_k\}$ with $k \ge N + 1$.

2.2 Correlating basis functions

From a given subset $\{\lambda_k\}(k \ge N + 1)$ of natural spin orbitals of an N-electron atom, we wish to construct a basis set $\{\chi_i\}$ of N_f correlating functions which would efficiently represent the subset $\{\lambda_k\}$. For this purpose, we minimize a functional

$$\Delta = \sum_{k=N+1}^{N+N_f} n_k \Delta_k \ , \tag{6}$$

in which the occupation numbers $\{n_k\}$ incorporate the relative significance of different natural orbitals and

$$\Delta_k \equiv \int dr |\lambda_k(\vec{r}) - \psi_k(\vec{r})|^2 w(\vec{r}) \ , \tag{7}$$

where $\psi_k(\vec{r})$ is a linear combination of correlating basis functions $\{\chi_i\}$ to be determined,

$$\psi_k(\vec{r}) = \sum_{i=1}^{N_f} C_{ki} \chi_i(\vec{r}) \ . \tag{8}$$

Note that in Eq. (7) we have suppressed the spin variable σ since as usual we assume a spin orbital to be a simple product of spatial and spin functions. Our choice of the weight function $w(\vec{r})$ will be discussed in the next section.

For an application of the present results to molecular calculations, we employ GTFs with exponents $\{\alpha_i\}$ as our basis functions $\{\chi_i\}$. The GTF principal quantum number n is taken to be the smallest value $n = l + 1$ of each symmetry specified by the azimuthal quantum number l. Then the functional (6) includes linear parameters $\{C_{ki}\}$ and non-linear parameters $\{\alpha_i\}$ to be optimized. The former can be immediately obtained by solving a set of linear equations for given values of $\{\alpha_i\}$. On the other hand, we have used the conjugated directions algorithm [7] for the non-linear optimization of the exponents $\{\alpha_i\}$. We note that for atoms the above determination of correlating functions can be independently performed for each symmetry l of natural orbitals.

3 Computational details

All the present atomic CI calculations were performed using the ATOMCI [8] program and test calculations on molecules were done with the ALCHEMY II program [9]. Our CI calculations used the well-tempered basis sets [10], $(17s10p10d10f10g)$ for He, $(20s13p13d13f13g)$ for Be, $(20s13p13d13f13g13h)$ for B through Ne, and included all the single and double (SD) substitutions from the HF configurations. The $1s$ orbital was, however, treated as a frozen core. In the case of the O(^3P) atom, for example, our CI wave function gave -74.994410 and -0.185358 hartrees for the total and correlation energies, respectively. The natural orbitals were then obtained by diagonalizing the density matrix.

To study the quality of the polarization functions, we used the HF occupied orbitals augmented with s correlation functions of $2s$–$4s$ (He atom) and $3s$–$6s$ (Be atom) natural orbitals orthogonalized to the occupied orbitals.

Table 1. Comparison of correlation energies of GTF sets generated by using three kinds of weight functions for O(^3P)

Set	r^0	r^{-1}	r^{-2}	Dunning	Natural orbitals
$+1d^a$	−0.136433	−0.138568	−0.138858	−0.138988	−0.147606
$+2d1f^a$	−0.167560	−0.168709	−0.168920	−0.169170	−0.172037
$+3d2f1g^a$	−0.178183	−0.178634	−0.178814	−0.178922	−0.179655
$+4d3f2g1h^b$	−0.182708	−0.182897	−0.183010	–	−0.183249

[a] $(20s13p)/[6s4p]$ was used for sp set
[b] $(20s13p)/[7s5p]$ was used for sp set

Similarly, the $1s$, $2s$, and $2p$ HF orbitals, augmented with the $3s$–$6s$ and $3p$–$5p$ or $3s$–$7s$ and $3p$–$6p$ natural orbitals, were employed for the atoms B through Ne.

For polarization sets, we applied truncations $1p$, $2p1d$, $3p2d1f$, and $4p3d2f1g$ for atoms He and Be, and truncations $1d$, $2d1f$, $3d2f1g$, and $4d3f2g1h$ for atoms B through Ne. We may expect these natural orbitals to be almost convergent to the exact natural orbitals and hereafter we refer them to as accurate natural orbitals. In the present study, we construct $1p$, $2p1d$, $3p2d1f$, $4p3d2f1g$ and $1d$, $2d1f$, $3d2f1g$, $4d3f2g1h$ correlating basis sets, respectively, for atoms He–Be and B–Ne to give a consistent treatment of correlation effects as Dunning's polarization basis sets [5].

We first carried out several test calculations on the ground ^3P state of the oxygen atom to find an appropriate form of the weight function $w(\vec{r})$ in Eq. (7). We assumed the functional form of the weight function simply to be r^n and tested it for $n = 0$, -1, and -2. The primitive GTF sets were generated by minimizing the functional (6) with these weight functions. The resultant polarization sets were added to the sp set of $(20s13p)/[6s4p]$ or $(20s13p)/[7s5p]$ and the CI calculations were carried out.

In Table 1, the resultant correlation energies are compared with those obtained from the correlation consistent basis set of Dunning and from the accurate natural orbitals. The weight function r^{-2} is seen to yield the best correlation energies among the three candidates for all the basis sets. It is natural than the correlation consistent sets gave a better description than the present polarization sets, because they were determined to minimize the CI energies. However, the differences are less than 0.25 mhartrees when the weight function r^{-2} is employed. Thus, we decided to use r^{-2} as the weight function $w(\vec{r})$. It may be rather surprising that our procedure described in Sect. 2 gives good correlation energies without energy variations.

Table 1 also shows an important fact that when compared with the accurate natural orbitals, both the present and Dunning's polarization sets have non-trivial discrepancies in the calculated correlation energies. The differences are remarkable for smaller sets such as $1d$ and $2d1f$, and amount to 8.6 mhartrees. These results suggest that the use of primitive GTFs for polarization functions has some limitations in quantitative applications.

To reduce the above discrepancies, we tested the use of *two* GTFs in a segmented contraction form for the *first* polarization function of *each* symmetry. The second and remaining polarization functions, if they exist, remained to be a single GTF. The idea comes from the fact that better description of the first natural orbital in polarization space, corresponding to $k = N + 1$ in Eq. (6), would be most important to improve the ability to incorporate the electron correlation. All the orbital exponents and contraction coefficients are fully optimized to minimize the functional (6). The resultant contracted polarization function sets were added to the sp sets to see how the calculated correlation energies are improved.

In Table 2, we summarize the correlation energies obtained for the oxygen atom. The table clearly shows a substantial improvement by the use of cGTFs over primitive GTFs. The differences from the accurate natural orbitals were reduced to less than 1 mhartree for any size of the basis sets. Since these results are quite satisfactory in the predicted correlation energies and yet the new polarization cGTF sets need few additional computations in practical applications, we decided to use the above-mentioned type of cGTF sets for the polarization functions of all the atoms examined in this study.

There are two exceptions, however. When we feed two or more basis functions for polarization space, the use of a cGTF for the first polarization function may not lead to an essential improvement due to the sufficient flexibility of the original primitive GTFs. In such cases, we use a *single* primitive GTF even for the first polarization function. Another exception is p polarization functions for the Be atom. They have a strong near degeneracy effect $2s^2 \to 2p^2$ and we found that a cGTF constructed by two primitive GTFs is not sufficiently accurate for the first polarization function. Thus we used *three* GTFs in a segmented contraction scheme for the first p polarization function of the Be atom. Further extensions were not examined, such as the use of a larger cGTF for the first polarization function and/or an additional introduction of cGTFs for the second polarization function of each symmetry, since we did not

Table 2. Comparison of correlation energies of the present cGTF sets with the correlation consistent set by Dunning and atomic natural orbitals for O(^3P)

Set	cGTF	Dunning	Natural orbitals
$+1d^a$	−0.146469	−0.138988	−0.147606
$+2d1f^a$	−0.171310	−0.169170	−0.172037
$+3d2f1g^a$	−0.179327	−0.178922	−0.179655
$+4d3f2g1h^b$	−0.183120	–	−0.183249

[a] $(20s13p)/[6s4p]$ was used for sp set
[b] $(20s13p)/[7s5p]$ was used for sp set

expect the essential improvement compared to the increased computational complexity.

4 Results and discussion

We have prepared [1p], [2p1d], [3p2d1f], and [4p3d2f1g] cGTF sets for atoms He and Be, and [1d], [2d1f], [3d2f1g], and [4d3f2g1h] cGTF sets for atoms B through Ne. The optimum exponents, contraction coefficients, and correlation energies are summarized in Tables 3–10. The percentages of the calculated correlation energies relative to the accurate natural orbitals of the same size are also given in the tables. The present polarization functions reproduce more than 99% of atomic correlation energies given by the accurate natural

Table 3. The helium atom ($E_{HF} = -2.861680$, $E_{corr} = -0.041828$)[a]

+1p[b]	$E_{corr} = -0.036472$			Percentage = 99.17%		
p	3.359247	0.772291				
	0.292946	0.811718				
+2p1d[b]	$E_{corr} = -0.039961$			**Percentage = 99.46%**		
p	10.426379	2.496391	/	0.723867		
	0.101569	0.940151	/	1.000000		
d	3.414102	1.014449				
	0.369140	0.749926				
+3p2d1f[b]	$E_{corr} = -0.041125$			**Percentage = 99.86%**		
p	19.345449	4.817907	/	1.650625	/	0.544814
	0.081805	0.951048	/	1.000000	/	1.000000
d	8.045128	2.832250	/	1.048274		
	0.172041	0.882127	/	1.000000		
f	3.790369	1.292498				
	0.407417	0.720330				
+4p3d2f1g[b]	$E_{corr} = -0.041562$			**Percentage = 99.96%**		
p	28.442409	7.548226 /	3.035456 /	1.247085 /	0.447417	
	0.082720	0.948315 /	1.000000 /	1.000000 /	1.000000	
d	13.262944	5.020687 /	2.244645 /	0.800640		
	0.142559	0.898617 /	1.000000 /	1.000000		
f	7.377672	3.023156 /	1.357886			
	0.255626	0.815184 /	1.000000			
g	4.208578	1.580725				
	0.431394	0.701978				

[a] For each polarization set, the first line gives exponents and the second line gives the contraction coefficients. Percentage shows the accuracy of the calculated correlation energy relative to that from the accurate natural orbitals of the same size
[b] (17s)/[6s] was used for s set

Table 4. The berrylium atom ($E_{HF} = -14.573023$, $E_{corr} = -0.046093$)[a]

+1p[b]	$E_{corr} = -0.044771$			Percentage = 98.77%		
p	3.677518	0.449702	0.121795			
	0.034651	0.361588	0.731713			
+2p1d[b]	$E_{corr} = -0.045637$			**Percentage = 99.60%**		
p	8.856237	1.364497	0.305026 /	0.100086		
	0.018971	0.144364	0.914035 /	1.000000		
d	0.235422	0.072231				
	0.916314	0.137593				
+3p2d1f[b]	$E_{corr} = -0.045890$			**Percentage = 99.81%**		
p	25.471750	4.559115	1.036918 /	0.283177/	0.096727	
	0.018829	0.172925	0.893965 /	1.000000/	1.000000	
d	0.276308		/	0.186784		
	1.000000		/	1.000000		
f	0.325876	0.129766				
	0.844392	0.222841				
+4p3d 2f1g[b]	$E_{corr} = -0.046023$			**Percentage = 99.95%**		
p	26.025899	4.694320	1.156310 /	0.373271/	0.166091 /	0.072338
	0.022255	0.201633	0.867662 /	1.000000/	1.000000 /	1.000000
d	1.483798		/	0.422360/	0.182247	
	1.000000		/	1.000000/	1.000000	
f	0.403226		/	0.235503		
	1.000000		/	1.000000		
g	0.412431	0.184147				
	0.796721	0.278844				

[a] See footnote (a) of Table 3
[b] (20s)/[6s] was used for s set

orbitals of the same size. It is remarkable that all the present correlating basis sets retain reasonable quality irrespective of their sizes. By contrast, Dunning's smaller correlation consistent sets, such as $(1d)$ and $(2d1f)$, have non-negligible discrepancies with ANO.

To assess the appropriateness of the present polarization sets for molecular calculations, we performed SDCI calculations on four diatomic molecules, O_2, CO, N_2, and BF, in their ground state at the experimental bond length. In these calculations, we used [74/7] cGTF sets of Tatewaki and Koga [11] decontracted to [7211/4111] for our sp set and augmented them with the $[1d]$ or $[2d1f]$ polarization set presented above. The excitations were limited on the valence shell. For comparison with the present sets, we also examined the basis sets of the same size prepared by Dunning [5]. The calculated HF and CI energies are summarized in Table 11, which shows that the present sets give better results for all the

Table 5. The boron atom ($E_{HF} = -24.529060$, $E_{corr} = -0.070510$)[a]

$+1d$[b]	$E_{corr} = -0.067058$		Percentage = 99.65%			
d	0.762491 0.212862					
	0.362599 0.764485					
$+2d1f$[b]	$E_{corr} = -0.069251$		Percentage = 99.89%			
d	1.632448 0.506731	/	0.169413			
	0.120119 0.926988	/	1.000000			
f	0.763370 0.285146					
	0.480326 0.637778					
$+3d2f1g$[b]	$E_{corr} = -0.069959$		Percentage = 99.91%			
d	4.206140 1.049788	/	0.425958	/	0.157721	
	0.053195 0.974562	/	1.000000	/	1.000000	
f	1.167911 0.683591	/	0.299277			
	0.232250 0.794594	/	1.000000			
g	0.838698 0.356540					
	0.539936 0.573260					
$+4d3f2g1h$[c]	$E_{corr} = -0.070330$		Percentage = 99.98%			
d	5.166457 1.345737	/	0.723954	/	0.338424 / 0.126624	
	0.070068 0.964619	/	1.000000	/	1.000000 / 1.000000	
f	1.135102	/	0.585554	/	0.245854	
	1.000000	/	1.000000	/	1.000000	
g	1.055648 0.505934	/	0.404186			
	0.586094 0.499531	/	1.000000			
h	0.975578 0.446594					
	0.534140 0.578020					

[a] See footnote (a) of Table 3
[b] $(20s13p)/[6s4p]$ was used for sp set
[c] $(20s13p)/[7s5p]$ was used for sp set

Table 6. The carbon atom ($E_{HF} = -37.688618$, $E_{corr} = -0.096629$)[a]

$+1d$[b]	$E_{corr} = -0.087057$		Percentage = 99.37%			
d	1.251463 0.337794					
	0.357205 0.773652					
$+2d1f$[b]	$E_{corr} = -0.093391$		Percentage = 99.76%			
d	3.014849 0.882064	/	0.285460			
	0.111984 0.935464	/	1.000000			
f	1.246825 0.439043					
	0.439685 0.686339					
$+3d2f1g$[b]	$E_{corr} = -0.095281$		Percentage = 99.89%			
d	5.794566 1.552194	/	0.618883	/	0.229676	
	0.066992 0.965356	/	1.000000	/	1.000000	
f	2.289495 1.074764	/	0.440597			
	0.162251 0.875347	/	1.000000			
g	1.339682 0.542915					
	0.498201 0.624605					
$+4d3f2g1h$[c]	$E_{corr} = -0.096185$		Percentage = 99.96%			
d	8.450287 2.202997	/	1.082378	/	0.515098 / 0.192955	
	0.069723 0.964774	/	1.000000	/	1.000000 / 1.000000	
f	1.892268	/	0.856724	/	0.352019	
	1.000000	/	1.000000	/	1.000000	
g	1.807632 0.946164	/	0.587089			
	0.500516 0.567212	/	1.000000			
h	1.537728 0.671233					
	0.499136 0.623768					

[a] See footnote (a) of Table 3
[b] $(20s13p)/[6s4p]$ was used for sp set
[c] $(20s13p)/[7s5p]$ was used for sp set

Table 7. The nitrogen atom ($E_{HF} = -54.400932$, $E_{corr} = -0.124004$)[a]

+1d[b] $E_{corr} = -0.105670$ Percentage = 99.17%

d	1.873384	0.493923
	0.353306	0.780050

+2d1f[b] $E_{corr} = -0.117997$ Percentage = 99.63%

d	4.586224	1.318772	/	0.421384
	0.118046	0.932695	/	1.000000
f	1.826455	0.622164		
	0.423955	0.706425		

+3d2f1g[b] $E_{corr} = -0.121539$ Percentage = 99.86%

d	8.048268	2.210969	/	0.870141	/	0.320020
	0.076810	0.959062	/	1.000000	/	1.000000
f	3.532326	1.531539	/	0.613041		
	0.158808	0.884846	/	1.000000		
g	1.942672	0.764057				
	0.477604	0.650608				

+4d3f2g1h[c] $E_{corr} = -0.123189$ Percentage = 99.94%

d	12.088422	3.215173	/	1.525997	/	0.729862	/	0.271863
	0.073610	0.961999	/	1.000000	/	1.000000	/	1.000000
f	5.191153	2.466317	/	1.182158	/	0.481013		
	0.084526	0.936039	/	1.000000	/	1.000000		
g	2.760197	1.432185	/	0.806356				
	0.425240	0.641359	/	1.000000				
h	2.210624	0.936235						
	0.482581	0.646798						

[a] See footnote (a) of Table 3
[b] (20s13p)/[6s4p] was used for sp set
[c] (20s13p)/[7s5p] was used for sp set

Table 8. The oxygen atom ($E_{HF} = -74.809395$, $E_{corr} = -0.185084$)[a]

+1d[b] $E_{corr} = -0.146469$ Percentage = 99.23%

d	2.615639	0.688518
	0.352039	0.781251

+2d1f[b] $E_{corr} = -0.171310$ Percentage = 99.58%

d	5.960330	1.764853	/	0.575660
	0.136289	0.919489	/	1.000000
f	2.414337	0.767660		
	0.424090	0.719405		

+3d2f1g[b] $E_{corr} = -0.179327$ Percentage = 99.82%

d	10.520368	2.971473	/	1.168394	/	0.426819
	0.083227	0.954324	/	1.000000	/	1.000000
f	4.891229	1.968653	/	0.747644		
	0.169480	0.883439	/	1.000000		
g	2.637797	0.972119				
	0.454800,	0.685744				

+4d3f2g1h[c] $E_{corr} = -0.183120$ Percentage = 99.93%

d	15.182044	4.171315	/	1.904788	/	0.912091	/	0.338252
	0.072133	0.961675	/	1.000000	/	1.000000	/	1.000000
f	7.718223	3.211763	/	1.478848	/	0.561169		
	0.098809	0.932253	/	1.000000	/	1.000000		
g	4.220059	2.079712	/	0.996373				
	0.309449	0.755373	/	1.000000				
h	2.949239	1.186975						
	0.466751	0.673858						

[a] See footnote (a) of Table 3
[b] (20s13p)/[6s4p] was used for sp set
[c] (20s13p)/[7s5p] was used for sp set

diatomics than the correlation consistent basis sets. This is true even for the HF energies. The differences between the two sets range between 0.010–0.014 hartrees and 0.002–0.003 hartrees for the 1d and 2d1f sets, respectively. The differences are slightly smaller in the molecular calculations than in the atomic calculations. In the case of the 1d set, the difference is 0.014 hartrees for the O atom, while it is 0.011 hartrees for the O_2 molecule, though the latter value includes the HF energy difference of 0.001 hartrees.

5 Summary

We determined [1p], [2p1d], [3p2d1f], and [4p3d2f1g] polarization sets for atoms He and Be, and [1d], [2d1f],

Table 9. The fluorine atom ($E_{HF} = -99.409344$, $E_{corr} = -0.244220$)[a]

$+1d$[b]	$E_{corr} = -0.186554$		Percentage = 99.24%		
d	3.495868 0.916030				
	0.349637 0.783737				
$+2d1f$[b]	$E_{corr} = -0.221956$		Percentage = 99.54%		
d	7.720164 2.308899	/	0.761876		
	0.148083 0.911198	/	1.000000		
f	3.150592 1.012297				
	0.425350 0.716358				
$+3d2f1g$[b]	$E_{corr} = -0.235109$		Percentage = 99.79%		
d	13.636461 3.910328	/	1.532431	/	0.556215
	0.087443 0.951233	/	1.000000	/	1.000000
f	6.267400 2.530864	/	0.997118		
	0.193041 0.865524	/	1.000000		
g	3.461730 1.242578				
	0.446017 0.699219				
$+4d3f2g1h$[c]	$E_{corr} = -0.241067$		Percentage = 99.92%		
d	19.751865 5.532033	/	2.508845 / 1.204119	/	0.442379
	0.073567 0.960189	/	1.000000 / 1.000000	/	1.000000
f	10.170172 4.189015	/	1.927177	/	0.723788
	0.108852 0.925688	/	1.000000	/	1.000000
g	5.851136 2.772200	/	1.258196		
	0.272221 0.793164	/	1.000000		
h	3.834909 1.510312				
	0.461949 0.683470				

[a] See footnote (a) of Table 3
[b] (20s13p)/[6s4p] was used for sp set
[c] (20s13p)/[7s5p] was used for sp set

Table 10. The neon atom ($E_{HF} = -128.547091$, $E_{corr} = -0.303429$)[a]

$+1d$[b]	$E_{corr} = -0.228162$		Percentage = 99.25%		
d	4.526627 1.177552				
	0.346926 0.786823				
$+2d1f$[b]	$E_{corr} = -0.271986$		Percentage = 99.53%		
d	9.724095 2.916678	/	0.969955		
	0.158554 0.904113	/	1.000000		
f	3.989071 1.343514				
	0.426979 0.705989				
$+3d2f1g$[b]	$E_{corr} = -0.290717$		Percentage = 99.76%		
d	17.075302 4.953333	/	1.932877	/	0.697703
	0.091931 0.948064	/	1.000000	/	1.000000
f	7.473217 3.051412	/	1.344705		
	0.240922 0.827311	/	1.000000		
g	4.391807 1.550355				
	0.441450 0.706784				
$+4d3f2g1h$[c]	$E_{corr} = -0.299013$		Percentage = 99.91%		
d	25.112499 7.106532	/	3.204619 / 1.539881	/	0.560171
	0.075053 0.958966	/	1.000000 / 1.000000	/	1.000000
f	12.917233 5.350112	/	2.465264 / 0.932040		
	0.114496 0.921287	/	1.000000 / 1.000000	/	
g	7.672740 3.534996	/	1.557886		
	0.254384 0.811918	/	1.000000		
h	4.834251 1.877080				
	0.460039 0.688631				

[a] See footnote (a) of Table 3
[b] (20s13p)/[6s4p] was used for sp set
[c] (20s13p)/[7s5p] was used for sp set

[3d2f1g], and [4d3f2g1h] polarization sets for atoms B through Ne. Both contraction coefficients and orbital exponents of the polarization cGTFs were optimized to minimize the error of contraction by fitting our cGTFs to accurate atomic natural orbitals, which have been generated by atomic CI calculations. Several test calculations were carried out on the oxygen atom and the present sets were shown to be superior to Dunning's correlation consistent sets at any size of the polarization set. Despite their smallness, the present sets reproduce more than 99% of the correlation energies predicted by the accurate atomic natural orbitals.

To check the appropriateness of the present polarization sets in molecular calculations, SDCI calculations were carried out on four diatomic molecules, O_2, CO, N_2, and BF, using the [1d] and [2d1f] sets. For all the diatomics examined, the present sets give correlation energies better than the correlation consistent basis sets.

Table 11. Comparison of the HF and SDCI energies with the present polarization sets and the correlation consistent sets of Dunning for diatomic molecules

Polarization set	E_{HF}		E_{CI}	
	Present	Dunning	Present	Dunning
The O$_2$ molecule ($r_e = 2.2824$ bohrs)				
+1d	−149.651273	−149.650045	−150.039327	−150.028501
+2d1f	−149.658346	−149.657986	−150.100118	−150.097314
The CO molecule ($r_e = 2.1327$ bohrs)				
+1d	−112.777541	−112.772913	−113.080008	−113.069722
+2d1f	−112.784139	−112.783355	−113.125562	−113.123657
The N$_2$ molecule ($r_e = 2.0698$ bohrs)				
+1d	−108.980603	−108.976090	−109.294183	−109.284438
+2d1f	−108.987082	−108.986323	−109.339210	−109.337440
The BF molecule ($r_e = 2.3856$ bohrs)				
+1d	−124.154936	−124.148677	−124.434717	−124.420718
+2d1f	−124.161024	−124.160260	−124.482129	−124.479832

The differences between the two sets range from 0.010 to 0.014 hartrees for the 1d set and from 0.002 to 0.003 hartrees for the 2d1f set.

References

1. Dunning TH Jr, Hay PJ (1977) In: Schaefer HF III (ed) Modern theoretical chemistry, vol 2, chap 1. Plenum, New York
2. Löwdin P-O, Shull H (1956) J Chem Phys 101:1730
3. Löwdin P-O (1955) Phys Rev 97:1474; Löwdin P-O (1959) Adv Chem Phys 2:207
4. Almlöf J, Taylor PR (1987) J Chem Phys 86:4070; Almlöf J, Helgaker T, Taylor PR (1988) J Chem Phys 92:3029
5. Dunning TH Jr (1989) J Chem Phys 90:1007
6. Pettersson GM, Siegbahn PEM (1985) J Chem Phys 83:3538
7. Powell MJD (1964) Comput J 7:155
8. Sasaki F (1974) Int J Quantum Chem 6:61; Sasaki F, Sekiya M, Noro T, Ohtuki K, Osanai Y (1990) In: Clementi E (ed) Modern techniques in computational chemistry MOTECC90, ESCOM, Leiden
9. Lengsfield BH III (1980) J Chem Phys 73:382; Lengsfield BH III, Liu B (1981) J Chem Phys 74:478; Liu B, Yoshimine M (1981) J Chem Phys 74:612
10. Huzinaga S, Miguel B (1990) Chem Phys Lett 175:289
11. Tatewaki H, Koga T (1996) J Chem Phys 104:8493