

Contracted polarization functions for B to Ar

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Abstract. Using optimal exponents for B through Ne given by Dunning and those for Al through Ar by Woon and Dunning, *d*-type contracted polarization functions ($2d/1d$), ($3d/1d$), and ($3d/2d$) are generated from natural orbitals of atomic single and double excitation configuration interaction (SDCI) calculations, where the numbers before and after the slash are those of the primitive and contracted Gaussian type functions. The resulting contracted functions are tested on N₂ and P₂ molecules by self-consistent field and SDCI calculations, which clarify characteristics of the present polarization functions.

Key words: Contracted *d*-type polarization functions – Atomic natural orbitals – First and second row atoms

1 Introduction

Many ab initio calculations are now performed by self-consistent field (SCF) and post-SCF methods. The quality of the investigations depends on the basis set employed. Basis sets are available [1–16] for all purposes except for polarization functions. Almloef and Taylor [2, 3] introduced polarization functions based on the atomic natural orbital (ANO), and Dunning [4] and Woon and Dunning [7] obtained correlation consistent (cc) polarization functions by minimizing the atomic single and double excitation configuration interaction (SDCI) energy. Polarization functions are required, first, to describe the molecular polarizations, and second to describe molecular extra correlations properly [17]. By using a large number of polarization functions, both claims are almost automatically satisfied. However, increasing the number of polarization functions used increases the difficulty of the calculations for two reasons. First, the angular momentum of the polarization functions is higher than that of the valence orbitals

for the typical elements, causing a large increase in the molecular integrals needed. Second, increasing the number of polarization functions brings an increase of the excited configurational space in the electron correlation treatment. We can lessen this second difficulty by reducing the number of polarization functions without sacrificing accuracy. Using the multi-configuration (MC) SCF method [18] of Sekiya [19], we have given the contracted polarization functions [17], revealing that a singly contracted polarization function gives much better SCF spectroscopic constants than the single primitive *d*-type polarization function. The same was true for the CI results.

The MCSCF method used in the previous work [17] has the limitation that only two electron excitation configurations from the main configuration are allowed; inclusion of a spin polarized excitation such as $ms \rightarrow nd$ is forbidden since, configurationally, this is a one electron excitation. In this work we examine the contracted polarization functions for B to Ne and Al to Ar generated from natural orbitals (NOs) of all single and double excitation CI from the main configuration of ($2s^m 2p^n$) and ($3s^m 3p^n$).

2 Polarization functions from B to Ne and Na to Ar

In previous work [17], we employed the MCSCF procedure to work out the contraction coefficients. In the present work we have performed the SDCI calculation including $s \rightarrow d$ transitions. NO iterations are performed until the optimal total energy results. More precisely, for B, C, Al and Si the NO iterations were found to be effective and were performed until n -th and $n+1$ -th iterations give the total energy difference of 10^{-7} a.u. For other atoms, NO iterations only lead to higher total energies. The contracted coefficients for the polarization functions are those of minimum energy. As in the previous work [17], we have employed one, two, and three primitive *d*-type Gaussian type polarization functions as given by Dunning [4] and by Woon and Dunning [7]. The *sp* sets are cc-pVTZ ($10s5p/4s3p$) for B to Ne⁴ and cc-pVTZ ($15s9p/5s4p$) for Al to Ar [7], where the numbers before and after the

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slash are those of the primitive and contracted Gaussian type functions (CGTFs) respectively. The polarization functions prepared are $(2d/1d)$, $(3d/1d)$, and $(3d/2d)$. The SDCI total energies for N 4S are presented in Table 1 and are compared with our own previous results [17] and those of Noro, Sekiya, and Koga (NSK) [20], who recently proposed contracted polarization functions. NSK have performed large SDCI calculations using a large GTF set of $(20s13p13d13f13g13h)$, and have obtained accurate NOs. The accurate NOs, for example the first and second d -type NOs, are expanded in two small CGTF sets which respectively consist of small primitive GTFs such as two and one primitive d -type ones [20]. Total SD energies calculated with these polarization functions are also given in Table 1.

Any singly contracted polarization function ($nd/1d$) gives remarkably lower total energies than a single primitive d -type GTF of $(1d/1d)$. In contraction schemes, the present method gives the best energy, as is expected. The difference in the total energy between the present $(3d/2d)$ and NSK's result is only 0.00025 a.u., suggesting that NSK's expansions are almost perfect. The exponent parameters [4, 7] and contracted coefficients are listed in

Table 2 and corresponding total energies are summarized in Table 3. The total energy difference between $(3d/1d)$ and $(2d/2d)$ and that between $(3d/2d)$ and $(3d/3d)$ is small.

Table 1. $(4s3p(n/m)d)$ SDCI total energies^a for N 4S (in a.u.)

$(1d/1d)$	-54.494568
$(2d/1d)$ -HHT ^b	-54.500692
$(2d/1d)$ -NSK ^c	-54.500719
$(2d/1d)$	-54.500877
$(3d/1d)$ -HHT ^b	-54.501306
$(3d/1d)$	-54.501458
$(2d/2d)$	-54.504011
$(3d/2d)$ -NSK ^c	-54.504575
$(3d/2d)$ -HHT ^b	-54.504798
$(3d/2d)$	-54.504825
$(3d/3d)$	-54.505444

^aThe total energy given by the SDCI calculations with cc-pVTZ $(10s5p/4s3p)$ plus m ($m = 3, 2,$ and 1) contracted or uncontracted d -type polarization functions generated from n primitive GTFs

^bContracted $3d$ polarization function(s) given by Hashimoto, Hirao, and Tatewaki (HHT)[17]

^cContracted $3d$ polarization function(s) given by Noro, Sekiya, and Koga (NSK)[20]

Table 2. Contracted $3d$ polarization functions from B to Ar

Atom		Coefficients			Atom		Coefficients		
		Exp.	$1d_{NO}$	$2d_{NO}$			Exp.	$1d_{NO}$	$2d_{NO}$
B	$1d$	0.343	1.000000		Al	$1d$	0.189		
	$2d$	0.661	-0.413742			$2d$	0.333	0.465395	
	$3d$	0.199	-0.710510			0.109	0.650550		
		1.110	0.135302	0.444769		0.494	0.187008	-0.559728	
		0.402	0.547802	0.655457		0.199	0.574395	-0.504675	
		0.145	0.473045	-1.027748		0.0804	0.374845	1.056540	
C	$1d$	0.550	1.000000		Si	$1d$	0.275		
	$2d$	1.097	-0.399353			$2d$	0.481	0.466550	
	$3d$	0.318	-0.728767			0.159	0.647795		
		1.848	-0.132298	-0.493651		0.760	0.169820	-0.446063	
		0.649	-0.541026	-0.594345		0.302	0.567587	-0.664029	
		0.228	-0.489346	0.975480		0.120	0.400825	1.117825	
N	$1d$	0.817	1.000000		P	$1d$	0.373		
	$2d$	1.654	-0.393295			$2d$	0.652	0.471817	
	$3d$	0.469	-0.737272			0.216	0.642548		
		2.837	-0.128936	-0.479847		1.036	-0.173461	-0.440226	
		0.968	-0.536910	-0.613957		0.413	-0.560284	-0.676908	
		0.335	-0.500594	0.971593		0.165	-0.405068	1.125607	
O	$1d$	1.185	1.000000		S	$1d$	0.479		
	$2d$	2.314	-0.400807			$2d$	0.819	0.483846	
	$3d$	0.645	-0.733765			0.269	0.632853		
		3.775	-0.141561	-0.487590		1.250	-0.197656	0.490952	
		1.300	-0.551222	-0.578560		0.504	-0.557402	0.596622	
		0.444	-0.478466	0.970044		0.203	-0.386142	-1.104252	
F	$1d$	1.640	1.000000		Cl	$1d$	0.600		
	$2d$	3.107	0.403873			$2d$	1.0460	-0.471879	
	$3d$	0.855	0.733264			0.344	-0.643758		
		5.014	0.143812	0.490932		1.551	0.204294	0.497209	
		1.725	0.553236	0.569243		0.628	0.551321	0.588999	
		0.586	0.475771	-0.966615		0.254	0.386503	-1.103967	
Ne	$1d$	2.202	1.000000		Ar	$1d$	0.738		
	$2d$	4.014	0.409078			$2d$	1.254	-0.490502	
	$3d$	1.096	0.730202			0.410	-0.627418		
		6.471	0.145904	0.490154		1.873	-0.213788	-0.507953	
		2.213	0.556655	0.564647		0.763	-0.544766	-0.575493	
		0.747	0.472147	-0.965467		0.311	-0.384137	1.104013	

Table 3. SDCI total energies^{a,b} given by respective polarization functions (in a.u.)

	Boron	Carbon	Nitrogen	Oxygen	Fluorine	Neon
(1d/1d)	-24.593786	-37.769441	-54.494568	-74.938161	-99.571106	-128.742205
(2d/1d)	-24.595894	-37.773753	-54.500877	-74.946103	-99.580683	-128.753314
(3d/1d)	-24.596067	-37.774135	-54.501458	-74.946826	-99.581558	-128.754301
(2d/2d)	-24.596474	-37.775404	-54.504011	-74.952735	-99.591058	-128.767623
(3d/2d)	-24.596644	-37.775874	-54.504825	-74.954000	-99.592837	-128.769960
(3d/3d)	-24.596817	-37.776241	-54.505444	-74.955339	-99.594893	-128.772777
	Aluminum	Silicon	Phosphorus ^c	Sulfur	Chlorine	Argon
(1d/1d)	-241.927090	-288.921738	-340.799237	-397.611082	-459.612007	-526.969778
(2d/1d)	-241.928762	-288.925283	-340.804634	-397.618842	-459.622402	-526.982824
(3d/1d)	-241.928893	-288.925588	-340.805107	-397.619580	-459.623377	-526.984152
(2d/2d)	-241.929473	-288.926661	-340.806912	-397.623794	-459.629815	-526.992892
(3d/2d)	-241.929606	-288.926974	-340.807378	-397.624539	-459.630846	-526.994196
(3d/3d)	-241.929691	-288.927122	-340.807625	-397.625057	-459.631625	-526.995250

3 Test calculations for N₂ and P₂

Spectroscopic constants for N₂ and P₂ by the SCF and valence SDCI calculations are given in Table 4. We first discuss the N₂ molecule. In SCF, the contracted polarization functions always show great improvement in the resulting constants over those given by the corresponding primitive GTFs. This suggests that the behavior of the tails of the polarization functions is important in describing molecular polarization. However, when a single polarization function is used in CI, only (nd/1d) given by us in [17] is superior to (1d/1d) in calculating D_e. The use of an accurate atomic correlating orbital harms the balance of atomic and molecular correlations. For example at R = 2.00 a.u., which is near to the equilibrium nuclear distance of N₂, molecular CI total energies for (2d/1d), (3d/1d), (2d/1d) [17], and (3d/1d) [17] are -109.2833, -109.2853, -109.2863, and -108.2886 a.u., although the atomic total energies are of the order of (2d/1d) [17], (2d/1d), (3d/1d) [17], and

(3d/1d) (see Table 1). Therefore, if accurate NOs are used, at least several NOs are necessary for CI calculations to generate adequate results. This is confirmed by the spectroscopic constants of (3d/2d) in Table 4.

The respective NSK polarization functions always give results close to the present ones, indicating that the NSK polarization functions are related to ours. Let us discuss this in more detail. The CI total energies for (3d/2d) and (3d/2d)-NSK at R = 2.0 a.u. are -109.3007 and -109.3006 a.u. respectively, while they are -109.2902 and -109.2900 a.u., at a larger distance of R = 2.2 a.u., showing a small increase in the difference of the two total energies. At infinite R, they are -109.0096 and -109.0092 a.u. A little crudeness of NSK in the atomic CI calculation brings a little larger D_e and ω_e than the present (3d/2d). We may, therefore, leave out the optimization procedure for the exponent parameters if we are not seeking a high degree of accuracy.

Results for P₂ are parallel to those for N₂, showing the adequacy of singly contracted polarization functions,

Table 4. Spectroscopic constants for N₂ and P₂

^a For N₂, Results are arranged according to the SCF and CI total energy at R = 2.0 a.u.
^b In CI for P₂, we used (15s9p/6s4p) instead of cc-pVTZ (15s9p/5s4p), because the molecular SCF program used cannot handle the contracted GTFs (CGTFs) with primitive GTFs > 12 and cc-pVTZ (15s9p/5s4p) requires CGTFs with 13 primitives. Instead of the atomic energies given by (15s9p/5s4pnd) in Table 3, we used the SDCI energies given by (15s9p/6s4pnd) for calculating D_es of (1d/1d), (2d/1d), (3d/1d), (2d/2d), (3d/2d). These are -340.799393, -340.804789, -340.805260, -340.807067, -340.807532, and -340.807777 a.u. These energies and corresponding energies in Table 3 differ by about 0.0002 a.u.

Basis	SCF for N ₂			CI for N ₂		
	D _e (eV)	R _e (a.u.)	ω _e (cm ⁻¹)	D _e (eV)	R _e (a.u.)	ω _e (cm ⁻¹)
(1d/1d)	4.883	2.028	2740	7.824	2.077	2488
(2d/1d)-NSK	5.025	2.022	2741	7.775	2.070	2488
(2d/1d)	5.037	2.022	2743	7.783	2.071	2491
(3d/1d)	5.071	2.022	2746	7.804	2.070	2495
(2d/1d)-HHT	5.068	2.018	2752	7.859	2.065	2508
(3d/1d)-HHT	5.096	2.019	2755	7.889	2.065	2512
(2d/2d)	5.109	2.017	2740	7.995	2.059	2513
(3d/2d)-HHT	5.131	2.017	2738	7.995	2.059	2507
(3d/2d)-NSK	5.137	2.017	2744	8.015	2.059	2517
(3d/2d)	5.137	2.017	2740	8.005	2.059	2511
(3d/3d)	5.145	2.017	2741	8.054	2.059	2510
Basis	SCF for P ₂			CI for P ₂		
	D _e (eV)	R _e (a.u.)	ω _e (cm ⁻¹)	D _e (eV)	R _e (a.u.)	ω _e (cm ⁻¹)
(1d/1d)	1.295	3.553	899	2.955	3.621	841
(2d/1d)	1.453	3.539	895	2.912	3.611	835
(3d/1d)	1.495	3.536	896	2.935	3.608	836
(2d/2d)	1.491	3.532	890	3.031	3.594	831
(3d/2d)	1.532	3.529	891	3.054	3.592	834
(3d/3d)	1.538	3.527	888	3.101	3.589	833

($nd/1d$), for the SCF calculations and their inadequacy for the CI calculations of D_{es} . The use of ($3d/2d$)s gives results close to ($3d/3d$) for SCF as well as CI as in the N_2 molecule.

4 Concluding remarks

We have proposed d -type contracted polarization functions of ($2d/1d$), ($3d/1d$), and ($3d/2d$) for Br to Ne and Al to Ar generated from atomic SDCI calculations. These polarization functions have been tested using the SCF and valence SDCI calculations on N_2 and P_2 . When the same numbers of polarization functions are used to ensure a fair comparison, the contracted polarization functions greatly improve the SCF spectroscopic constants given by the primitive polarization functions. However, this is not true for the CI calculations when one polarization function is employed. The first $3d$ NO obtained by CI calculations is too accurate in describing atomic correlations to describe the molecular and atomic correlations properly. The ($3d/2d$) gives spectroscopic constants close to ($3d/3d$). The CI dimension for ($3d/2d$) is 3026, and is 4570 for ($3d/3d$) in P_2 . Reduction of the calculation time in ($3d/2d$) is greater for more complicated systems, and we therefore recommend using ($3d/2d$) instead of ($3d/3d$), when accurate calculations of the electronic structure are required. We also recommend using the contraction of Hashimoto and co-workers [17], ($2d/1d$), when the number of polarization functions available is limited.

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