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Valence *p* functions for alkali and alkaline-earth atoms

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Abstract Contracted Gaussian-type function (CGTF) basis sets are reported for valence *p* orbitals of the six alkali and alkaline-earth atoms Li, Be, Na, Mg, K, and Ca for molecular applications. These sets are constructed by Roothaan–Hartree–Fock calculations for the $ns \rightarrow np$ excited states of atoms, in which both linear and nonlinear parameters of CGTFs are variationally optimized. The present CGTF sets reproduce well the numerical Hartree–Fock $ns \rightarrow np$ excitation energies: the largest error is 0.0009 hartrees for Li. New CGTFs are tested with diatomic Li_2, Na_2, K_2, and MH molecules, where M = Li, Be, Na, Mg, K, and Ca, by self-consistent-field (SCF) and multiconfiguration SCF calculations. The resultant spectroscopic constants compare well with those of more elaborate calculations and are sufficiently close to experimental values, supporting the efficiency of the present set for the valence *p* orbitals.

Key words: Valence *p* orbitals – Contracted Gaussian-type functions – Alkali atoms – Alkaline-earth atoms

1 Introduction

Many Gaussian-type function (GTF) basis sets have been developed for molecular calculations, in either uncontracted [1–14], contracted [15–22], or intermediate form [23, 24], where the last applies contracted functions to inner shells and uncontracted ones to outer shells. For the alkali and alkaline-earth atoms, however, basis sets for valence *p* orbitals are very rare. For this reason, studies [25–37] on molecules containing alkali and alkaline-earth atoms usually take the *sp* sets from the literature [1–24], and add the valence *p* sets, whose sizes are often very large in order to avoid inaccuracies, in an ad hoc manner. To our knowledge, however, there are four exceptions. McLean and Chandler [38] reported contractions of Huzinagas 12*s*8*p* and 12*s*9*p* GTF sets for the Na ^{2}P and Mg ^{3}P atoms. Sadlej and Urban [25] constructed so-called polarized basis sets. Sadlej-Urban sets gave excellent polarizabilities and electronic moments, but they used relatively many *p*- and *d*-type primitive GTFs (pGTFs); the Li and Be atoms, for example, have six 2*p* and four 3*d* pGTFs. Based on Roothaan–Hartree–Fock (RHF) calculations [39] of the first excited state, Koga and coworkers [40–42] constructed valence *p* basis functions with five and seven pGTFs for Li and Be and with eight and nine pGTFs for Na and Mg with and without contractions. Noro et al. [43] developed contracted polarization functions for the atoms He and Be-Ne, where the contracted functions were generated by fitting them to accurate correlating orbitals obtained by large atomic configuration interaction (CI) calculations.

Recently, we developed minimal-type contracted GTF (CGTF) sets with high accuracy for the atoms Li to Ne [20], Na to Ar [21], and K to Kr [22], using the RHF method. Since the valence *p* function sets in the literature [25, 38, 40–44] are relatively large for practical molecular applications, we report in the present study alternative compact yet reliable CGTF sets for the valence *p* orbitals of six alkali and alkaline-earth atoms Li, Be, Na, Mg, K, and Ca, as a natural extension of the minimal-type CGTF sets [20–22] constructed by us. In order to obtain polarization functions, we apply the atomic RHF method to the excited *np* ^{2}P state, instead of the ground *ns* ^{2}S state, for the alkali atoms and the excited *nsnp* ^{3}P state, instead of the ground ns^2 ^{1}S state, for the alkaline-earth atom as done in Refs. [38, 40–42]. These states are the lowest excited states for the respective atoms, and the *np* orbital has a radial size not very different from the *ns* orbital in the ground state; in the Ca atom, for example, the ground state $\langle r \rangle_{4s}$ is 4.22 bohrs while the ^{3}P state $\langle r \rangle_{4p}$ is 5.10 bohrs [45]. We therefore expect that valence basis sets for these *np* ^{2}P or *nsnp* ^{3}P states give a good description for valence and correlating orbitals simultaneously. Our computational details on valence *p* basis sets are summarized in the next section. The atomic results are discussed in Sect. 3. Molecular tests are presented in Section 4 to demon-

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strate the usefulness of the present sets, and the present valence $2p$ sets are compared with those of Sadlej and Urban [25], Thakkar et al. [41], and Noro et al. [43] in Sect. 5.

2 Method of calculation

In our previous work on the construction of CGTF sets [20–22], the nonlinear optimization in a coupled manner was found to be important for contraction coefficients and exponents. The conjugate directions algorithm [46] was sufficiently efficient to determine their optimum values with respect to the total energy. The method is again used in this work. We use three pGTFs for the valence p CGTFs. Thus the sizes of our CGTF sets are (7/3) for Li ^{2}P, (74/3) for Be ^{3}P, (74/73) for Na ^{2}P, (743/73) for Mg ^{3}P, (743/743) for K ^{2}P, and (7433/743) for Ca ^{3}P, respectively, where the slash separates the s and p symmetries and the single digit figures give the numbers of the pGTFs of the respective symmetries. Additionally, CGTF sets with four p-type pGTFs are also developed for the Li and Be atoms as will be described later.

3 Atomic results

Calculated total energies, $ns \rightarrow np$ excitation energies, and orbital energies of the highest occupied orbitals of each symmetry are given in Table 1 together with the corresponding numerical HF (NHF) values [45, 47]. We see that for third- and fourth-period atoms the error of the np orbital energies relative to those of the NHF is quite small (<0.0002 hartrees) and the error of the excitation energies (<0.0003 hartrees) is as small as that of the orbital energies. For the second-period atoms, the situation is slightly different. The errors in the $2p$ orbital energy for Li ^{2}P and Be ^{3}P is about 10 times larger than those of the third- and forth-period atoms. The error in the calculated excitation energy for Li ^{2}P and Be ^{3}P is again 10 times larger. We therefore recalculated these two atoms with four pGTFs for the valence p set. The results compared in Table 1 show that the errors for the $2p$ orbitals are much reduced and are now similar to those of the $3p$ and $4p$ orbitals. The valence $3p$ and $4p$ orbitals can penetrate into the core region with the help of CGTFs which describe the inner p orbitals, but for the $2p$ orbitals there is no such p core and a pGTF with a larger exponent is necessary to obtain preferable behavior in this region. The exponents and contraction coefficients for the three- and four-term expansions for the valence p CGTF sets are given in Tables 2 and 3, respectively. We found that the largest p exponent of the $3p$ orbitals for Na and Mg lies outside the p exponents of the ion core, while the largest p exponent of the $4p$ orbitals for K and Ca lies within those of the ion core. We symbolically write the distribution of the exponents for Na and Mg as (out, out, out) and that for K and Ca as (in, out, out). For Na and Mg atoms, a set with (in, out, out) distribution gives a total energy slightly higher (0.0002 hartrees for Na and 0.0003 hartrees for Mg) than the optimum sets with (out, out, out) distribution. For K and Ca, we also found that CGTF sets with (out, out, out) exponents give total energies higher (0.0005 hartrees for K and 0.0001 hartrees for Ca) than the optimum sets. It will be shown in the next section that for the MgH molecule, the dissociation energies calculated with the (in, out, out) set are smaller than those with the (out, out, out) set both in uncorrelated and correlated methods. We therefore list only the optimum sets in Table 2.

4 Molecular applications

For all the diatomic molecules examined, we performed self-consistent-field (SCF) calculations and complete-active-space multiconfiguration SCF (MCSCF) calculations where only the valence electrons were taken into account. In MCSCF calculations, all the molecular orbitals (MOs) except for the core MOs are treated as valence orbitals. The dissociation energy was obtained by subtracting the sum of the atomic total energies from the molecular total energy.

4.1 Diatomic molecules with alkali atoms

We first examined three homonuclear alkali diatomics Li_2, Na_2, and K_2. The SCF configurations for these

Table 1. Total energy, excitation energy, and highest occupied orbital energies obtained by numerical Hartree–Fock (*NHF*) and contracted Gaussian-type function (*CGTF*)-Roothaan–Hartree–Fock (*RHF*) calculations. [a] All values in hartrees

Atom	Electronic configuration (state)	Method	Total energy	Excitation energy	Highest orbital energy	
					s	p
3 Li	[He]$2p^1$	NHF	−7.3650697	0.067657	−2.530726	−0.128673
	(^{2}P)	CGTF	−7.3639051	0.068400	−2.532000	−0.127847
		CGTF (4)	−7.3645237	0.067781	−2.530832	−0.128467
4 Be	[He]$2s^1 2p^1$	NHF	−14.511502	0.061521	−0.394376	−0.241500
	(^{3}P)	CGTF	−14.508188	0.063924	−0.394187	−0.238935
		CGTF (4)	−14.510165	0.061945	−0.394106	−0.240955
11 Na	[Ne]$3p^1$	NHF	−161.786408	0.072504	−2.874286	−0.109454
	(^{2}P)	CGTF	−161.779285	0.072679	−2.872697	−0.109395
12 Mg	[Ne]$3s^1 3p^1$	NHF	−199.546712	0.067924	−0.339594	−0.179645
	(^{3}P)	CGTF	−199.539131	0.067707	−0.339407	−0.179478
19 K	[Ar]$4p^1$	NHF	−599.113145	0.051642	−1.800916	−0.095579
	(^{2}P)	CGTF	−599.096117	0.051481	−1.800087	−0.095522
20 Ca	[Ar]$4s^1 4p^1$	NHF	−676.718768	0.039418	−0.259628	−0.152584
	(^{3}P)	CGTF	−676.700328	0.039102	−0.259361	−0.152492

[a] CGTF means the use of three p-type primitive GTFs (pETFs) for all the valence p functions. For Li and Be atoms, CGTF (4) means the use of four p-type pETFs for the valence $2p$ function

Table 2. Valence *p* CGTF sets with three pGTFs

Li	Be	Na	Mg	K	Ca
Exponents					
0.5637243	1.4803675	0.0878596	0.1841341	0.3248641	0.5436812
0.1046111	0.2884656	0.0338632	0.0713423	0.0390478	0.0753727
0.0289100	0.0753751	0.0140172	0.0281681	0.0143781	0.0274271
Contraction coefficients					
0.0732779	0.0890732	0.2244348	0.2613636	−0.0202812	−0.0249064
0.4261883	0.4494644	0.5645339	0.5577647	0.5041802	0.5417034
0.6551705	0.6338700	0.3163652	0.2945075	0.5716647	0.5380417

molecules are written as [core] $(ms\sigma_g)^2$, where $m = 2$, 3, and 4 for Li_2, Na_2, and K_2, respectively. The basis sets for Li are (7211/211), (7211/111), and (7211/21) generated by decontracting the outermost CGTFs of the (74/4) or the (74/3) set. The *s*-type CGTF sets were discussed in Ref. [20] and are given at http://202.35.198.41/~htatewak, and the valence *p* CGTF sets are given in Tables 2 and 3. The calculated spectroscopic constants are summarized in Table 4, where D_e, R_e, and ω_e denote the dissociation energy, equilibrium bond length, and vibrational constant, respectively. The SCF calculation with (7211/211) gives $D_e = 0.154$ eV and $R_e = 5.274$ bohrs, which are reasonably close to $D_e = 0.175$ eV and $R_e = 5.216$ bohrs obtained with a large set of Slater-type functions (STFs) including up to *g*-type functions [27]. We may say that the present set for the valence 2*p* orbital acts well as polarization functions. The valence 2*p* set spanned by three pGTFs simulates the results of (211) if it is used in a triple zeta (TZ) form (111), but gives somewhat inaccurate results if it is used in a double zeta (DZ) form (21). The results of MCSCF calculations, where all the MOs except for $1\sigma_g$ and $1\sigma_u$ were treated as valence orbitals, are also given in Table 4. Inclusion of the correlation effects improves D_e by 0.7 eV, R_e by 0.1 bohrs for all the basis sets examined. The results are close to the experimental values and also to reference MCSCF values ($D_e = 1.029$ eV, $R_e = 5.087$ bohrs) [27]. We thus see that the present valence 2*p* sets work well as correlating sets.

For the Na_2 molecule, the two basis sets (74111/7111) and (74111/721) were examined. The CGTFs other than the valence 3*p* are discussed in Ref. [21] and given at http://202.35.198.41/~htatewak. As summarized in Table 4, the SCF calculations give negative D_es and larger R_es compared with experiment. An MCSCF calculation with the (74111/7111) set, in which the electron occupations for Ne-like core MOs are frozen, gives a larger D_e and a shorter R_e than the SCF results, but an MCSCF with (74111/721) gives a little large R_e compared with the SCF R_e, although the calculated D_e is positive. These MCSCF results suggest that the valence 2*p* set should be used in a TZ form. Stevens et al. [28] performed MCSCF calculations of the Na_2 molecule with STFs including $d\pi$ functions. Using their total energies, we obtained $D_e = 0.73$ eV and $R_e = 5.95$ bohrs compared to $D_e = 0.62$ eV and $R_e = 6.02$ bohrs of the present work. These results again suggest that the valence 3*p* set can act as a good correlating set in its TZ form.

Table 3. Valence 2*p* CGTF set with four pGTFs for the Li and Be atoms

Li	Be
Exponents	
1.5337950	3.6308772
0.2748596	0.7126356
0.0735992	0.1952460
0.0240213	0.0602015
Contraction coefficients	
0.0227743	0.0289887
0.1391018	0.1691259
0.5004399	0.5135609
0.5084286	0.4795887

Table 4. Spectroscopic constants for Li_2, Na_2, and K_2 molecules

Method	Basis	D_e/eV	R_e/bohr	ω_e/cm^{-1}	*p*-GAOP
Li_2					
SCF	(7211/211)	0.154	5.274	337	0.085
	(7211/111)	0.152	5.291	339	0.083
	(7211/21)	0.145	5.299	338	0.079
MCSCF	(7211/211)	0.881	5.157	335	0.122
	(7211/111)	0.878	5.165	337	0.118
	(7211/21)	0.862	5.170	336	0.114
Exptl.		1.046	5.051	351	
Na_2					
SCF	(74111/7111)	−0.025	6.032	157	0.058
	(74111/721)	−0.032	6.045	156	0.056
MCSCF	(74111/7111)	0.619	6.018	147	0.078
	(74111/721)	0.578	6.107	142	0.073
Exptl.		0.720	5.818	159	
K_2					
SCF	(743111/74111)	−0.144	7.916	84	0.049
	(743111/7421)	−0.144	7.914	84	0.060
MCSCF	(743111/74111)	0.402	7.944	77	0.079
	(743111/7421)	0.401	7.946	77	0.089
Exptl.		0.514	7.380	92	

The basis sets tested for K_2 were (743111/74111) and (743111/7421). The CGTFs other than the valence 4*p* set were discussed in Ref. [22]. The results for K_2 are shown in the final part of Table 4. The MCSCF calculations with the valence 4*p* in DZ and TZ forms considerably increase D_e and the resultant D_es are much closer to experimental values than to SCF values. We, note, however, that the MCSCF R_e is larger than the SCF R_e and moves away from the experimental value. We could not find ab initio SCF and MCSCF calculations with sufficiently large basis sets for this molecule. The coupled

Table 5. Spectroscopic constants for LiH, NaH, and KH molecules[a]

Method	Basis for alkali atom	D_e/eV	R_e/bohr	ω_e/cm^{-1}	Charges at alkali atom	
					Total GAOP	p GAOP
LiH						
SCF	(7211/111)	1.449	3.061	1466	2.531	0.202
MCSCF	(7211/111)	2.376	3.057	1429	2.553	0.194
Exptl.		2.429	3.015	1406		
NaH						
SCF	(74111/7111)	0.886	3.629	1194	10.417	0.087
MCSCF	(74111/7111)	1.844	3.633	1154	10.480	0.084
Exptl.		1.88	3.567	1172		
KH						
SCF	(743111/74111)	0.671	4.470	972	18.310	0.067
MCSCF	(743111/74111)	1.617	4.468	945	18.382	0.072
Exptl.		1.86	4.238	984		

[a] The basis set for H is (511/111) in all calculations

cluster calculation for valence electrons with $16s14p4d$ pGTFs contracted to $9s9p4d$ gave $D_e = 0.526$ eV and $R_e = 7.842$ bohrs [29]. A large difference between calculations and experiment remains for R_e, indicating the necessity of the inclusion of core-valence correlations [29].

SCF and MCSCF calculations were performed for three diatomic hydrides LiH, NaH, and KH. The SCF configuration is [core] $(m\sigma)^2$, where $m = 2$, 4, and 6 for LiH, NaH, and KH, respectively. The basis sets for Li, Na, K, and H atoms are (7211/111), (74111/7111), (743111/74111), and (511/111), respectively, where the valence $2p$ function for H is taken from Ref. [48]. In MCSCF calculations, the number of electrons in the core MOs is fixed. We see that gross atomic orbital population (GAOP) for $2p$ is as large as 0.20 for LiH, which should be compared with 0.33 ($= 2.53 - 2.00 - 0.20$) GAOP for valence $2s$. We thus infer that this $2p$ acts not as a polarization function but as a real valence function. We also see from the SCF and MCSCF D_es that the valence ps in a TZ form also work as correlating functions. All the spectroscopic constants calculated by MCSCF are close to experimental values.

Some accurate calculations are available for the three diatomic hydrides. Using uncontracted $9s9p$ GTFs for both Li and H, Cardelino et al. [30] performed SCF calculations of LiH. They obtained $D_e = 1.469$ eV and $R_e = 3.034$ bohrs, which are close to the present SCF values. For NaH, Sachs et al. [31] performed valence MCSCF calculations with extensive STF functions, and reported that $D_e = 1.878$ eV and $R_e = 3.608$ bohrs, in good agreement with the present MCSCF results of $D_e = 1.844$ eV and $R_e = 3.633$ bohrs. For the KH molecule, we only found pseudopotential CI calculations with GTFs [32] and pseudopotential MCSCF calculations with STFs [33]. The STF MCSCF calculations include core polarization in its pseudopotential and the GTF CI calculations include relativistic effects. The present calculations include neither core-valence correlation effects nor relativistic effects, but the latter contribution is expected to be small for the K atom. We compare the present SCF ($D_e = 0.67$ eV, $R_e = 4.47$ bohrs) and MCSCF ($D_e = 1.62$ eV, $R_e = 4.47$ bohrs) results with the GTF SCF ($D_e = 0.68$ eV, $R_e = 4.47$ bohrs) and CI ($D_e = 1.64$ eV, $R_e = 4.46$ bohrs) results [32], where $8s6p2d$ pGTFs are contracted to $6s4p2d$. The agreement is almost perfect. We can again say from the results for hydrides that the p functions optimized for the atomic lowest excited states perform well as polarization functions and correlating functions.

4.2 Diatomic molecules with alkaline-earth atoms

Three diatomic hydrides BeH, MgH, and CaH were chosen for our test. The SCF configuration is [core] $[(m-1)\sigma]^2(m\sigma)^1$, where $m = 3$, 5, and 7 for BeH, MgH, and CaH, respectively. We examined three basis sets for Be, (7211/211), (7211/111), and (7211/21), two sets for Mg, (74111/7111) and (74111/721), and two sets for Ca. (743111/74111) and (743111/7421). When the valence p set is used in a TZ form, the basis set for H is (511/111), while when p is in a DZ form it is (511/21). The results are given in Table 6. These molecules have a charge polarization of M^+H^- as shown in the columns of charges at the alkaline-earth atom. Large GAOPs for nps suggest that these nps are not polarization functions but are real valence orbitals. For BeH, we observe that D_es calculated with SCF are larger than those of MCSCF. The D_e obtained with the present best SCF calculation is larger than the experimental value. (Note that the experimental D_e given in the table includes vibrational energies and when these are excluded it is 2.16 eV). One may doubt basis set superposition error (BSSE) [49–52], but the (74) set for Be has a total energy only 0.02 eV above the NHF value [20], showing there is no chance for BSSE to explain a large SCF D_e. We therefore performed GTF calculations with a HF quality set [6, 7] plus present valence $2p$ at the calculated R_e of 2.538 bohrs: the basis sets for the molecular calculation were (16,1111/211) for Be and (511/111) for H. We obtained $D_e = 2.140$ and 1.990 eV by SCF and MCSCF, respectively. A large STF SCF gives 2.183 eV [34], also confirming the present results. In this molecule, the molecular extra correlation energy (MECE) is almost zero. Since electrons in molecules are confined in a small space, the MECE is usually negative and enlarges molecular bonding energies. In this sense, BeH is

Table 6. Spectroscopic constants for BeH, MgH, and CaH molecules

Method	Basis for alkaline-earth atom	D_e/eV	R_e/bohr	ω_e/cm^{-1}	Charges at alkaline-earth atom	
					Total GAOP	p GAOP
BeH						
SCF	(7211/211)[a]	2.149	2.538	2280	3.596	0.709
	(7211/111)[a]	2.095	2.545	2253	3.616	0.723
	(7211/21)[b]	2.072	2.556	2253	3.619	0.726
MCSCF	(7211/211)[a]	1.998	2.550	2182	3.633	0.679
	(7211/111)[a]	1.961	2.559	2148	3.655	0.692
	(7211/21)[b]	1.939	2.570	2150	3.659	0.697
Exptl.		2.034	2.537	2061		
MgH						
SCF	(74111/7111)[a]	1.098	3.276	1616	11.441	0.507
	(74111/7111)-i[a,c]	1.086	3.275	1610	11.442	0.509
	(74111/721)[b]	1.068	3.267	1609	11.515	0.546
MCSCF	(74111/7111)[a]	1.278	3.303	1515	11.508	0.472
	(74111/7111)-i[a,c]	1.269	3.301	1509	11.508	0.473
	(74111/721)[b]	1.241	3.291	1510	11.573	0.507
Exptl.		1.36	3.269	1495		
CaH						
SCF	(743111/74111)[a]	1.183	4.037	1288	19.284	0.420
	(743111/7421)[b]	1.177	4.036	1285	19.290	0.426
MCSCF	(743111/74111)[a]	1.425	4.044	1238	19.346	0.403
	(743111/7421)[b]	1.371	4.051	1218	19.390	0.426
Exptl.		<1.70	3.784	1298		

[a] The basis set for H is (511/111)
[b] The basis set for H is (511/21)
[c] The symbol "-i" means the (in, out, out) p-type CGTF set. See text

exceptional. We see from Table 6 that the GAOPs of valence $2s$ and $2p$ in the largest SCF calculation are 0.89 ($= 3.60 - 2.00 - 0.71$) and 0.71. The 2σ MO is condensed in a molecular region but the strongly hybridized 3σ MO is not. We note that the Be atom has a very concentrated $2s^2$ electron pair, whose correlation effects are well described by the valence p sets. Thus we infer that it is difficult to get balanced atomic and molecular correlations, if only the valence p set is used. With the (7211/211) set, we showed in Table 6 that MCSCF calculations give $D_e = 1.998$ eV (and $R_e = 2.550$ bohrs) smaller than the SCF $D_e = 2.149$ eV (and $R_e = 2.538$ bohrs). A large CI calculation [34] with an STF basis set including up to Be $4f$ and H $3d$ functions gave $D_e = 2.115$ eV and $R_e = 2.542$ bohrs. A similar CI calculation by Larsson [35] gave a D_e of 2.162 eV.

For the MgH molecule, the GAOPs for the valence $3s$ and $3p$ orbitals are 0.93 and 0.51. This shows the sp hybridization in the MgH 5σ MO is smaller than that in the BeH 3σ MO, indicating that valence electron charge in a molecular region is larger in MgH than in BeH. In contrast to BeH, the MCSCF D_es increase relative to the SCF D_es in MgH, reflecting an increase in the number of valence electrons in a molecular region. Large valence CI calculations [36] gave $D_e = 1.385$ eV and $R_e = 3.294$ bohrs compared with the present best calculation of $D_e = 1.241$ eV and $R_e = 3.291$ bohrs. For MgH, we also performed SCF and MCSCF calculations with the (in, out, out) set described at the end of the previous section: the results are given in Table 6. Although we have not shown the molecular total energies, the values from the (in, out, out) set are always higher than those from the optimum (out, out, out) set. Moreover, as shown in Table 6, the (out, out, out) set gave better spectroscopic constants than the (in, out, out) set.

In CaH, the $4p$ GAOP decreases further. In alkaline-earth hydrides, the smaller the np GAOPs the larger the correlation effects. Pettersson et al. [37] performed valence CI calculations with a large basis set including an f-type GTF and obtained $D_e = 1.444$ eV and $R_e = 3.886$ bohrs. Comparison of these results with $D_e = 1.425$ eV and $R_e = 4.051$ bohrs from the present largest calculation suggests that GTFs with high angular momenta are necessary to obtain better molecular geometry. The proper geometry is obtained with CI calculations including core-valence correlations [37].

In summary, we can say that the present np sets for alkaline-earth atoms are appropriate for describing valence p orbitals and molecular correlations.

5 Comparison with other valence $2p$ sets

Since there are no inner p orbitals for the valence $2p$s, comparison of the different $2p$ sets is less ambiguous than for the $3p$s. We compare the present set with those given by Sadlej and Urban (SU) [25], Thakkar et al. (TKSH) [41], and Noro et al. (NSK) [43].

Using these sets, we first examined the Li_2 molecule. The basis set for s was (7211). The present, SU, and TKSH sets are denoted by (7211/211), (7211/411)-SU, and (7211/4111)-TKSH, respectively. We failed to obtain MCSCF solutions for (7211/411)-SU, and we therefore performed valence full CI (VFCI) calculations which give results close to MCSCF; the main difference between the two is that the former takes $1s$ core relaxations into account but the latter does not. In the top half of Table 7, we give the spectroscopic constants, molecular total energies at $R = 5.2$ bohrs, and atomic SCF total energies which are common to all the sets

Table 7. Spectroscopic constants for Li_2 and BeH obtained with different valence $2p$ sets[a]

Method	Basis for alkaline-earth atom	D_e/eV	R_e/bohr	ω_e/cm^{-1}	Molecular and atomic total energies/hartree	
					Li_2 ($R = 5.2$)/ BeH ($R = 2.4$ bohr)	Li/Be
Li_2						
SCF	(7211/411)-SU[b]	0.147	5.298	338	−14.869984	−7.4323195
	(7211/211)	0.154	5.274	337	−14.870241	−7.4323195
	(7211/4111)-TKSH[c]	0.158	5.273	339	−14.870387	−7.4323195
VFCI	(7211/411) SU[b]	0.868	5.169	336	−14.896524	−7.4323195
	(7211/211)	0.881	5.159	334	−14.896988	−7.4323195
	(7211/4111)-TKSH[c]	0.892	5.151	337	−14.897397	−7.4323195
Exptl.		1.046	5.051	351		
BeH						
SCF	(7211/411)-SU[b]	1.999	2.561	2221	−15.143153	−14.572138
	(7211/311)-NSK[d]	2.143	2.538	2267	−15.149060	14.572138
	(7211/211)	2.149	2.538	2280	−15.149256	−14.572138
	(7211/3111)-NSK[d]	2.155	2.539	2269	−15.149489	−14.572138
	(7211/4111)-TKSH[c]	2.161	2.538	2277	−15.149717	−14.572138
MCSCF	(7211/411)-SU[b]	1.879	2.575	2117	−15.181047	−14.614679
	(7211/311)-NSK[d]	1.990	2.551	2164	−15.188161	−14.617085
	(7211/211)	1.998	2.550	2182	−15.188293	−14.616909
	(7211/3111)-NSK[d]	2.002	2.552	2168	−15.188687	−14.617166
	(7211/4111)-TKSH[c]	2.007	2.550	2177	−15.188830	−14.617119
Exptl.		2.034	2.537	2061		

[a] The basis set for H is (511/111)
[b] See Ref. [25]
[c] See Ref. [41]
[d] See Ref. [43]

examined. (If the Li_2 results in Tables 4 and 7 are compared, the effect of $1s$ relaxation is found to be very small.) We see the present set gives better results than SU, although its size is smaller than that of the set of SU. This originates from the fact that SU [25] aimed to construct p functions appropriate for molecular polarizabilities and electronic moments; inclusion of very diffuse pGTFs which hardly affect energetics is inevitable for these molecular properties. The best one is (7211/4111)-TKSH. However, the D_e and R_e values given by the present set differ from those of TKSH by only 0.01 eV and 0.01 bohr, showing the set developed is preferable in view of its size.

We next performed comparative calculations on the BeH molecule. In addition to (7211/211), (7211/411)-SU, and (7211/4111)-TKSH sets, we examined two correlation oriented valence $2p$ sets developed by NSK [43] for the Be atom. They are referred to as (7211/311)-NSK and (7211/3111)-NSK. The (511/111) set was used for H. The results are summarized in the bottom half of Table 7. If three CGTFs are used, the present (7211/211) is the best, despite the fact that the number of pGTFs is the smallest. The origin of the difference between the present and the SU sets has already been mentioned. The difference between the present and the NSK sets is that the NSK set is oriented to atomic correlation and the atom-like electron correlation is assumed to be also important in molecules, while the present set is oriented to molecular polarization and the atomic $ns \rightarrow np$ excitation is assumed to be important in molecules. The conceptual difference in developing the p sets leads to relatively tight pGTFs for the correlation oriented set and relatively diffuse pGTFs for the molecular polarization oriented set, if the size of the sets is small: the smallest p exponents of (7211/311)-NSK and (7211/211) are 0.097 and 0.060, respectively. In SCF calculations, the polarization effect is important. It is therefore natural that the present (7211/211) set gives better SCF molecular total energies and dissociation energies. The (7211/311)-NSK set describes molecular correlation effects better than the present (7211/211) set, but it is not large enough to invert the molecular MCSCF energies around R_e. As a result, the MCSCF D_e with (7211/311)-NSK is worse than that with (7211/211). The present D_e is close to the value predicted by the (7211/3111)-NSK set. The best molecular results are not given by (7211/3111)-NSK but by (7211/4111)-TKSH, again showing the importance of molecular polarization. As pointed out previously [53], the NSK sets may describe the atomic correlation too accurately. We finally comment that the atomic correlation energies (Be near degeneracy) calculated with (7211/3111)-NSK and (7211/211) are −1.225 and −1.218 eV, respectively, again showing that the present set is preferable for describing the correlation effects.

Although we have not included the results of the (7211/111) set in Table 7, they surpass those of (7211/411)-SU and are closer to those of (7211/211) for Li_2 and to those of (7211/311)-NSK for BeH (cf. Tables 4, 6, 7).

6 Conclusion

We have developed CGTF basis sets for the valence np orbitals ($n = 2$, 3, and 4) of six alkali and alkaline-earth atoms. The sets with three pGTFs were prepared for all the atoms, but examinations of errors in the p orbital energies lead to additional four-term expansions for the Li and Be atoms. The new CGTF sets were tested by molecular SCF and MCSCF calculations of three homonuclear alkali diatomics and six diatomic alkali/alkaline-earth hydrides. We found that the calculated spectroscopic constants almost always simulate well the results of more elaborate calculations and of experiment. The present valence sets are concluded to describe valence *p* orbitals as well as correlating *p* orbitals adequately in spite of their compactness.

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