

# Contracted Gaussian-type basis functions revisited II. Atoms Na through Ar

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**Abstract.** We report five minimal-type contracted Gaussian-type function (CGTF) basis sets of the second-row atoms, Na – Ar, for molecular applications. Three of the present CGTF sets are revised versions of those given by Huzinaga and co-workers and the other two are newly developed for more accurate calculations. Practical utility and improved reliability of the present basis sets, augmented by polarization functions, are confirmed by test calculations on the P atom and P<sub>2</sub> molecule both at the self-consistent field (SCF) and configuration interaction (CI) levels.

**Key words:** Contracted Gaussian-type function – Minimal-type basis sets – Second-row atoms – Self-consistent field – Configuration interaction

## 1 Introduction

Many Gaussian-type function (GTF) basis sets have been developed for molecular calculations. They may be classified into two categories: one characterized by describing self-consistent field (SCF) atomic orbitals (AOs) with common primitive GTFs (PGTFs) for the respective symmetries of *s*, *p*, *d*, ..., and the other characterized by describing SCF AOs with the contracted GTFs (CGTFs). Typical examples of the former are basis sets given by Raffanetti [1] and van Duijneveldt [2]. They have recently been used in the form of natural orbitals [3, 4] or general contractions [5–8] with augmented correlation (polarization) functions. Typical examples of the latter are 4–31G [9, 10] and MINI/MIDI [11–13] sets. Intermediate basis sets are those of Schaefer et al. [14, 15], in which CGTFs and PGTFs are employed mainly for inner and outer shells, respectively.

Recently, we reported [16] accurate minimal-type CGTF sets for the atoms Li to Ne, after careful reinvestigation of the CGTF sets previously given by

Tatewaki and Huzinaga [12, 13]. Improved quality of the new basis sets [16] was verified through atomic and molecular calculations by adding various correlation/polarization functions. The improvement observed for the first-row atoms showed insufficient optimality of the original CGTF sets reported by Tatewaki and Huzinaga, and suggested that a similar refinement is needed for the remaining atoms, since their basis sets have been frequently used in molecular applications.

In the present paper we report five minimal-type CGTF sets for the second-row atoms from Na to Ar. Three of the present CGTF sets, (333/33), (433/43) and (533/53), are improved versions of those reported by Huzinaga and co-workers [13]. The remaining two, (633/63) and (743/74), are newly developed for more accurate molecular calculations, where the single digit numbers in parentheses indicate the numbers of the PGTFs which span the CGTFs and the symbol / separates the *s* and *p* symmetries. The quality of the new basis sets is tested in atomic and molecular calculations by adding the correlation functions given by Woon and Dunning [7]. We find that the effects of the correlation functions on the molecular calculations are almost the same irrespective of the basis sets, and the quality of molecular calculations is essentially parallel to that of *s* and *p* basis sets; the valence-split sets derived from the present (433/43) and (533/53) CGTF sets are suited for molecular calculations with moderate accuracy, while those from the (633/63) and (743/74) are for more accurate calculations.

## 2 Computational details

In their construction of the CGTF sets, Tatewaki and Huzinaga [12, 13] treated contraction coefficients of the CGTFs as linear parameters and used the Fock equation to determine the coefficients. On the other hand, they determined each exponent by a single-line search based on the presumed quadratic dependence of the total energy on the exponent. However, in our construction of accurate Roothaan-Hartree-Fock wave functions [17, 18] we experienced that the directly coupled variation of exponents is significant for finding a better energy

**Table 1.** Total energy errors (in hartrees) of the CGTF sets relative to the NHF values (sign reversed in hartrees). For each atom, the first line shows the present results and the second line shows results from Ref. [13]

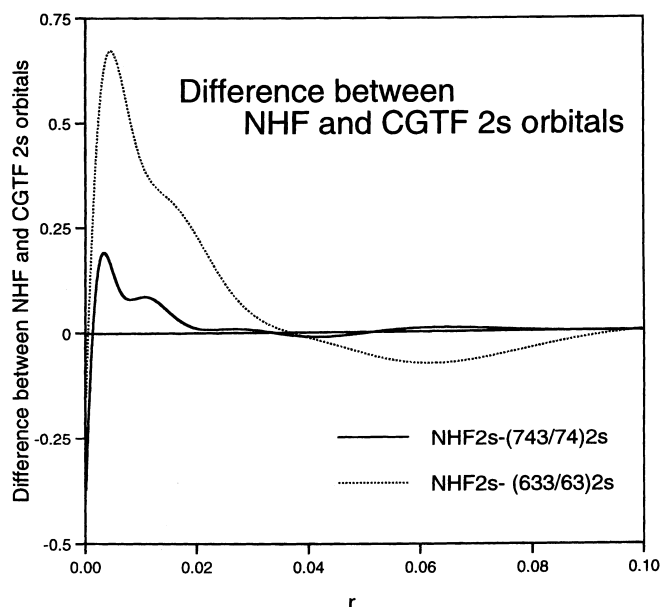
Atom	NHF (Ref. [22])	(333/33)	(433/43)	(533/53)	(633/63)	(743/74)
11 Na ( $^2S$ )	161.8589116	0.9815001 0.9824512	0.2353931 0.2355859	0.0648860 0.0650288	0.0218353 —	0.0069478 —
12 Mg ( $^1S$ )	199.6146364	1.1549442 1.1561333	0.2753512 0.2756628	0.0758239 0.0928510	0.0256642 —	0.0077979 —
13 Al ( $^2P$ )	241.8767072	1.3183923 1.3221717	0.3124646 0.3128310	0.0860432 0.0864000	0.0294337 —	0.0086344 —
14 Si ( $^3P$ )	288.8543625	1.5150108 1.5174138	0.3576311 0.3579862	0.0986536 0.0990703	0.0341128 —	0.0098257 —
15 P ( $^4S$ )	340.7187810	1.7278804 1.7300394	0.4069570 0.4073709	0.1125514 0.1131523	0.0393682 —	0.0112626 —
16 S ( $^3P$ )	397.5048959	1.9591830 1.9613210	0.4608606 0.4613928	0.1278903 0.1286611	0.0453194 —	0.0129588 —
17 Cl ( $^2P$ )	459.4820724	2.2067938 2.2091563	0.5186412 0.5192834	0.1444527 0.1453882	0.0518811 —	0.0149350 —
18 Ar ( $^1S$ )	526.8175128	2.4711607 2.4738270	0.5803932 0.5813154	0.1622707 0.1634900	0.0590715 —	0.0172112 —

minimum. For CGTF sets, we found [16] that the approximate treatment of the contraction coefficients as linear parameters is insufficiently accurate and an additional coupling of exponent and contraction coefficient optimizations is needed. We have thus performed fully coupled nonlinear optimizations of CGTF exponents and contraction coefficients using the conjugate directions method [19, 20]. Concerning the exponents, the present method of optimization is essentially the same as that proposed by Faegri and Almlöf [21] for PGTF sets.

In the present study, we have first developed (333/33), (433/43), (533/53), (633/63) and (743/74) sets for the atoms Na to Ar. The differences of their total energies from the numerical Hartree-Fock (NHF) values [22] are given in Table 1, where the results of the previous calculations [13] are also included for comparison. We find that the optimizations used by Tatewaki and Huzinaga are rather rough for the (333/33) set. In particular, the previous (533/53) set for Mg is erroneous, since the total energy improvement is extremely large (about 0.02 hartrees) compared with the other cases. However, we have found that the orbital energies predicted by the present and previous CGTF sets are more or less the same, though the details are omitted here.

The contraction pattern of the present largest set is not (833/74) but (743/74). We first imagined that the (833/74) set would be better than (743/74), but found that the latter gives a lower total energy (for example, the difference is 0.004025 hartrees for the Cl atom). The improvement of the second innermost orbital is more important than that of the innermost one after seven PGTFs have been used for the innermost orbital. Figure 1 compares the accuracies of the  $2s$  AOs obtained from the (633/63) and (743/74) sets for the P atom in the region close to the nucleus. It is clearly seen that the last added PGTF in the second  $s$  CGTF is effectively used to improve the very inner distribution of the  $2s$  AO, which would indirectly improve the  $1s$  AO too.

In the case of the P ( $^4S$ ) atom, for example, Schaefer and co-workers [14, 15] gave  $-340.597368$  and  $-340.709515$  hartrees using the (5311/511) and (73211/6111) sets, respectively. When the present minimal-type



**Fig. 1.** Difference between the numerical Hartree-Fock (NHF) and contracted Gaussian-type function (CGTF)  $2s$  atomic orbitals (AOs) for the P atom

( $n33/n3$ ) sets ( $n=4, 5, 6$ ) are decontracted into ( $n321/n21$ ) sets, the total energy is worse for  $n=4$  and better for  $n=5$  and 6 (see Table 2) than that of the (5311/511) set. We expect that the present ( $n321/n21$ ) sets give nearly the same results in atomic and molecular calculations as (5311/511), except for the total energies. Although the total energies of ( $n321/n111$ ) are higher than that of (73211/6111) [15], all of these basis sets would work analogously in the electronic structure calculations.

### 3 Effects of polarization functions on atomic correlations

Splitting the outermost CGTFs, we prepared two types of basis sets, ( $n321/n21$ ) and ( $n321/n111$ ), where  $n=3, 4, 5$  and 6. The largest (7421/71111) set

**Table 2.** Atomic SCF energies and correlation energies (sign reversed in hartrees) for the P atom. *Reference* stands for the (12, 12, 1, 1/88111) CGTF set derived from the 14s12p GTF set and *sp* stands for CGTF sets

CGTF	SCF energy	Correlation energy			
		<i>sp</i>	<i>sp+1d</i>	<i>sp+2d</i>	<i>sp+2d+1f</i>
(3321/321)	339.030760	0.015252	0.078881	0.086051	0.095114
(4321/421)	340.320712	0.014764	0.078558	0.085672	0.094775
(5321/521)	340.608491	0.014526	0.078317	0.085430	0.094536
(6321/621)	340.680136	0.014471	0.078255	0.085371	0.094476
(3321/3111)	339.049503	0.017953	0.081422	0.088916	0.097935
(4321/4111)	340.321379	0.017984	0.081428	0.088913	0.097934
(5321/5111)	340.608498	0.017997	0.081408	0.088904	0.097924
(6321/6111)	340.680187	0.018000	0.081405	0.088906	0.097925
(7321/71111)	340.707981	0.018181	0.081660	0.089103	0.098105
<i>Reference</i>	340.717745	0.019330	0.082718	0.090190	0.099174

belongs to the second type. A Raffanetti-type (12, 12, 12, 1, 1/88111) is also prepared from a new uncontracted 14s11p set as the reference (*ref*) set in the present study. Prior to molecular calculations, we have examined the role of polarization functions in atomic configuration interaction (CI) calculations as before [16]. For this purpose, four types of basis sets are prepared: (1) the CGTF sets given above (hereafter abbreviated as *sp*), (2) *sp+1d*, (3) *sp+2d*, and (4) *sp+2d+1f*, where the augmented *d*- and *f*-type polarization functions (*pol*) are those of Woon and Dunning [7]. The single and double (SD) excitations from the 3s and 3p orbitals to all the SCF virtual orbitals and the symmetry orbitals generated from the polarization functions were considered. The calculated correlation energies defined by

$$E^{\text{corr}} = E^{\text{CI}} - E^{\text{SCF}} , \quad (1)$$

are listed in Table 2 for the P atom. We find in the table that

$$\Delta E_{\text{atom}}^{\text{corr}}(sp + pol) \cong \Delta E_{\text{atom}}^{\text{corr}}(sp) , \quad (2a)$$

where

$$\Delta E_{\text{atom}}^{\text{corr}}(sp + pol) \equiv E_{\text{atom}}^{\text{corr}}(sp + pol) - E_{\text{atom}}^{\text{corr}}(ref + pol) \quad (2b)$$

and *pol* = 0, 1d, 2d, or 2d+1f. The relation in Eq. (2a) is important, since it indicates the ‘stability’ of the *sp* space of all the present CGTF sets in the sense that additional polarization functions change the value of  $E_{\text{atom}}^{\text{corr}}(sp)$  by very little. We note that the present correlation energies (−0.0979 hartrees) calculated with (n321/n111)+2d+1f compare well with that (−0.1054 hartrees) of Woon and Dunning [7] who used 15s-, 5p-, 3d- and 2f-type active orbitals.

#### 4 SCF and CI calculations on the P<sub>2</sub> molecule

Using the (n321/n21) and (n321/n111) sets discussed in the previous section, we have performed SCF calculations on the P<sub>2</sub> molecule in its ground  $^1\Sigma_g^+$  state. The

resultant spectroscopic constants are collected in the left half of Table 3. A stepwise improvement of the spectroscopic constants is observed when the number of augmented polarization functions is increased, and the improvement is most remarkable for the dissociation energy  $D_e$ .

The  $D_e$  predicted by (3321/321) and its family is always larger than that predicted by the family of the reference set and the difference of the dissociation energies between (3321/321)+*pol* and *ref*+*pol* increases as the number of polarization functions increases. This shows that the basis set superposition error (BSSE) [24–27] is enhanced by the polarization functions. We also see that a small BSEE appears in (3321/3111) and its family. On the other hand, the (4321/421), (5321/521), (6321/621) sets and their families give acceptable results. The results of (4321/4111), (5321/5111), (6321/6111), (7421/71111) and their families show almost complete agreement with the corresponding reference values, except for  $D_e$ ’s which show small but stubborn BSSE. If we intend to obtain an accuracy of 0.02 eV we should use the (6321/6111) set or greater.

As in the case of the P atom, we have performed SD-CI calculations for the P<sub>2</sub> molecule, using all the virtual SCF orbitals and the same polarization functions; the basis sets employed are *sp*, *sp+1d*, *sp+2d* and *sp+2d+1f*. The reference configuration for the CI calculations is  $(4\sigma_g)^2(4\sigma_u)^2(5\sigma_g)^2(2\pi_u)^4$ . We define the difference of the molecular correlation energy of the respective basis relative to the reference by

$$\Delta E_{\text{mol}}^{\text{corr}}(R, sp + pol) = E_{\text{mol}}^{\text{corr}}(R, sp + pol) - E_{\text{mol}}^{\text{corr}}(R, ref + pol) , \quad (3)$$

where  $R$  denotes the internuclear distance. As an example,  $\Delta E_{\text{mol}}^{\text{corr}}(R, sp + pol)$  and  $2\Delta E_{\text{atom}}^{\text{corr}}(sp)$  are plotted in Fig. 2 for the (6321/621) and (6321/6111) sets. From the figure, we find that

$$\Delta E_{\text{mol}}^{\text{corr}}(R, sp + pol) \cong 2\Delta E_{\text{atom}}^{\text{corr}}(sp) . \quad (4)$$

Equation (4) states that, at any internuclear distance, the error in the *molecular* correlation energy calculated with *sp+pol* functions is twice the error in the *atomic* correlation energy with *sp*. The relation holds almost

**Table 3.** Spectroscopic constants of the P<sub>2</sub> molecule obtained by SCF and CI calculations

CGTF	SCF			CI		
	$D_e/\text{eV}$	$R_e/\text{bohr}$	$\omega_e/\text{cm}^{-1}$	$D_e/\text{eV}$	$R_e/\text{bohr}$	$\omega_e/\text{cm}^{-1}$
(3321/321)	-0.563	3.688	844	2.176	3.785	761
(4321/421)	-0.648	3.691	841	2.110	5.791	758
(5321/521)	-0.672	3.693	840	2.090	3.794	756
(6321/621)	-0.678	3.694	840	2.085	3.795	755
Reference	-0.677	3.676	815	2.094	3.770	735
(3321/321)+1d	1.470	3.552	907	3.111	3.625	850
(4321/421)+1d	1.268	3.559	899	2.926	3.635	841
(5321/521)+1d	1.237	3.560	898	2.898	3.636	840
(6321/621)+1d	1.232	3.560	898	2.893	3.637	840
Reference+1d	1.257	3.552	895	2.935	3.619	839
(3321/321)+2d	1.716	3.533	899	3.256	3.601	843
(4321/421)+2d	1.463	3.543	893	3.020	3.614	835
(5321/521)+2d	1.426	3.544	892	2.986	3.615	834
(6321/621)+2d	1.421	3.544	892	2.981	3.616	834
Reference+2d	1.475	3.531	890	3.075	3.590	836
(3321/321)+2d+1f	1.955	3.515	898	3.778	3.570	850
(4321/421)+2d+1f	1.589	3.532	894	3.435	3.589	845
(5321/521)+2d+1f	1.539	3.534	892	3.390	3.591	843
(6321/621)+2d+1f	1.531	3.535	892	3.383	3.592	843
Reference+2d+1f	1.564	3.528	893	3.402	3.581	847
(3321/3111)	-0.601	3.683	824	2.170	3.776	745
(4321/4111)	-0.628	3.680	824	2.148	3.774	744
(5321/5111)	-0.643	3.681	822	2.135	3.775	742
(6321/6111)	-0.648	3.681	821	2.130	3.775	741
(7421/71111)	-0.607	3.674	832	2.174	3.765	753
Reference	-0.677	3.676	815	2.094	3.770	735
(3321/3111)+1d	1.375	3.547	902	3.040	3.615	845
(4321/4111)+1d	1.305	3.550	897	2.976	3.619	841
(5321/5111)+1d	1.282	3.551	896	2.953	3.621	839
(6321/6111)+1d	1.274	3.552	896	2.946	3.622	839
(7421/71111)+1d	1.274	3.552	897	2.965	3.621	841
Reference+1d	1.257	3.552	895	2.935	3.619	839
(3321/3111)+2d	1.583	3.526	893	3.157	3.586	837
(4321/4111)+2d	1.522	3.528	890	3.102	3.589	834
(5321/5111)+2d	1.497	3.530	890	3.079	3.591	833
(6321/6111)+2d	1.487	3.530	890	3.070	3.592	833
(7421/71111)+2d	1.483	3.532	889	3.083	3.593	834
Reference+2d	1.475	3.531	890	3.075	3.590	836
(3321/3111)+2d+1f	1.847	3.520	917	3.679	3.569	872
(4321/4111)+2d+1f	1.669	3.523	900	3.507	3.575	854
(5321/5111)+2d+1f	1.608	3.526	896	3.447	3.579	850
(6321/6111)+2d+1f	1.587	3.527	894	3.427	3.580	848
(7421/71111)+2d+1f	1.576	3.528	893	3.425	3.580	848
Reference+2d+1f	1.564	3.528	893	3.402	3.581	847
Experimental data (Ref. [23])	5.033	3.578	781	5.033	3.578	781

perfectly for ( $n321/n111$ ), ( $7421/71111$ ) and their families, moderately for ( $n321/n21$ )+ $2d+1f$  and approximately for ( $n321/n21$ ), ( $n321/n21$ )+ $1d$ , and ( $n321/n21$ )+ $2d$ .

We collect the spectroscopic constants calculated by SD-CI in the right half of Table 3. Except for those from ( $3321/321$ ) and its family, all  $D_e$ 's from ( $n321/n21$ ) and their families agree with the corresponding ones of the reference set and its derivatives. Except for  $D_e$ 's of ( $3321/3111$ ) and ( $4321/4111$ ), almost perfect agreements result for the case of ( $n321/n111$ ) when polarization functions are added. If we define the difference of the bonding energies from the reference CI calculations at the respective distance  $R$  by

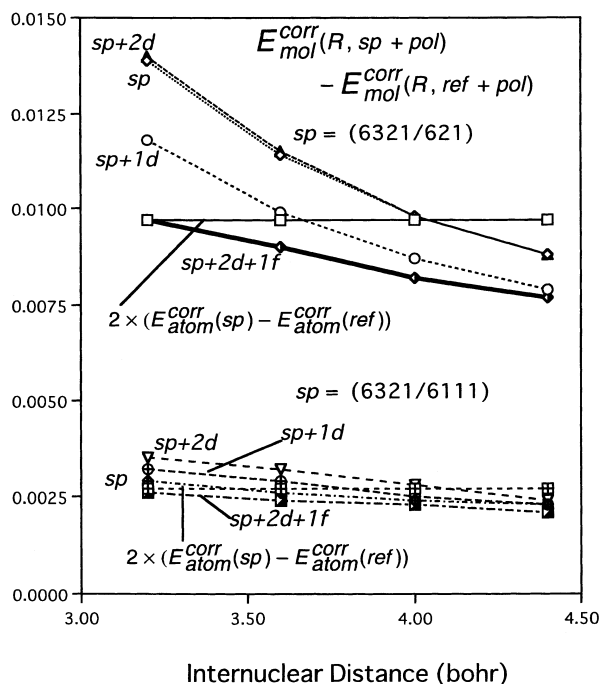
$$\Delta D_{\text{mol}}^{\text{CI}}(R, sp + pol) = \{E_{\text{mol}}^{\text{CI}}(R, sp + pol) - 2E_{\text{atom}}^{\text{CI}}(sp + pol)\}$$

$$- \{E_{\text{mol}}^{\text{CI}}(R, ref + pol) - 2E_{\text{atom}}^{\text{CI}}(ref + pol)\} ,$$

then using Eq. (4), we find

$$\begin{aligned} \Delta D_{\text{mol}}^{\text{CI}}(R, sp + pol) &= \Delta D_{\text{mol}}^{\text{SCF}}(R, sp + pol) \\ &+ \Delta E_{\text{mol}}^{\text{corr}}(R, sp + pol) - 2\Delta E_{\text{atom}}^{\text{corr}}(sp) \\ &\cong \Delta D_{\text{mol}}^{\text{SCF}}(R, sp + pol) , \end{aligned} \quad (5)$$

which shows that the error of CI calculations with  $sp + pol$  in the dissociation energy is approximately equal to that of SCF calculation. The relation in Eq. (5) holds well for ( $n321/n111$ ), ( $7421/71111$ ) and their derivatives but is only approximate for ( $n321/n21$ ), ( $n321/n21$ )+ $1d$  and ( $n321/n21$ )+ $2d$ , reflecting the fact that Eq. (4) is approximately valid for these basis sets.



**Fig. 2.** Difference of the correlation energies of the (6321/621)+*pol* and (6321/6111)+*pol* sets from the reference values for the  $P_2$  molecule

## 5 Concluding remarks

We have developed the five minimal-type basis sets for the atoms Na to Ar. The quality of the new basis sets was tested on the P atom and  $P_2$  molecule, using two types of the derived basis sets, ( $n321/n21$ ) and ( $n321/n111$ ). The results were analysed and compared to those of the reference (12, 12, 12, 1, 1/88111) set generated from the uncontracted  $14s11p$  basis set. We recommend the basis sets ( $n321/n21$ )+*pol* with  $n > 3$  for molecular calculations which are expected to give reasonably accurate molecular constants compared with *ref + pol*. The (6321/6111)+*pol* and (7421/71111)+*pol* are recommended for higher quality molecular calculations. All the ( $n321/n111$ ) and (7421/71111) sets are efficient to calculate the excitation energies, since they gave almost the same molecular correlation energies as the reference family. All the present CGTF sets are available at [28].

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## References

- Raffenetti RC (1973) *J Chem Phys* 58:4452
- van Duijneveldt FB (1971) IBM technical report RJ945
- Almlöf J, Taylor PR (1987) *J Chem Phys* 86:4070
- Almlöf J, Taylor PR (1991) *Adv Quantum Chem* 22:301
- Dunning TH Jr (1989) *J Chem Phys* 90:1007
- Kendall RA, Dunning TH Jr (1992) *J Chem Phys* 96:6796
- Woon DE, Dunning TH Jr (1993) *J Chem Phys* 98:1358
- Woon DE, Dunning TH Jr (1993) *J Chem Phys* 99:1914
- Ditchfield R, Hehre WJ, Pople JA (1971) *J Chem Phys* 54:724
- Hehre WJ, Pople JA (1972) *J Chem Phys* 56:4233
- Easton RE, Giesen DJ, Welch A, Cramer CJ, Truhlar DG (1996) *Theor Chim Acta* 93:281
- Tatewaki H, Huzinaga S (1979) *J Chem Phys* 71:4339; Tatewaki H, Huzinaga S (1980) *J Comput Chem* 1:205
- Huzinaga S (ed) Andzelm J, Klobukowski M, Radio-Andzelm E, Sakai Y, Tatewaki H (1984) *Gaussian basis sets for molecular calculations*. Elsevier, Amsterdam
- Schaefer A, Horn H, Ahlrichs R (1992) *J Chem Phys* 97:2571
- Schaefer A, Huber C, Ahlrichs R (1994) *J Chem Phys* 100:5829
- Tatewaki H, Koga T (1996) *J Chem Phys* 104:8493
- Koga T, Omura M, Teruya H, Thakkar AJ (1995) *J Phys B* 28:3113
- Koga T, Watanabe S, Kanayama K, Yasuda R, Thakkar AJ (1995) *J Chem Phys* 103:3000
- Powell MJD (1964) *Comput J* 7:155
- Kuester JL, Mize JH (1973) *Optimization techniques with fortran*. McGraw-Hill, New York, pp 331–343
- Faegri K Jr, Almlöf J (1986) *J Comp Chem* 7:396
- Tatewaki H, Koga T, Thakkar AJ, Sakai Y (1994) *J Chem Phys* 101:4945
- Huber KP, Herzberg G (1979) *Molecular spectra and molecular structure. IV. Constants of diatomic molecules*. Van Nostrand Reinhold, New York
- Boys SF, Bernardy F (1970) *Mol Phys* 19:553
- Meunier A, Levy B, Berthier G (1973) *Theor Chim Acta* 29:49
- Johansson A, Kollmann P, Rothenberg S (1973) *Theor Chim Acta* 29:167
- Urban M, Hobza P (1975) *Theor Chim Acta* 36:215
- <http://202.35.198.41/~htatewak>
- Kashiwagi H, Takeda T, Miyoshi E, Obara S, Sasaki F (1987) A library program of the Computer Center of the Institute for Molecular Science, Okazaki, Japan
- Murakami A, Iwaki H, Terashima H, Shoda T, Kawaguchi T, Noro T (1985) A library program of the Computer Center of the Institute for Molecular Science, Okazaki, Japan