MEDIUM-SIZE POLARIZED BASIS SETS APPLICABILITY FOR INTERACTION ENERGY CALCULATIONS: He_2 AND Be_2 van der WAALS SYSTEMS

Andrzej NOWEK

Institute of Chemistry,
Pedagogical University, al. Armii Krajowej 13/15, 42200 Czestochowa, Poland

Received July 28, 1992
Accepted December 1, 1992

Polarized basis set approach has been applied for preparation of medium-size contracted GTO basis sets starting from various standard energy-optimized and even-tempered isotropic atomic basis sets. Their usefulness for calculation of the SCF interaction energy and its components as well as dispersion energy consistently determined within the dimer basis set were studied for He_2 and Be_2 systems for intermediate internuclear separations. The results obtained with polarized basis sets indicate their good performance in comparison with property oriented ones.

It is well known that one of the determining factors for the reliability of an *ab initio* calculation of intermolecular energies is the choice of the molecular basis set. As a rule the two-step procedure is applied: (i) selection of the appropriate isotropic part and (ii) its saturation with some additional orbitals which are necessary if molecular properties and intermolecular interactions are to be properly accounted for. Until nowadays various standardized isotropic basis sets augmented with polarization functions have been generated and less or more commonly used for molecular calculations[1]. For van der Waals systems where interaction potential is the net result of a balance of opposite contributions evaluated at the SCF as well as a higher level electron correlation theories, very good quality basis sets are needed[2,3]. Therefore, a large (of double zeta or better quality) energy-optimized or well-tempered[4] and even-tempered[5] isotropic part of the basis set is augmented with additional diffuse and polarization functions. Moreover, orbital exponents of these additional functions should be optimized at molecular level if accurate results are to be expected. For these reasons the standard basis sets available in many libraries and collections need far from trivial refinements and optimizations.

A few years ago, Sadlej[6] proposed a simple and general procedure for the construction of polarized GTO/CGTO atomic basis sets. He has considered a many-electron system in the presence of the external perturbation and its influence onto spinorbitals described by using some finite set of basis functions (e.g. primitive GTO's constituting an isotropic atomic basis set). As the result a contracted polarized part of

the basis set for molecular use at SCF HF and correlated level without any further optimizations is derived. In the case of the external electric field the basis sets as generated within this technique seem to be very useful for calculations of electric properties of molecular systems[6,7] and even with moderately large basis sets high accuracy results are obtained[6]. It is very important in this technique that it takes into account that accurate calculation and prediction of molecular electric properties are closely related to the determination of intermolecular interaction energies[8]. In principle the basis set polarization scheme can be applied to any atomic GTO basis set. Depending on the size and flexibility of the basis set and the accuracy requirements, its polarized part can be decontracted and some of the component functions deleted[6].

The aim of this study is to investigate the usefulness of the basis set polarization approach for preparation of medium-size contracted basis sets suitable for calculations of the intermolecular interaction energy and its components. For simplicity two atomic dimers have been selected: He_2 and Be_2 for which medium-size property-oriented optimized[9] and also very accurate results are available in the literature[10].

METHODS AND COMPUTATIONAL DETAILS

The medium-size basis sets were used by Rybak[9] in the exchange-perturbation study of the interaction energy for He_2 and Be_2. He has used the energy-optimized 10*s* GTO's for He and 12*s* for Be of van Duijneveldt[11] augmented with *p* and *d* orbitals contracted as [61111/111/11] for He and [6111111/111/1] for Be atoms. The uncontracted polarized part of these basis sets were fitted with respect to the lowest values of dispersion energy. First we have used the above noted uncontracted GTO isotropic parts for He and Be as initial basis sets and with the basis set polarization method the four-component *p* and two-component *d* orbitals formed from the most diffuse functions were derived. Next, *s* subsets have been contracted as in Rybak's scheme and *p* subsets decontracted into two CGTO's ($4 \Rightarrow 2 + 2$) according to Sadlej's suggestions[6] or three CGTO's ($4 \Rightarrow 1 + 2 + 1$). As the results, the following CGTO basis sets were derived: [61111/22/2] 10*s* DP for He ($E_{SCF} = -2.8616729$ a. u.)* and [6111111/22/2] 12*s* DP and [6111111/121/2] 12*s* DP for Be ($E_{SCF} = -14.57293044$ a. u.). In our notation, n*s* DP denotes polarized contracted basis set generated from van Duijneveldt's n*s* GTO's. It seems that the structure of the derived contracted polarized basis sets is compatible with those of Rybak. Hence, in this case the performance of the polarized basis sets can be checked against the results for interaction energy and its components computed with the property-oriented optimized basis sets.

* The SI expressions of atomic units of energy and length are $E_h = 2.6255 \cdot 10^6$ J mol^{-1} and $^a0 = 0.52917706 \cdot 10^{-10}$ m. The atomic unit of energy is also called Hartree and referred to as 1 H.

The usefulness of the basis set polarization method for preparation of the contracted polarized basis sets was also investigated for other initial isotropic basis sets: regularized even-tempered basis set of Schmidt and Ruedenberg[5] (denoted RP) and energy-optimized basis sets of Huzinaga[12] (denoted HP). In the similar manner as described above the following basis sets have been derived: [61111/22/2] 10*s* RP (E_{SCF} = – 2.86164882 a. u.), [67111/22/3] 16*s* RP (E_{SCF} = –2.86167953 a. u., contracted *d* orbital consists of the three outermost primitives) for He and [8441111/22/2] 20*s* RP (E_{SCF} = 14.5692451 a. u.) for Be starting from 10, 16 and 20-component regularized even-tempered uncontracted *s*-basis sets, respectively. For Be atom a smaller initial energy-optimized 7*s*, 9*s* and 10*s* GTO sets of Huzinaga[15] were also used. As the result, the following polarized basis sets of comparable size were generated: [1111111/22/2] 7*s* HP (E_{SCF} = –14.55130386 a. u.), [3111111/22/2] 9*s* HP (E_{SCF} = –14.57207543 a. u.), [3111111/22/3] 9*s* HP (E_{SCF} = –14.57213993 a. u.) and [31111111/112/2] 10*s* HP (E_{SCF} = –14.57231927 a. u.). Frequently, the energy-optimized medium-size basis sets are considered as not sufficiently flexible for proper description of the properties, which depend on the "tail" region of the wavefunction. Therefore, they need to be augmented with some diffuse functions of the same symmetry as those already present in the given basis set[6]. Hence, we have extended 9*s* of the Huzinaga set by adding one 1s function with orbital exponent derived from the two outermost exponents by assuming they form a geometrical sequence. As the result [31111111/22/2] 9*s* + 1*s* HP (E_{SCF} = – 14.57214867 a. u.) basis set was obtained. The SCF interaction energy and its components have been calculated within the reduced basis set dependence approach proposed by Sokalski et al.[13], according to which the interaction energy ΔE_{SCF} is obtained from equation

$$\Delta E_{SCF}(D) = E_{AB}(D) - E_A(D) - E_B(D) , \qquad (1)$$

where $E_{AB}(D)$, $E_A(D)$ and $E_B(D)$ denote the total SCF energies of the AB dimer and of the A and B monomers as calculated with the dimer basis set. In this way, the non-physical effect known as the basis set superposition error (BSSE) is removed[14 - 16] by Boys–Bernardi's counterposition correction (CP) method[17]. First order interaction energy $E^{(1)}(D)$ is evaluated as the zeroth-iteration energy[18] starting from the mutually orthogonal eigenvectors of A and B subsystems calculated in the dimer basis set. Further it is partitioned into the electrostatic $ES^{(1)}(D)$ and exchange $EX^{(1)}(D)$ components by extracting $ES^{(1)}(D)$ as calculated with the usual perturbational approach using dimer-centered eigenvectors of the interacting subsystems (see Eq. (*3*) in ref.[13]). The first order exchange term $EX^{(1)}(D)$ is then determined as the residue

$$EX^{(1)}(D) = E^{(1)}(D) - ES^{(1)}(D) , \qquad (2)$$

and the basis set consistent decomposition of $\Delta E_{SCF}(D)$ has the form

$$\Delta E_{SCF}(D) = ES^{(1)}(D) + EX^{(1)}(D) + E^{(R)}(D)\,, \qquad (3)$$

where delocalization or deformation term[15] $E^{(R)}(D)$ collects higher order contributions to the SCF interaction energy. The correlated part of the total interaction energy has been monitored with its main attractive term $E_{disp}^{(20)}(D)$, the second order Möller–Plesset polarization dispersion energy calculated in the full dimer basis set for each monomer. All calculations were carried out with MICROMOL program[26] in which we have implemented energy decomposition and dispersion energy routines.

RESULTS AND DISCUSSION

The values of the SCF interaction energy and its components as calculated in the various basis sets for several near equilibrium (R = 5.6 a.u.) internuclear distances for the He_2 system are collected in Table I. With all the basis sets used almost identical values of $\Delta E_{SCF}(D)$, $ES^{(1)}(D)$, $EX^{(1)}(D)$ and $E^{(R)}(D)$ were obtained and they were close to the near Hartree–Fock of Gutowski et al.[16]. This is not surprising since the He_2 system the SCF interaction energy is dominated by the first order components and the use of 10s-type GTO's is sufficient to reproduce these terms accurately[13,19]. On the other hand, the polarized parts of these basis sets are large enough for proper description of the induction components of $\Delta E_{SCF}(D)$. The dispersion energy $E_{disp}^{(20)}(D)$ values calculated with 10s DP, 10s RP and 16s RP polarized basis sets are very close to the corresponding values obtained with property-optimized Rybak's basis set (Table II). The best of our results $E_{disp}^{(20)}(D)$ = −48.99 μH at R = 5.6 a.u. obtained with [67111/22/3] 16s RP correlates very well with the value reported by Roszak et al.[20] $E_{disp}^{(20)}(D)$ = −49.52 μH and obtained with $[1^s/2^p/1^d]$ where a 12 lobe function representation for the ^{d} orbital with dispersion energy optimized exponent was used. It should be noted that significantly better values for dispersion energy are obtained with basis sets that are augmented with higher orbital momentum polarization orbitals, $E_{disp}^{(20)}(D)$ = −51.02 μH in $[1^s/2^p/1^d/1^f]$ (ref.[21]) and $E_{disp}^{(20)}(D)$ = −53.8 μH in $[1^s/3^p/2^d/2^f/2^g/2^h/2^i]$ (ref.[22]) for R = 5.6 a.u. The nature of bonding in Be_2 is not that of a simple van der Waals complex. Considerable theoretical and experimental problems[23] have been involved with definitive determination of the potential curve for this system connected with a near 2^s–2^p degeneracy of Be. The values of the SCF interaction energy and its components evaluated at intermediate internuclear distances, R = 4.0, 5.0, 6.0 and 7.0 a. u. are presented in Table III. For all of the basis sets used here $\Delta E_{SCF}(D)$ values are too repulsive when compared with the results obtained by Lee and Bartlett[24] with the [6111111/311/1] basis set of Dykstra[25] optimized for energy of Be_2 (12s GTO's were taken from van Duijneveldt's tables[11]). From analysis of the SCF interaction energy components (Table III) it is found that changes of $\Delta E_{SCF}(D)$ values as calculated with different basis

TABLE I
He_2 interaction energy components and $\Delta E_{SCF}(D)$ (in μH) for several different basis sets

R(He...He), a.u.	$ES^{(1)}$	$EX^{(1)}$	$E^{(R)}$	$\Delta E_{SCF}(D)$
		[61111/111/11] 10*s* of Rybak		
5.0	−22.80	156.06	−7.64	125.62
5.6	−4.93	35.63	−1.50	29.21
6.0	−1.77	13.20	−0.50	10.93
7.0	−0.14	1.08	0.00	0.94
		[61111/22/2] 10*s* DP		
5.0	−22.76	156.09	−7.59	125.74
5.6	−4.93	35.64	−1.48	29.23
6.0	−1.77	13.20	−0.49	10.94
7.0	−0.13	1.08	−0.04	0.91
		[61111/22/2] 10*s* RP		
5.0	−22.72	156.04	−7.60	125.72
5.6	−4.93	35.60	−1.48	29.19
6.0	−1.77	13.18	−0.50	10.91
7.0	−0.14	1.07	−0.03	0.90
		[67111/22/3] 16*s* RP		
5.0	−22.83	156.05	−7.59	125.63
5.6	−4.94	35.64	−1.48	29.22
6.0	−1.77	13.21	−0.50	10.94
7.0	−0.13	1.08	−0.04	0.91
		[10*s*/4*p*/3*d*/1*f*] Gutowski et al.[a]		
5.0	−22.82	156.1	−7.67	125.57
5.6	−4.94	35.63	−1.49	29.21
6.0	−1.77	13.21	−0.50	10.94
7.0	−0.13	1.08	−0.03	0.915

[a] Taken from ref.[16]; $EX^{(1)} = E_{exch}^{(10)} + \Delta_M$, where Δ_M denotes Murell's zeroth-order exchange term.

sets are closely related to the corresponding changes in the $E^{(R)}$(D) term. This regularity follows from a very little dependency of the first order $ES^{(1)}$(D) and $EX^{(1)}$(D) components determined consistently with the dimer basis set on its size and contraction scheme used even if the higher order contributions to the interaction energy are not properly accounted for. Somewhat to our surprise, very poor values for $E^{(R)}$(D), and as the result also ΔE_{SCF}(D), are obtained with the [31111111/22/2] 9*s* + 1*s* HP basis set for all of the internuclear distances assumed.

TABLE II
He_2 dispersion energy $E_{disp}^{(20)}$(D), CP(DISP) and BSSE(SCF) (in μH) for several different basis sets

R(He...He), a.u.	$E_{disp}^{(20)}$(D)	BSSE(SCF)	CP(DISP)[a]
	[61111/111/11] 10*s* of Rybak		
5.0	−101.92	−0.25	−7.00
5.6	−48.88	−0.22	−1.97
6.0	−31.16	−0.21	−0.82
7.0	−11.53	−0.15	−0.13
	[61111/22/2] 10*s* DP		
5.0	−101.16	−0.20	−6.43
5.6	−48.82	−0.21	−1.92
6.0	−31.21	−0.21	−0.88
7.0	−11.52	−0.14	−0.12
	[61111/22/2] 10*s* RP		
5.0	−101.86	−1.47	−6.89
5.6	−48.84	−1.32	−2.12
6.0	−31.22	−1.09	−0.98
7.0	−11.48	−0.70	−0.14
	[67111/22/3] 16*s* RP		
5.0	−102.09	−0.01	−7.13
5.6	−48.99	−0.01	−2.13
6.0	−31.24	−0.01	−0.93
7.0	−11.51	−0.01	−0.12

[a] CP(DISP) = $E_{disp}^{(20)}$(D) − $E_{disp}^{(20)}$(M).

TABLE III
Be_2 interaction energy components and $\Delta E_{SCF}(D)$ (in μH) for several different basis sets

R(Be...Be), a.u.	$ES^{(1)}$	$EX^{(1)}$	$E^{(R)}$	$\Delta E_{SCF}(D)$
		[6111111/111/11] 12*s* of Rybak		
4.0	−51.31	138.19	−55.92	30.96
5.0	−20.36	51.42	−20.58	10.21
6.0	−7.12	17.66	−6.36	4.18
7.0	−2.25	5.72	−1.81	1.66
		[6111111/22/2] 12*s* DP		
4.0	−51.30	138.17	−52.48	34.38
5.0	−20.63	51.54	−19.24	11.54
6.0	−7.12	17.66	−6.09	4.45
7.0	−2.25	5.71	−1.72	1.72
		[6111111/121/2] 12*s* DP		
4.0	−51.28	138.18	−57.71	29.19
5.0	−20.61	51.41	−21.11	9.69
6.0	−7.12	17.66	−6.46	4.08
7.0	−2.25	5.71	−1.82	1.64
		[1111111/22/2] 7*s* HP		
4.0	−51.31	138.08	−51.13	35.64
5.0	−20.61	51.38	−19.19	11.58
6.0	−7.10	17.66	−5.96	4.56
7.0	−2.24	5.71	−1.73	1.74
		[3111111/22/2] 9*s* HP		
4.0	−51.51	138.00	−55.09	31.44
5.0	−20.66	51.31	−20.65	10.00
6.0	−7.12	17.62	−6.14	4.41
7.0	−2.24	5.68	−1.83	1.61
		[3111111/22/3] 9*s* HP		
4.0	−51.39	138.12	−53.40	33.33
5.0	−20.59	51.37	−20.05	10.73
6.0	−7.08	17.62	−6.22	4.32
7.0	−2.24	5.69	−1.76	1.69

TABLE III
(*Continued*)

R(Be...Be), a.u.	$ES^{(1)}$	$EX^{(1)}$	$E^{(R)}$	ΔE_{SCF}(D)
		[31111111/22/2] 9*s* + 1*s* HP		
4.0	−51.43	138.15	−41.45	45.27
5.0	−20.60	51.42	−15.09	15.73
6.0	−7.09	17.67	−4.69	5.86
7.0	−2.25	5.71	−1.36	2.10
		[31111111/112/2] 10*s* HP		
4.0	−51.42	138.18	−54.96	31.80
5.0	−20.64	51.40	−20.19	10.57
6.0	−7.10	17.66	−6.22	4.34
7.0	−2.24	5.71	−1.78	1.69
		[8441111/22/2] 20*s* RP		
4.0	−51.96	139.13	−54.79	32.38
5.0	−21.01	52.04	−20.42	10.61
6.0	−7.22	17.97	−6.37	4.38
7.0	−2.31	5.83	−1.82	1.70

A similar behaviour is also observed for the dispersion energy (Table IV). Usually, diffuse functions are added to the energy-optimized atomic basis sets independently in the sense that they do not change the inner structure of the parent basis (orbital exponents and contraction coefficients remain unchanged). It is not the case in the polarized basis set approach adopted here; orbital exponents and contraction coefficients of the polarization functions are derived directly from corresponding ones of the initial isotropic set. Therefore, if the same size and contraction scheme are assumed for the polarized part in both the standard and diffuse augmented basis sets, as it is with [3111111/22/2] 9*s* HP and [31111111/22/2] 9*s* + 1*s* HP, their *p* and *d* shells may differ significantly. Hence, the four outermost orbital exponents in the standard 9*s* GTO basis of Huzinaga are 2.185, 0.859, 0.1807 and 0.05835, respectively, and they form the set from which *p* and *d* (the last two) contracted polarized set of 9*s* HP is generated. If a diffuse function is added, the polarized set of 9*s* + 1*s* basis is shifted toward smaller orbital exponents i.e. instead of a *p* orbital with the exponent of 2.185 another one appears with the exponent of 0.0189. As th result underestimated values of delocalization $E^{(R)}$ and dispersion energy terms are obtained, especially for shorter

TABLE IV
Be_2 dispersion energy $E_{disp}^{(20)}$(D), CP(DISP) (in μH) and BSSE(SCF) (in μH) for several different basis sets

R(Be...Be), a.u.	$E_{disp}^{(20)}$(D)	BSSE(SCF)	CP(DISP)[a]
	[6111111/111/11] 12*s* of Rybak		
4.0	−23.20	−1.17	−5.12
5.0	−11.72	−1.12	−2.37
6.0	−5.77	−1.10	−1.02
7.0	−2.82	−1.03	−0.41
	[6111111/22/2] 12*s* DP		
4.0	−21.71	−0.12	−4.70
5.0	−11.50	−0.12	−2.32
6.0	−5.90	−0.16	−1.09
7.0	−2.95	−0.27	−0.49
	[6111111/121/2] 12*s* DP		
4.0	−24.17	−0.47	−5.69
5.0	−12.18	−0.42	−2.85
6.0	−5.88	−0.32	−1.27
7.0	−2.82	−0.36	−0.52
	[1111111/22/2] 7*s* HP		
4.0	−23.13	−935.27	−5.29
5.0	−12.30	−540.53	−2.87
6.0	−6.16	−321.55	−1.34
7.0	−2.98	−224.30	−0.56
	[3111111/22/2] 9*s* HP		
4.0	−25.82	−7.97	−6.37
5.0	−13.44	−15.21	−3.89
6.0	−6.40	−14.46	−1.99
7.0	−2.89	−15.10	−0.89
	[3111111/22/3] 9*s* HP		
4.0	−24.07	−5.58	−9.73
5.0	−11.68	−7.54	−4.50
6.0	−5.23	−9.67	−4.44
7.0	−2.25	−12.01	−0.77

TABLE IV
(*Continued*)

R(Be...Be), a.u.	$E_{disp}^{(20)}$(D)	BSSE(SCF)	CP(DISP)[a]
	[31111111/22/2] 9*s* + 1*s* HP		
4.0	-13.50	-1.86	-5.24
5.0	-7.05	-1.97	-2.40
6.0	-3.73	-1.17	-1.14
7.0	-1.95	-1.23	-0.50
	[31111111/112/2] 10*s* HP		
4.0	-22.65	-31.72	-6.77
5.0	-11.84	-23.63	-2.83
6.0	-5.91	-19.33	-1.20
7.0	-2.90	-17.05	-0.47
	[8441111/22/2] 20*s* RP		
4.0	-22.42	-15.22	-5.42
5.0	-11.31	-27.62	-2.43
6.0	-5.61	-20.32	-1.01
7.0	-2.80	-25.22	-0.40

[a] See footnote in Table II.

internuclear distances (Tables III and IV). It seems that this shortcoming can be simply eliminated by adding the omitted large exponent orbital or by replacing the most diffuse function (with the orbital exponent of 0.0189) by a function with a higher exponent (2.185), for example. Indeed, in the later case we have obtained, respectively, -19.79, 11.00 and -11.23 μH for $E^{(R)}$, ΔE_{SCF}(D) and $E_{disp}^{(20)}$(D) at R = 5.0 a. u. Analysis of the results of calculations for the SCF interaction energy and its components as well as dispersion energy term for the model Be_2 system indicates that with the [6111111/121/2] 12*s* DP contracted polarized basis set even slightly better values of corresponding terms are obtained as compared with the dispersion energy refined [6111111/111/1] 12*s* basis set of Rybak of comparable size and concentration scheme. The results obtained with smaller 9*s* HP and 10*s* HP basis sets for the SCF contributions are worse but still of reasonable accuracy. It is interesting, that $E_{disp}^{(20)}$(D) values calculated with 9*s* HP and 7*s* HP basis sets better than those obtained with the property optimized 12*s* basis set of Rybak (Table IV). It should be noted that for the Be_2 system the SCF interaction energy suffers from the basis set superposition error very little

(note that values of BSSE(SCF) quoted in Table IV are given in microhartrees) whereas remarkably large counterpoise corrections CP(DISP) to the dispersion energy are found for all of the basis sets studied here. Even-tempered basis sets can be considered as an effective substitute of the energy-optimized ones. It seems, however, that their applicability for preparing the polarized basis sets is rather limited for systems larger than He_2. As it follows from our calculations for Be_2 in [8441111/22/2] 20*s* RP basis set with a rather large isotropic part, the obtained results are not better than those obtained with the less expensive [3111111/22/2] 9*s* HP.

CONCLUSION

It is found that the polarized basis set approach[6] seems to be an elegant and powerful tool for preparing medium-size contracted basis sets useful for calculations of the interaction energies at both the SCF and correlated levels. The results obtained for He_2 and Be_2 systems with polarized basis sets indicate their good performance in comparison with property-oriented optimized basis sets of comparable size. The values of dispersion energy for Be_2 obtained with even smaller polarized basis sets are superior to those calculated in property-oriented basis sets. As indicated above, the polarized basis set technique should be used with care and further studies on larger systems are strongly recommended.

The author wishes to thank Drs W. A. Sokalski and S. Roszak for illuminating discussions and Prof. H. Chojnacki for reading and commenting on the manuscript. The author is also grateful to Dr S. M. Colwell for making a copy of MICROMOL program[26] available.

REFERENCES

1. Davidson E. R., Feller D.: Chem. Rev. *86*, 681 (1986).
2. Hobza P., Zahradník R.: Chem. Rev. *88*, 871 (1988).
3. Chalasinski G., Gutowski M.: Chem. Rev. *88*, 943 (1988).
4. Huzinaga S., Klobukowski M., Tatewaki H.: Can. J. Chem. *63*, 1812 (1985).
5. Schmidt M. W., Ruedenberg K.: J. Chem. Phys. *71*, 3951 (1979).
6. Sadlej A. J.: Collect. Czech. Chem. Commun. *53*, 1995 (1988).
7. Roos B. O., Sadlej A. J.: Chem. Phys. *94*, 43 (1985).
8. Hobza P., Zahradník R.: *Weak Interactions in Chemistry and Biology*. Elsevier, New York 1980.
9. Rybak S.: *Ph.D. Thesis*. University of Warsaw, Warsaw 1988.
10. Gutowski M., van Duijneveldt F. B., Chalasinski G., Piela L.: Mol. Phys. *61*, 233 (1987).
11. van Duijneveldt F. B.: IBM Techn. Report, RJ945 (1971).
12. Huzinaga S.: J. Chem. Phys. *42*, 1293 (1965); Huzinaga S., Andzelm J., Klobukowski M., Radzio-Andzelm E., Sakai Y., Tatewaki H.: *Gaussian Basis Sets for Molecular Calculations*. Elsevier, New York 1984.
13. Sokalski W. A., Roszak S., Pecul K.: Chem. Phys. Lett. *153*, 153 (1988).
14. Kolos W.: Theor. Chim. Acta *51*, 219 (1979).
15. Gutowski M., van Duijneveldt F. B., Chalasinski G., Piela L.: Chem. Phys. Lett. *129*, 325 (1986).

16. Gutowski M., van Duijneveldt F. B., Chalasinski G., Piela L.: Mol. Phys. *61*, 233 (1987).
17. Boys S. F., Bernardi F.: Mol. Phys. *19*, 533 (1970).
18. Urban H., Hobza P.: Theor. Chim. Acta *36*, 215 (1975).
19. Gutowski M., Chalasinski G., van Duijneveldt-van de Rijdt J.: Int. J. Quantum Chem. *26*, 971 (1984).
20. Roszak S., Sokalski W. A., Hariharan P. C., Kaufman J. J.: Theor. Chim. Acta *70*, 81 (1986).
21. Chalasinski G., Jeziorski B.: Mol. Phys. *32*, 81 (1976).
22. Gutowski M., Verbeek J., van Lenthe J. H., Chalasinski G.: Chem. Phys. *111*, 271 (1987).
23. Harrison R. J., Handy N. C.: Chem. Phys. Lett. *123*, 321 (1986).
24. Lee Y. S., Bartlett R. J.: J. Chem. Phys. *80*, 4371 (1984).
25. Dykstra C. E., Schaefer III H. F.: J. Chem. Phys. *65*, 5141 (1977).
26. Amos R. D., Colwell S. M.: *MICROMOL 5, IBM PS/2 Version.* University of Cambridge, Cambridge 1988.