

Regular article

Relativistic atomic natural orbital type basis sets for the alkaline and alkaline-earth atoms applied to the ground-state potentials for the corresponding dimers

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Abstract. New basis sets of the atomic natural orbital (ANO) type have been developed for the atoms Li–Fr and Be–Ra. The ANOs have been obtained from the average density matrix of the ground states and the lowest excited states of the atom, the positive ion, and the dimer at its equilibrium geometry. Scalar relativistic effects are included through the use of a Douglas–Kroll Hamiltonian. Multiconfigurational wave functions have been used with dynamic correlation included using second-order perturbation theory (CASCF/CASPT2). The basis sets are applied in calculations of the ground-state potentials for the dimers. Computed bond energies are accurate to within 0.05 eV for the alkaline dimers and 0.02 eV for the alkaline-earth dimers (except for Be₂).

Keywords: Relativistic basis sets – Atomic natural orbitals – Douglas–Kroll – Complete-active-space self-consistent field/complete-active-space second-order perturbation theory

1 Introduction

A new general contraction scheme for Gaussian-type basis sets was suggested by Almöf and Taylor in 1987, the so-called atomic natural orbitals (ANOs) [1]. The idea was to obtain the contraction coefficients from correlated calculations on the atoms. The ANOs are chosen as the natural orbitals, which have an occupation number larger than a given threshold. Such orbitals will in an optimal way describe the atomic correlation effects, using the smallest possible number of basis functions. Their ordering after decreasing occupation number

implies that an extension of the basis set will include finer details of the atomic correlation effects.

However, the ANOs of Almöf and Taylor are based on singles and doubles configuration interaction (CI) calculations on ground-state atoms. Eventhough it was shown in some molecular test cases that the contraction errors were small in molecules like N₂ and H₂O, it is clear that such a procedure will favor the atoms. Higher angular momentum functions will describe atomic correlation effects more than polarization due to chemical bonding. In order to relax this bias to free atoms, Widmark and coworkers [2, 3, 4, 5] devised ANOs based on an average density matrix that was obtained from calculations on atoms in different electronic states, negative (or positive) ions, and also the atom in an electric field, in order to mimic molecular polarization. Two sets of basis functions were generated, one set, ANO-L, for the atoms H–Zn based on a larger number of primitives (14s9p4d3f for Li–Ne, 17s12p5d4f for Na–Ar, and 21s15p10d6f4g for Sc–Zn) [2, 3, 5] and one smaller set, ANO-S, for the atoms H–Kr [4]. These basis sets have since been used in a large number of applications. As with all general contraction schemes it is important to use an integral code that is effective in handling such basis functions, also when the number of primitive functions becomes large. SEWARD is such a code. It was developed with the specific aim to handle effectively general contractions [6]. This integral code together with the ALASKA [7] code for first and the MCKINLEY code [8] for second derivatives were developed for the quantum chemistry software MOL-CAS [9], but they are also used today with the MOL-PRO and ACES-II quantum chemistry codes.

Work has now started to construct a new ANO type basis set which can be considered as an extension and modification of the ANO-L set. The aim is to cover the entire periodic system with basis sets of the same quality. Here, we present results for the group Ia (Li–Fr) and group IIa (Be–Ra) elements. The inclusion of heavy elements, makes it necessary to include also relativistic effects in the basis set generation. This was done here

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using the Douglas–Kroll Hamiltonian [10, 11], which makes it possible to introduce the scalar relativistic effects in a basically nonrelativistic formulation. Another feature which needs to be taken into account for heavier elements is correlation of the semicore electrons. This is particularly important for the Ia and IIa elements. Consequently, these electrons are included in the correlation treatment and basis functions, which include such effects, are generated. By necessity, such basis sets will be larger and are not so easily labeled as single-double-zeta, etc. Polarization functions for the ANO-L and ANO-S basis sets were constructed by including in the density-averaging calculations on the atom in an external electric field. This procedure leads to polarization functions that are somewhat diffuse. Here, we have instead included in the calculation not only the atom but also the dimer and extracted the contraction coefficients from a density matrix that is a linear combination of atomic densities (50%) and the atomic density in the dimer at its equilibrium geometry (50%).

Multiconfigurational wave functions have been used (complete-active-space self-consistent held CASSCF) with the most important orbitals in the active space and dynamic correlation treated using complete-active-space second-order perturbation theory (CASPT2) [12, 13, 14]. This approach was used because it is general and can be applied to all electronic states and also to the dimers without loss of accuracy. A multireference CI method might have been preferable, since it is variational. The increased computational costs would, however, have been prohibitive, in particular for the calculations on the dimers in the uncontracted basis set.

In the following we present first the general features of the new basis sets and some results obtained for the atoms. We then present the ground-state potentials for all corresponding homonuclear dimers. The actual basis sets are available in the MOLCAS basis set library (www.teo-kem.lu.se/MOLCAS) under the heading ANO-RCC.

2 Primitive basis sets and density averaging

The sets of primitive Gaussian functions chosen are presented in Table 1. For atoms Li, Be, Na, and Mg, the

Table 1. Size of the primitive basis sets and the contraction range

Atom	Primitive	Contraction range
Alkaline atoms		
Li	14s9p4d3f	2s–8s7p4d2f
Na	17s12p5d4f	3s1p – 9s8p5d4f
K	21s16p5d4f	4s2p – 10s9p5d3f
Rb	23s19p11d4f	5s3p1d – 10s10p5d4f
Cs	26s22p15d4f	6s4p2d – 12s10p8d4f
Fr	28s25p17d12f	7s5p3d1f – 12s11p8d5f
Alkaline earth atoms		
Be	14s9p5d2f	2s – 9s8p5d2f
Mg	17s12p6d2f	3s1p – 9s8p6d2f
Ca	20s16p6d2f	4s2p – 10s9p6d2f
Sr	23s19p12d4f	5s3p1d – 11s10p7d4f
Ba	26s22p15d4f	6s4p2d – 12s10p8d4f
Ra	28s25p17d12f	8s6p3d1f – 12s11p8d5f

ANO-L primitives were used. The primitives for the other atoms were based on the Faegri set [15]. The s- and p sets were extended with more diffuse functions in an even-tempered way. For atoms Li–Ca, exponents for d-type functions were optimized for core correlation and additional diffuse functions were added. For the heavier elements, the d-sets were extended using even-tempered exponents. Exponents for the f-type functions were obtained from the most important d-type functions by using a scale factor of 4/3.

Calculations with the primitive basis set performed for each atom in its ground state and in the lowest $s \rightarrow p$ excited state (2P for the Ia elements and 3P for IIa). For Cs, Ba, Fr, and Ra the $s \rightarrow d$ excited state was also included. In addition, calculations were performed around the minimum geometry for the dimer and the CASPT2 orbitals obtained at the geometry closest to equilibrium were used in the contraction. The average density matrix was constructed as

$$\rho_{av} = \sum_i \omega_i \rho_i, \quad (1)$$

where ρ_i are the density matrices obtained from the different CASPT2 wave functions. The weights ω_i were taken as 0.5 for the dimer and $0.5/n$ for each of the n atomic states (3 or 4). The final ANOs were obtained as the eigenfunctions of ρ_{av} . All orbitals with occupation numbers larger than 10^{-6} were kept in the final basis set. This give the maximum sizes given in Table 1. The calculations were performed using the GENANO utility of the MOLCAS program system.

3 The alkaline atoms and dimers

3.1 The atoms Li–Fr

The group Ia elements were treated with one active orbital (s , p , or d), or none for the positive ion. The active space used for the dimer included the s and p orbitals on each atom. The $1s$ electron pair was correlated for Li and Be, while the $(n-1)s$ and $(n-1)p$ electrons were correlated for the heavier elements. The dimer was not included in the generation of the basis set for Fr. Instead a calculation was performed on the ground-state atom in an electric field of 0.001 au.

We present Table 2 results for excitation and ionization energies obtained with the largest contracted set (cf. Table 1). A direct comparison with experiment is somewhat hampered by the inherent error in the CASPT2 approximation to the dynamic correlation effects. We note that the error in the computed excitation energies are a few hundredth of an electron volt. The error for the 2D state is somewhat larger owing to lack of very diffuse d-type functions in the basis sets. It was not found meaningful to include more functions of this type because they will be of less importance in molecular applications. The difference between the CASSCF and CASPT2 results shows the importance of core–core and core–valence correlation for the ionization energies. It increases from 0.04 eV for Li to about 0.4 eV for the heaviest elements. These effects are only included with

Table 2. Calculated and experimental excitation and ionization energies (electronvolts) for the alkaline atoms. Experimental data within *parentheses*. Experimental data from Ref. [24] averaged over the J quantum number

Atom	2P (CASPT2)	2D (CASPT2)	1S (CASSCF)	1S (CASPT2)
Li	1.850(1.845)		5.342	5.381(5.390)
Na	2.094(2.103)		4.957	5.117(5.137)
K	1.645(1.614)		4.020	4.313(4.339)
Rb	1.591(1.579)		3.799	4.146(4.176)
Cs	1.398(1.432)	1.891(1.804)	3.473	3.826(3.893)
Fr	1.559	2.064	3.535	3.929(3.942)

rather large basis sets. For example, the basis set 5s4p1d gives an Ionization Potential (IP) for K of 4.18 eV, which is in error by 0.16 eV. With the largest basis sets the error in the computed IP varies between 0.01 and 0.06 eV at the CASPT2 level. A plot of the IPs as a function of the atomic number is given in Fig. 1. At first the IP decreases with increasing atomic number, but for the heavier elements the curve flattens out and finally increases slightly. This is an effect of the relativistic contraction of the s orbital with increasing atomic number.

3.2 The dimers Li_2 – Fr_2

We first attempted to generate the present basis sets using only results from calculations on the free atoms. The results were then used for the dimers. For Li_2 we obtained a binding energy of 0.848 eV using the contracted set 5s4p2d. The experimental value is 1.046 eV [16]. We first suspected that the error was due to the use of the CASPT2 approximation, but a recalculation using the primitive basis set gave a binding energy of 1.024 eV, only 0.022 eV smaller than experiment. It was clear that something else was wrong. Inspection of the ANOs showed that those with the larger occupation numbers were core-correlating orbitals. Because only

atomic calculations had been performed, the basis sets included polarization functions only when the contracted set became very large. It was concluded that molecular calculations should be included in the generating set of densities. Thus, calculations were performed for all dimers around the equilibrium geometry using the primitive basis set. The density obtained at the point closest to the equilibrium distance was included in the generating set together with the atomic densities. The weight factor 0.5 was used for the dimer density. These calculations became rather time-consuming for the heavier elements; therefore, no attempt was made to generate full potential curves with the primitive basis sets, and for Fr the diatomic calculation was replaced by a calculation on the atom in an electric field.

The recalculation of the potential curve for Li_2 with the ANOs generated including the dimer density and using the same 5s4p2d contraction gave a binding energy of 1.006 eV. The contraction error was reduced to 0.018 eV. Some molecular constants for this and the other alkaline dimers can be found in Table 3. The calculations were performed with an active space including the atomic ns and np orbitals. The basis set superposition error (BSSE) was treated using full counterpoise. Large contracted sets were used in all cases, so the contraction error is small with negligible effects of BSSE. The remaining errors are due to limitations in the primitive

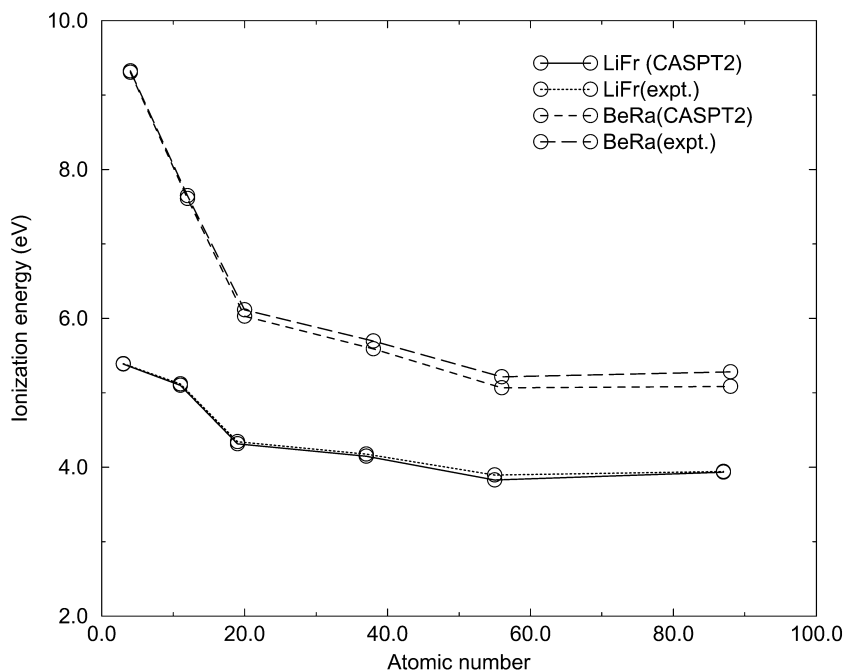


Fig. 1. The ionization energies for the alkaline and alkaline-earth atoms as a function of the atomic number

Table 3. Calculated and experimental spectroscopic constants for the alkaline dimers. Results obtained at the complete-active-space second-order Perturbation theory (CASPT2) level of theory including basis set superposition error (BSSE). Experimental data within parentheses

Dimer	Contraction	R_e (Å)	D_0 (eV)	ω_e (cm ⁻¹)
Li ₂	5s4p2d	2.681(2.673)	1.006(1.046)	351(351) ^a
Na ₂	6s6p3d1f	3.105(3.078)	0.717(0.720)	157(159) ^a
K ₂	9s9p4d3f	3.905(3.905)	0.454(0.510)	89(92) ^a
Rb ₂	10s9p5d3f	4.217(4.213)	0.434(0.491)	57(58) ^b
Cs ₂	12s10p8d4f	4.692(4.648)	0.438(0.450)	42(42) ^c
Fr ₂	12s11p8d5f	4.665	0.407	33

^aRef. [16]

^bRef. [17]

^cRef. [18]

basis set, in particular the lack of higher angular momentum functions, and of course the use of the CASPT2 approximation. Computed dissociation energies are accurate to about 1 kcal mol and distances to about 0.02 Å, except for Cs₂, where the error is somewhat larger. The computed ω_e values show that the potential curves are well described in the neighborhood of the equilibrium geometry. It should maybe be emphasized that these calculations merely serve as illustrations. They have not been pushed to the limit. We notice that all bond distances are larger than the experimental values and the bond energies are smaller. Increased basis sets are thus likely to lead to better agreement with experiment.

The experimental data for Rb₂ and Cs₂ were taken from the very extensive accurate experimental information compiled by Amiot [17, 18]. The present rovibrational data were obtained by a numerical solution of the Schrödinger equation for the nuclear motion, using the VIBROT program in MOLCAS. Thus, we can make a direct comparison of computed G_v values with the experimental data. This comparison is made in Table 4 for $v = 1 - 9$. The agreement is surprisingly good, which shows that even if the computed bond energies and bond distances are not perfect, the shape of the potential curves around the minimum is accurate. We have added the corresponding data for Fr₂ in Table 4 even though it is not likely that this elusive molecule will ever be studied. Notice that the computed bond distance for Fr₂ is

Table 4. Calculated and experimental G_v values (reciprocal centimeters) for the heavier alkaline dimers. Results obtained at the CASPT2 level of theory including BSSE. Experimental data within parentheses. Experimental data from Ref. [17] (Rb₂) and Ref. [18] (Cs₂)

v	Rb ₂	Cs ₂	Fr ₂
0	28.74(28.83)	21.03(20.98)	16.45
1	86.01(86.34)	62.95(62.84)	49.28
2	142.94(143.55)	104.68(104.53)	81.99
3	199.51(200.50)	146.24(146.06)	114.55
4	255.72(257.15)	187.61(187.42)	146.93
5	311.56(313.53)	228.77(228.61)	179.11
6	367.03(369.61)	269.68(269.64)	211.08
7	422.13(425.41)	310.33(310.49)	242.82
8	476.84(480.92)	350.70(351.18)	274.30
9	531.16(536.14)	390.77(391.71)	305.52

shorter than for Cs₂, while the bond energy is still decreasing. We attribute this effect to the relativistic contraction of the s orbital.

4 The alkaline-earth atoms and dimers

The group IIa elements give quite different computational problems than the group Ia elements. It is well known that a large fraction of the valence correlation is covered by the $ns^2 \rightarrow np^2$ excitation (95% for the Be atom). Thus, the np shell has to be included in the active space. The dimers constitute an additional problem. It was shown in a recent paper by Martin [19] that an accurate description of the Be dimer required a large active space including both the $2s, 2p$ and $3s, 3p$ shells. The binding energy was also shown to converge very slowly with the basis set. The reason for this is an avoided crossing between the $2s^2 + 2s^2$ van der Waals curve and the $2s2p_z + 2s2p_z$ “covalent” curve. The present dimer calculations were therefore performed with 16 active orbitals for all dimers, even if it may be assumed that van der Waals curve will dominate the potential for the heavier dimers.

4.1 The atoms Be–Ra

We present Table 5 results for excitation and ionization energies obtained with the largest contracted set (cf. Table 1). The corresponding states were included in the density averaging together with results for the dimers, except for Ra, where instead the atom in an electric field was used to generate the polarization functions. The errors in the excitation energy to the ³P state are all smaller than 0.05 eV, while the computed ³D excitation energies for Ba and Ra are too large, again because of the lack of enough diffuse d -type functions. The computed ionization energies are all smaller than the experimental values. The error goes from 0.02 eV for Be to 0.17 eV for Ra. We notice that the CASSCF results are even smaller, showing that there is an appreciable effect of core–core and core–valence correlation on the IPs. It is likely that the lack of higher polarization functions is the reason for the increased error for the heavier atoms. The effect of core correlation increases from 0.06 eV for Be to about 0.3 eV for Ra. Again, we

Table 5. Calculated and experimental excitation, ionization energies (electron volts), and polarizabilities (atomic units) for the alkaline-earth atoms. Experimental data within *parentheses*

Atom	$^3P(\text{CASPT2})^a$	$^3D(\text{CASPT2})^a$	$^2S(\text{CASSCF})$	$^2S(\text{CASPT2})^a$	Polarizability ^b
Be	2.776(2.725)		9.238	9.299(9.320)	37.2(37.8)
Mg	2.752(2.714)		7.471	7.611(7.644)	70.9(71.5)
Ca	1.903(1.892)		5.867	6.044(6.111)	163(169)
Sr	1.816(1.823)		5.394	5.612(5.692)	210(186)
Ba	1.591(1.622)	1.259(1.166)	4.867	5.089(5.210)	312(268)
Ra	1.850(1.908)	1.807(1.769)	4.829	5.110(5.277)	283(259)

^aExperimental data from Ref. [24] averaged over the J quantum number

^bExperimental data from the compilation in Ref. [20] (for Ca, see Ref. [21])

emphasize that these effects will only be included with rather large basis sets. As can be seen in Fig.1, the IPs for the alkaline-earth atoms show the same trends as the alkaline atoms did: first a sharp decrease of the energy with increasing atomic number, then a flat region and finally a slight increase for Ra. Again, the reason is the competition between the increased shell number and the relativistic contraction of the ns orbital.

We present in Table 5 computed values for the static electric polarizabilities of the atoms. They were obtained at the CASPT2 level of theory using finite-field perturbation theory. The experimental data were taken from the compilation of Nagle [20]. These data are, however, quite uncertain for the heavier atoms. For example, Nagle quotes the value 154 au for the Ca atom, which is smaller than the computed value, 163 au. A newer measurement gives, however, the value 169 au, which is much closer to the theoretical estimate [21]. It is not unlikely that the experimental data for the heavier atoms also need to be modified. We notice that the relativistic contraction makes the polarizability for Ra smaller than that of Ba. This is also true for the experimental values, even if they are all smaller than the theoretical estimates for Sr, Ba, and Ra.

4.2 The dimers Be_2 – Ra_2

As already mentioned, the calculation of accurate potential curves for the alkaline-earth dimers is a demanding task, which requires a very careful treatment of the dynamic correlation energy and extensive basis sets. The basis sets presented here are not large enough to come close to the basis set limit. They would have to be complemented with higher-order angular momentum functions both in the valence and core regions. Still, we computed the potential curves for the dimers using the largest contracted sets and an active space consisting of two sets of s, p orbitals on each atom (four electrons in 16 orbitals). The importance of the second set of s, p orbitals is nicely illustrated in Fig. 2, which shows the potential curves for the Be dimer with 8 and 16 active orbitals, respectively.

The eight-orbital calculation gives a double minimum, one outer, corresponding to the dispersion interaction, and one inner, which gives the “covalent” bonding. The outer minimum is, however, deeper, leading to a very long and weak bond, with a bond energy smaller than 0.01 eV. Addition of the second s, p shell increases the strength of the “covalent” bond

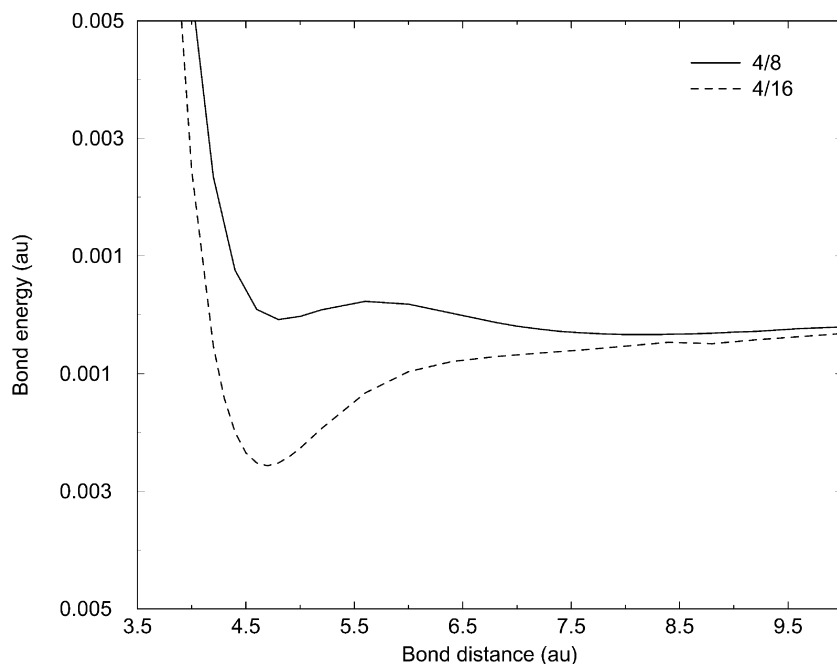


Fig. 2. Computed potential curves (Complete-active-space second order perturbation theory) for the beryllium dimer using two different active spaces. The *full curve* obtained with four electrons in eight orbitals ($2s, 2p$), the *dashed curve* with four electrons in 16 orbitals ($2s, 2p, 3s, 3p$)

Table 6. Calculated and experimental spectroscopic constants for the alkaline-earth dimers. Results obtained at the CASPT2 level of theory including BSSE. Experimental data within *parentheses*

Dimer	Contraction	R_e (Å)	D_0 (eV)	ω_e (cm ⁻¹)
Be ₂	7s6p4d2f	2.484(2.47)	0.070(0.12)	180(224) ^a
Mg ₂	9s8p6d2f	4.012(3.89)	0.039(0.05) ^b	45
Ca ₂	10s9p6d2f	4.449(4.28)	0.109(0.13) ^c	55
Sr ₂	11s10p7d4f	4.772(4.45)	0.111(0.13) ^d	36
Ba ₂	12s10p8d4f	5.100(4.87)	0.141(0.20) ^e	31
Ra ₂	12s11p8d5f	5.478	0.079	17

^aRef. [19]

^bRef. [22]

^cRef. [25]

^dRef. [26]

^eTheoretical estimates from Ref. [23]

considerably and gives with the present basis set a binding energy of 0.07 eV, which is still 0.05 eV smaller than the estimate reported by Martin [19], even though it is closer to the first experimental estimate, 0.098 eV, given by Bondybey [22]. Comparing the ω_e value computed here, 180 cm⁻¹, with Martin's estimate, 224 cm⁻¹, and the experimental value 223.8 cm⁻¹, indicates strongly that the bond energy given by Martin is accurate. The present error is clearly dominated by the basis set, as analyzed by Martin. His CAS(4/16) averaged coupled pair functional calculation with a corresponding basis set gives a bond energy of about 0.09 eV. We can thus attribute about half of the error to the basis set and half to the CASPT2 approximation.

For the heavier atoms, the dimerization energy will be more and more dominated by the dispersion interaction. The "covalent" contribution can, however, not be neglected. For example, a calculation for Ca₂ with eight active orbitals gives a binding energy of 0.08 eV, while the result with 16 active orbitals is 0.11 eV. The results for all the dimers is presented in Table 6.

The experimental data for the heavier dimers are somewhat uncertain. For Ba, the only estimates available are based on theoretical calculations using a relativistic pseudopotential, which are not likely to be more accurate than the present results [23]. We have not found any information (experimental or theoretical) on the radium dimer. The experimental data available seem to indicate that the present bond energies are about 0.02 eV too small. The effect of this error on the bond distance is, of course, appreciable (0.1–0.3 Å) because of the small total bond energy.

5 Conclusions

New basis sets of the ANO type have been generated for the group Ia and IIa elements. Scalar relativistic effects were included using the Douglas–Kroll Hamiltonian (notice that this implies that the basis sets should be used with a nonrelativistic Hamiltonian). The basis sets were generated using an average atomic density where 50% comes from calculations on the free atom and the positive ion, and the remaining 50% from calculations on the dimer. The basis sets includes up to f-type functions, but can, of course, easily be extended with

higher angular momentum components. The CASSCF/CASPT2 method was used to generate the densities. Calculations were performed on all the dimers as an illustration of the accuracy that may be obtained.

The new basis sets will be named ANO-RCC in the MOLCAS basis set library. They can be obtained from the MOLCAS homepage (www.teokem.lu.se/MOLCAS) or by contacting one of the authors.

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