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# Main Group Atoms and Dimers Studied with a New Relativistic ANO Basis Set

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New basis sets of the atomic natural orbital (ANO) type have been developed for the main group and rare gas atoms. The ANO's have been obtained from the average density matrix of the ground and lowest excited states of the atom, the positive and negative ions, 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 (CASSCF/CASPT2). The basis sets are applied in calculations of ionization energies, electron affinities, and excitation energies for all atoms and the ground-state potentials for the dimers. These calculations include spin−orbit coupling using the RASSCF State Interaction (RASSI-SO) method. The spin−orbit splitting for the lowest atomic term is reproduced with an accuracy of better than 0.05 eV, except for row 5, where it is 0.15 eV. Ionization energies and electron affinities have an accuracy better than 0.2 eV, and atomic polarizabilities for the spherical atoms are computed with errors smaller than 2.5%. Computed bond energies for the dimers are accurate to better than 0.15 eV in most cases (the dimers for row 5 excluded).

## 1. Introduction

This report is part of an ongoing effort to develop a new set of AO basis sets for molecular calculations. The aim is to cover the entire periodic system with basis sets of the same quality.We have recently presented results for the group Ia (Li−Fr) and group IIa (Be−Ra) elements.[1] Here we continue to explore the periodic table and present the basis sets for the main group (IIIa−VIIa) and rare gas elements (VIIIa). The basis sets are of the ANO type, as was originally suggested by Almlöf and Taylor in 1987.[2] They can be considered as an extension of the so-called ANO-L basis sets developed by Widmark and coworkers[3−5] for the first- and second-row atoms and the first-row transition metals. These basis sets were developed using average density matrices obtained from CI calculations on ground and excited states of the atom, the positive and negative ions, and the atom in an electric field (to obtain polarization functions).

The extension to heavy elements in the new basis sets makes it necessary to include relativistic effects also in the basis set generation. This has been done here using the Douglas−Kroll Hamiltonian,[6,7] which makes it possible to add 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. Consequently, such electrons are included in the correlation treatment, and basis functions that include such effects are generated. Polarization functions for the ANO-L 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%). Such a procedure is too cumbersome for row 5 elements (Tl−Rn). For them we have used the atom in an electric field for the generation of polarization functions. Multiconfigurational wave functions have been used (CASSCF) with the most important orbitals in the active space, and dynamic correlation treated using second-order perturbation theory (CASPT2).[8−10] 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, because 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. All CASPT2 calculations were performed with the so-called gl correction to the zeroth-order Hamiltonian, to correct for the systematic error in the CASPT2 method[11] for systems with many open shells. For the main group elements it is also important to include the effects of spin−orbit coupling in the calculations. The basis sets were generated without such effects, but the test calculations performed on the atoms, ions, and dimers with the new basis sets include spin−orbit coupling. The newly developed RAS State Interaction (RASSI-SO) method was used for this purpose.[12]

Below, we shall present first the general features of the new basis sets and some results obtained for the atoms. We shall then also present the ground-state potentials for the homonuclear dimers. The dimers for row 5 present special problems due to the strong spin−orbit effects and results for them will be presented separately. The actual basis sets will be available in the MOLCAS basis set library under the heading ANO−RCC (for directions go to http://www.teokem.lu.se/MOLCAS).

Relativisitc effects in heavy element systems have been studied for some time now and the literature on the subject is steadily growing. Many of the results obtained here have also been obtained in earlier work by different authors. It would be impossible to attempt to quote all these earlier papers on the different atoms and diatomics. Many of them are using effective core potentials, whereas this work is based on an all-electron

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**TABLE 1: Size of the Primitive Basis Sets and the Contraction Range**

| atoms | primitive | contraction range |
|---|---|---|
| B−Ne | 14s9p4d3f2g | MB-DZP-TZP-QZP-9s8p5d3f2g |
| Al−Ar | 17s12p5d4f2g | MB-DZP-TZP-QZP-9s9p5d3f2g |
| Ga−Kr | 20s17plld5f2g | MB-DZP-TZP-QZP-10s9p8d5f2g |
| In−Xe | 22sl9p13d5f3g | MB-DZP-TZP-QZP-l0s9p8d5f3g |
| Tl−Rn | 25s22p16d12f4g | MB-DZP-TZP-QZP-1lsl0p9d6f4g |

basis set. A general reference would be ref 13 and other articles in the same book.

## 2. Primitive Basis Sets and Density Averaging

The chosen sets of primitive Gaussian functions are presented in Table 1. For first- and second-row atoms the ANO-L primitives were used. The primitives for the other atoms were based on the Faegri primitive sets.[14] They were extended with more diffuse functions in an even-tempered way. Higher angular momentum functions were added and exponents were optimized for the ground-state atoms (at the CASPT2 level of theory) using an even-tempered extension with a ratio of 0.4.

Calculations with the primitive basis set were performed for each atom in its ground state ($(ns)^2(2p)^x$, high spin); one excited state ($(ns)^1(2p)^{x+1}$ or $(ns)^2(2p)^x$, low spin); the positive ion; and the negative ion (except for nitrogen and the rare gases). 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. This procedure was not practical for row 5 atoms. Instead, the atom was placed in an electric field of strength 0.01 au. An average density matrix was constructed as

$$\rho_{\text{av}} = \sum_i \omega_i \rho_i \tag{1}$$

where $\rho_i$ are the density matrixes obtained from the different CASPT2 wave functions. The weights $w_i$ were taken as 0.5 for the dimer and 0.5/$n$ for each of the $n$ atomic states. The final ANO's were obtained as the eigenfunctions of $\rho_{\text{av}}$. All orbitals with occupation number larger than $10^{-6}$ were kept in the final basis set. This gives the maximum sizes shown in Table 1. The calculations were performed using the GENANO utility of the MOLCAS program system.[15]

Correlation of semi-core electrons was applied as follows: B(ls), Al(2p), Ga, Ge(3d), In−Xe(4d), Tl−Rn(5d). Because the basis sets have been constructed including such correlation effects, semicore correlation should also be included when the basis set is used. In particular, one should note that correlation functions of f- and g-type have been optimized with large exponents. Other core electrons are described with minimal basis set quality and should not be included in any correlation treatment, because that could cause large basis set superposition errors (BSSE). All calculations have been performed with the s- and p-orbitals active (four active orbitals for the atoms and eight for the diatoms).

## 3. Ionization Energies, Electron Affinities, and Excitation Energies for the Atoms

In this section we shall present results for the free atoms obtained with the largest contracted basis sets. These results are a test not only of the basis sets but also of the computational approach adopted in this study, the CASSCF/CASPT2 method. They are not aiming at spectroscopic accuracy but should rather be considered as calibration data for the molecular calculations that these basis sets are constructed for.

**3.1. Spin−Orbit Coupling.** The electronic structures of the heavier main group elements show the largest effect of spin−orbit coupling (SOC) in the entire periodic system. The spin-orbit splitting of the lowest term ($^2$P) in the astatine atom (At) is as large as 20 000 cm$^{-1}$ (2.5 eV). Calculations on systems comprising such atoms must therefore include these effects. Here they are included by using the newly developed RASSI-SO code in MOLCAS.[12] In this approach, spin−orbit coupling is introduced a posteriori by letting a set of CASSCF wave functions mix under the influence of a spin−orbit Hamiltonian, which is approximated as an effective one-electron operator (for details see ref 12). Dynamic correlation effects are included by shifting the diagonal elements of the SOC Hamiltonian to the CASPT2 energies. This approach has been shown to give results of chemical accuracy in a number of earlier studies. Whether the approach will work satisfactorily in the extreme case of the heavier main group atoms will be investigated in the present report. One would not expect so, because the approach does not take into account the effect of SOC on the shape of, in particular, the p shell orbitals. As will be shown below, this effect is only of chemical significance for the last-row atoms, and even there the errors in computed relative energies are not larger than about 0.1 eV.

The spin−orbit effects are computed by including in the SOC Hamiltonian matrix all terms arising from the electronic configuration $(ns)^2(np)^x$, where $n = 2-6$ and $x = 1-5$. In Table 2 we present the results obtained for the spin−orbit splitting of the lowest term in each of the atoms (except of course group Va with the $^4$S ground state). An overview of the results is also presented in Figure 1.

The strength of the SOC increases about 1 order of magnitude for each row and also along each row, reflecting the strong

**TABLE 2: Spin−Orbit Splitting (eV) of the Lowest Term in the Main Group Atoms (Experimental Values in Parentheses[a])**

| $\Delta J$ | B($^2$P) | Al($^2$P) | Ga($^2$P) | In($^2$P) | Tl($^2$P) |
|---|---|---|---|---|---|
| 3/2−1/2 | 0.0018 (0.0020) | 0.013 (0.014) | 0.099 (0.102) | 0.261 (0.274) | 0.893 (0.966) |
| $\Delta J$ | C($^3$P) | Si($^3$P) | Ge($^3$P) | Sn($^3$P) | Pb($^3$P) |
| 1−0 | 0.0019 (0.0020) | 0.0082 (0.0096) | 0.060 (0.069) | 0.179 (0.210) | 0.826 (0.970) |
| 2−0 | 0.0055 (0.0054) | 0.0240 (0.0277) | 0.154 (0.175) | 0.378 (0.425) | 1.195 (1.320) |
| $\Delta J$ | O($^3$P) | S($^3$P) | Se($^3$P) | Te($^3$P) | Po($^3$P) |
| 1−2 | 0.0186 (0.0197) | 0.0460 (0.0492) | 0.229 (0.246) | 0.537 (0.589) | 1.134 (0.935) |
| 0−2 | 0.0277 (0.0281) | 0.0673 (0.0711) | 0.302 (0.315) | 0.600 (0.584) | 1.817 (2.087) |
| $\Delta J$ | F($^2$P) | CI($^2$P) | Br($^2$P) | I($^2$P) | At($^2$P) |
| 1/2−3/2 | 0.050 (0.050) | 0.102 (0.109) | 0.422 (0.457) | 0.863 (0.942) | 2.517 (−) |

[a] From Moore's tables.[28]

**TABLE 3: Atomic Ionization Energies (eV)[a]**

| B | C | N | O | F | Ne |
|---|---|---|---|---|---|
| 8.10 (8.10)<br>8.30 | 11.05 (11.05)<br>11.26 | 14.39 (14.39)<br>14.54 | 13.32 (13.36)<br>13.62 | 17.26 (17.27)<br>17.42 | 21.59 (21.61)<br>21.56 |
| Al | Si | P | S | Cl | Ar |
| 5.78 (5.79)<br>5.98 | 7.99 (8.01)<br>8.15 | 10.43 (10.46)<br>10.49 | 10.13 (10.13)<br>10.36 | 12.76 (12.77)<br>13.01 | 15.62 (15.66)<br>15.75 |
| Ga | Ge | As | Se | Br | Kr |
| 5.96 (5.91)<br>6.00 | 7.90 (7.91)<br>7.90 | 9.79 (9.90)<br>9.81 | 9.47 (9.39)<br>9.75 | 11.57 (11.62)<br>11.81 | 13.82 (14.22)<br>14.00 |
| In | Sn | Sb | Te | I | Xe |
| 5.80 (5.62)<br>5.79 | 7.37 (7.39)<br>7.34 | 8.69 (9.22)<br>8.64 | 8.80 (8.61)<br>9.01 | 10.30 (10.45)<br>10.45 | 12.01 (12.37)<br>12.13 |
| Tl | Pb | Bi | Po | At | Rn |
| 6.08 (5.47)<br>6.11 | 7.31 (7.12)<br>7.42 | 7.37 (8.87)<br>7.29 | 8.29 (8.21)<br>8.43 | 9.13 (9.92)<br>9.54 | 10.58 (11.69)<br>10.75 |

[a] The values within parenthesis have been obtained without inclusion of spin−orbit coupling. Experimental values are given in the second row.[b]
[b] From Moore's tables.[28]

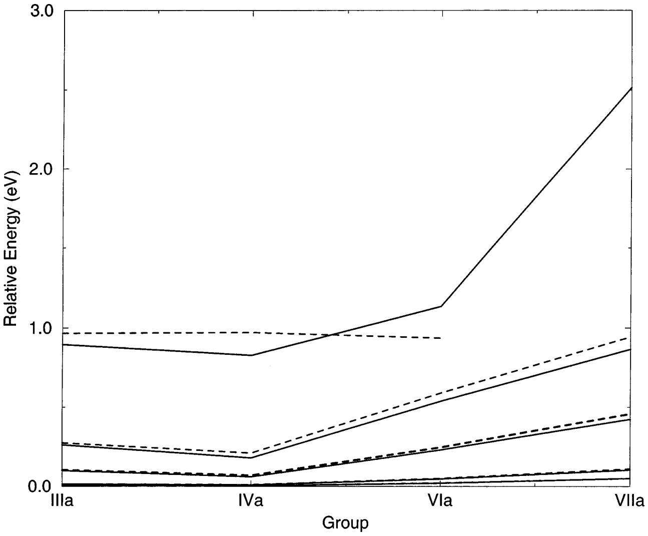

**Figure 1.** Spin−orbit splitting (eV) in the lowest term of the main group atoms: solid lines, computed values; dashed lines, experiment.[28] From bottom up: rows 1−4.

dependence on the nuclear charge. The calculations reproduce these changes well with errors in computed relative energies in most cases less than 10%. Only for row 5 will the maximum error become larger than 0.1 eV (0.199 eV for Po). The stabilization of the lowest level is only a fraction of the spin−orbit splitting. We conclude that the effect on such molecular quantities as binding energies can be well reproduced using the RASSI methodology with the largest uncertainty for chemical bonds involving row 5 atoms. However, it is clear that chemical bonds involving main group elements heavier than chlorine cannot be studied with quantitative accuracy without invoking the effects of spin−orbit coupling.

**3.2. Ionization Energies.** The first ionization energy of the atoms are computed from the lowest level of the neutral atom to the lowest level of the ion. The largest contracted set has been used (cf. Table 1), except that no g-type functions were used for first-row atoms. The results are presented in Table 3 and in Figure 2.

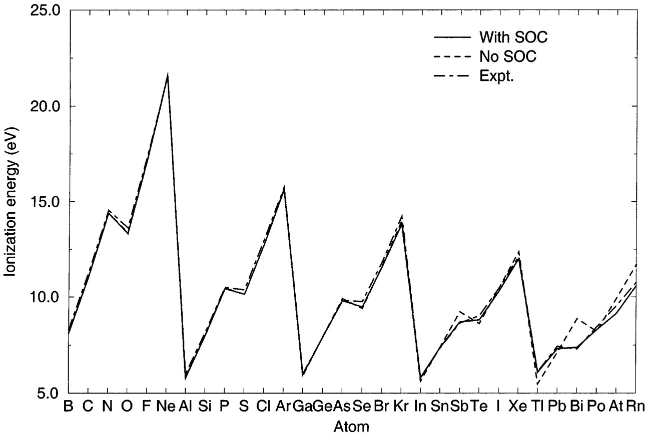

**Figure 2.** Ionization (eV) energies for main group atoms. Computed IPs with and without the inclusion of spin−orbit coupling are shown together with the experimental data.

Let us first take a look at the overall accuracy. The largest error (0.41 eV) occurs for the astatine atom. This is certainly due to an inadequate treatment of the spin−orbit coupling effects. As pointed out above, the splitting of the $^2$P term is computed to be 2.52 eV. The corresponding values for At$^+$ is 1.39 and 2.59 eV for $\Delta J = 2$ and 1, respectively. The experimental values are not known, but it may be assumed that the error is of the order of a few tenths of an electronvolt. Apart from this rather extreme case, the largest errors occur for group Va with oxygen as the worst case, with an IP that is 0.30 eV too small. A calculation with the two g-type functions added to the basis set reduces the error to 0.24 eV, about the same as for the heavier elements in this group. The error is most certainly due to the CASPT2 treatment of the correlation effects. The approach has a small systematic error, which leads to too low energies for systems with many open shells. One would therefore expect a too large IP for group IIa−Va elements and a too small IP for groups VIa−VIIa. Most of the IPs are, however, too low, which is an indication that even with these rather extensive basis sets we have not reached the converged limit for the lighter elements. The effect of g-type functions on the result for the oxygen atom is an illustration if this.

Figure 2 gives a nice illustration of how the IPs vary along the series of atoms. It shows the extra stability of the closed and half-closed shells. We notice that the extra stability of the half-closed shell remains through all atoms only for the results obtained without spin−orbit coupling. Inclusion of this effect

**TABLE 4: Atomic Electron Affinities (eV)**[a]

| B | C | N | O | F |
|---|---|---|---|---|
| 0.03 (0.03) | 1.07 (1.07) | 0.00 (0.00) | 1.38 (1.38) | 3.54 (3.54) |
| 0.28 | 1.26 | 0.00 | 1.46 | 3.40 |
| Al | Si | P | S | Cl |
| 0.25 (0.26) | 1.33 (1.31) | 0.51 (0.54) | 1.91 (1.92) | 3.53 (3.40) |
| 0.43 | 1.39 | 0.75 | 2.08 | 3.63 |
| Ga | Ge | As | Se | Br |
| 0.19 (0.21) | 1.21 (1.31) | 0.58 (0.55) | 1.84 (1.88) | 3.25 (3.37) |
| 0.43 | 1.23 | 0.81 | 2.02 | 3.37 |
| In | Sn | Sb | Te | I |
| 0.34 (0.39) | 1.10 (1.46) | 0.82 (0.73) | 1.82 (1.91) | 2.94 (3.21) |
| 0.30 | 1.11 | 1.05 | 1.97 | 3.06 |
| Tl | Pb | Bi | Po | At |
| 0.24 (0.34) | 0.39 (1.40) | 0.75 (0.66) | 1.25 (1.81) | 2.22 (3.04) |
| 0.20 | 0.36 | 0.95 | 1.9? | 2.82 |

[a] The values within parenthesis have been obtained without inclusion of spin−orbit coupling. Experimental values are given in the second row.[b] [a] From ref 17.

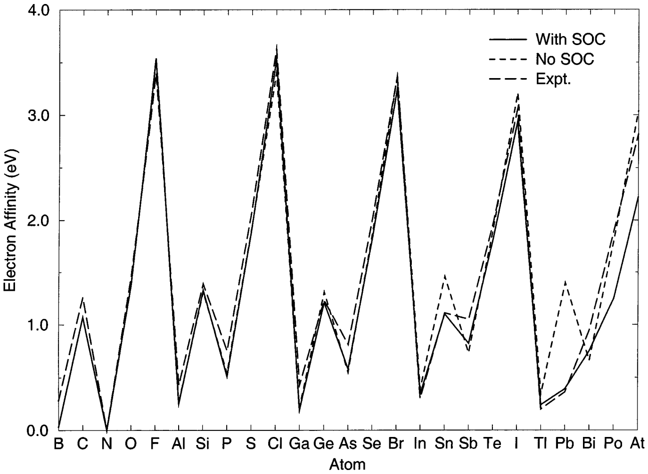

**Figure 3.** Electron affinities (eV) for main group atoms. Computed EAs with and without the inclusion of spin−orbit coupling are shown together with the experimental data.

removes the secondary peak for the heavy atoms. Instead, the group IVa atoms Sb and in particular Pb show an increased stability. This is due to the increased importance of jj-coupling. Pure jj-coupling would give these atoms a closed-shell structure described as $p_{1/2}{}^2$.[16]

The effect of spin−orbit coupling on the IPs becomes larger than 0.1 eV for Kr and heavier atoms (except Sn and Po). The effect is largest for Bi, 1.50 eV. The agreement with computed and experimental data shows that the spin−orbit contribution to the IPs is well described with the present approach.

**3.3. Electron Affinities.** All main group elements have positive electron affinities except nitrogen. The negative ions were included in the construction of the basis set. The EAs have then been computed using the largest basis set but without g-type functions for first-row atoms. Again, spin−orbit coupling is included for both the neutral atom and the negative ion. The results are presented in Table 4 and Figure 3. Experimental results have been taken from the compilation in *The Handbook in Chemistry and Physics*,[17] which we refer the reader to for more detailed references.

All computed electron affinities (EA), excepting Po and At, have errors smaller than 0.25 eV. The largest errors occur, as for the IPs, for group Va atoms. The errors are larger for Po and At, but here the experimental data are more uncertain and we suggest that the computed values have error bars smaller than 0.3 eV. This would, for example, give an electron affinity for At in the range 2.2−2.5 eV.

**TABLE 5: Atomic Excitations Energies (eV)**[a]

| B($^4P_{1/2}$) | C($^5S_2$) | N($^2D_{3/2}$) | O($^1D_2$) |
|---|---|---|---|
| 3.55 (3.55) | 4.09 (4.09) | 2.45 (2.45) | 1.99 (1.99) |
| 3.57 | 4.18 | 2.38 | 1.96 |
| Al($^4P_{1/2}$) | Si($^1D_2$) | P($^2D_{3/2}$) | S($^1D_2$) |
| 3.58 (3.58) | 0.77 (0.80) | 1.51 (1.45) | 1.22 (1.16) |
| 3.61 | 0.78 | 1.41 | 1.15 |
| Ga($^4P_{1/2}$) | Ge($^1D_2$) | As($^2D_{3/2}$) | Se($^1D_2$) |
| 4.71 (4.72) | 0.93 (0.81) | 1.39 (1.41) | 1.24 (1.10) |
| 4.71 | 0.88 | 1.31 | 1.19 |
| In($^4P_{1/2}$) | Sn($^1D_2$) | Sb($^2D_{3/2}$) | Te($^1D_2$) |
| 4.42 (4.41) | 1.06 (0.71) | 1.14 (1.20) | 1.31 (0.91) |
| 4.35 | 1.07 | 1.06 | 1.31 |
| Tl($^4P_{1/2}$) | Pb($^1D_2$) | Bi($^2D_{3/2}$) | Po($^1D_2$) |
| 5.81 (5.95) | 2.36 (0.69) | 1.31 (1.20) | 2.48 (0.86) |
| 5.61 | 2.66 | 1.42 | 2.69 |

[a] The values within parenthesis have been obtained without inclusion of spin−orbit coupling. Experimental values are given in the second row.[b] [a] From Moore's tables.[28]

Most computed EAs are smaller than experiment. The reason is the same as for the IPs; a combination of the CASPT2 error and remaining basis set effects. This is in particular the case for atoms with small EAs. Here, one can expect that the negative ion has a more diffuse electronic structure than the basis set permits.

The variation of the EAs with the atomic number is shown in Figure 3. We notice the same general structure as for the IPs with peaks corresponding to closed and half-closed shells. We notice also that the specific stability of the half-filled shell disappears for the heavier atoms, where the electronic structure is better described by jj-coupling.

**3.4. Excitation Energies.** We present also some results for excitation energies in Table 5. For group IIIa atoms and carbon, excitation is to the "valence state" $sp^{n+1}$, high spin. For the other atoms to the low spin term of the same configuration as the ground state. The calculations including spin−orbit coupling are from and to the $J$ value of lowest energy.

These results are certainly converged with respect to the basis set, and remaining errors thus reflect the ability of the CASPT2 method to describe relative energies. We notice that the errors are, with the exception of row 5, well below 0.1 eV in most cases. This is quite satisfactory and shows that the approach can describe spin-flip excitations with high accuracy for the p-elements. The situation is more complex for row 5. Here, the larger errors are a reflection of the approximate treatment of spin−orbit coupling. The largest error, 0.30 eV, occurs for Pb. For the other atoms it is less than 0.1 eV for rows 1−4 and less than 0.21 eV for row 5.

**3.5. Atomic Polarizabilities.** We finally present the polarizabilities for the group Va elements and the rare gases, both with a spherically symmetric ground state. These values are a good test of the ability of the basis set to respond to an external perturbation, whether it is an electric field or an approaching other atom, or ion.

The results presented in Table 6 have been obtained at the CASPT2 level of theory (using finite field perturbation theory)

**TABLE 6: Atomic Polarizabilities (au) (Experimental Values in Parenthesis[a])**

| N | P | As | Sb | Bi |
|---|---|---|---|---|
| 7.41 (7.42) | 24.9 (24.5) | 29.8 (29.1) | 42.2 (44.5) | 48.6 (49.9) |
| Ne | Ar | Kr | Xe | Rn |
| 2.61 (2.67) | 11.1 (11.1) | 16.6 (16.8) | 26.7 (26.9) | 32.6 (33.2) |

[a] From ref 17.

with the largest contracted basis sets given in Table 6. As can be seen from the data in the table, there is good agreement between experiment and theory for all atoms with errors smaller than 2.5%. The largest error occurs for Sb and Bi. It is most likely due to spin−orbit effects, which have not been included in these calculations. The convergence of the polarizability with an increasing basis set is slow. At least a quadruple quality basis set is needed to come within 1% of the results presented in Table 6.

## 4. Homonuclear Diatomics

As mentioned above, calculations around the equilibrium were performed for all the homonuclear diatomics of rows 1−4 in the primitive basis set. These results were used together with the atomic data for the construction of the ANOs. To test the performance of the basis set on a molecular case, we have then used the largest contracted basis sets in a calculation of the full potential curve for the ground state of the same molecules. These calculations were performed using the s- and p-orbitals in the active space (8 orbitals) with the number of active electrons varying from 3 to 16. For the rare gas dimers this corresponds of course to a standard MP2 calculation. Spin−orbit coupling was included only in a final calculation at the equilibrium geometry and the dissociation limit. Such an approximation is accurate enough for the molecules studied here but will be completely unsatisfactory for row 5 dimers, where SOC has to be included also in the calculation of the potential curves. These results will be presented in a forthcoming paper.

The calculations comprised 20−30 points on the potential curve with the highest density around equilibrium. The program VIBROT in the MOLCAS system was then used to derive the spectroscopic constants. The program solves the ro-vibrational Schrödinger equation numerically. A wealth of spectroscopic data is obtained, which will not be presented here. Only bond distances, energies, and vibrational frequencies will be listed. Reference will usually only be made to the compilations in *The Handbook of Chemistry and Physics* (HCP).[17] A wealth of experimental and theoretical data is available for most of these molecules, and it is impossible to make a more detailed citation. For some of the heavier diatomics, there is, however, more scarce and less accurate data, and a more detailed discussion is needed. We shall discuss the results row by row.

**4.1. First-Row Diatomics.** These molecules are very well-known and have been studied extensively by quantum chemists, and very accurate results are available in the literature for the ground and lower excited states. The present results are a measure of the accuracy that the used method gives with the ANO−RCC basis sets. The basis set used here is 8s7p4d3f.

The results are presented in Table 7. The bond distances are generally 0.005 Å too long (except for $F_2$ where the error is 0.009 Å). The bond energies are correspondingly smaller than experiment, the error varying from 0.02 to 0.28 eV. An exception is $O_2$ where the computed D0 is 0.18 eV larger than experiment. The largest error occurs for $N_2$. It is well-known that a very large basis set is required to converge $D_0$ for this triple-bonded molecule. A test was made by extending the present basis set with two g-type functions.

The error then decreases to 0.20 eV. The remaining error is mostly due to the approximate treatment of dynamic electron correlation. The table also shows the contribution to the bond energy from spin−orbit coupling. It starts to become nonnegligible for $O_2$ and $F_2$.

**4.2. Second-Row Diatomics.** Most of these molecules have also been studied extensively, maybe with the exception of $Al_2$. The present results are given in Table 8. The errors in computed bond distances are now larger, between 0.010 and 0.017 Å. They are all too long. Not unexpectedly, the largest error is found for the triple-bonded $P_2$ molecule. The errors in the bond energies vary between −0.15 and +0.23 eV, the largest error for $P_2$. Again the group VIa dimer $S_2$ is special with a too large $D_0$ (0.15 eV). We have no explanation for this deviation from the trend. We notice that it is no longer possible to neglect the influence of spin−orbit coupling on the bond energies.

The Al2 dimer deserves special attention. One would believe that the ground state here is the same as in $B_2$, ${}^3\Sigma_g^-$ with two $\pi$-electrons. This is, however, not the case; instead, the ${}^3\Pi_u$ state with only one $\pi$-electron falls below. Here, the computed $T_e$ is only 34 $\text{cm}^{-1}$. An MRCI study by Bauschlicher et al. from 1987[18] yields the difference 174 $\text{cm}^{-1}$. Their spectroscopic constants for the ${}^3\Pi_u$ state are very similar to the present results. $D_0$ was 1.39 eV to be compared to 1.38 for CASPT2 and the experimental value of 1.34 ± 0.06 eV. All heavier group IIIa dimers have the same ground state as $Al_2$.

**4.3. Third-Row Diatomics.** Less is known for the diatomics of the first members in this row and HCP only lists bond energies for $Ga_2$ and $Ge_2$. Both measurements of the bond energies and large CI calculations have been performed by

**TABLE 7: Spectroscopic Constants for the First-Row Diatomics (Experimental Values in Parenthesis[a])**

| | $B_2({}^3\Sigma_g^-)$ | $C_2({}^1\Sigma_g^+)$ | $N_2({}^1\Sigma_g^+)$ | $O_2({}^3\Sigma_g^-)$ | $F_2({}^1\Sigma_g^+)$ |
|---|---|---|---|---|---|
| $R_e$ (Å) | 1.595 (1.590) | 1.248 (1.243) | 1.102 (1.097) | 1.214 (1.208) | 1.421 (1.412) |
| $D_0$ (eV) | 2.84 (2.95) | 6.26 (6.29) | 9.48[b] (9,76) | 5.31 (5.13) | 1.59 (1.61) |
| $\omega_e$ ($\text{cm}^{-1}$) | 1042 (1051) | 1847 (1855) | 2340 (2359) | 1568 (1580) | 888 (917) |
| SOC[c] (eV) | −0.00 | −0.00 | −0.00 | −0.02 | −0.03 |

[a] From ref 17. [b] 9.56 eV with two g-type functions added to the basis set. [c] Effect of spin−orbit coupling on the bond energy.

**TABLE 8: Spectroscopic Constants for the Second-Row Diatomics (Experimental Values in Parenthesis[a])**

| | $Al_2({}^3\Pi_u)$ | $Si_2({}^1\Sigma_g^+)$ | $P_2({}^1\Sigma_g^+)$ | $S_2({}^3\Sigma_g^-)$ | $Cl_2({}^1\Sigma_g^+)$ |
|---|---|---|---|---|---|
| $R_e$ (Å) | 2.479 (2.466) | 2.263 (2.246) | 1.910 (1.893) | 1.899 (1.889) | 2.000 (1.988) |
| $D_0$ (eV) | 1.39 (1.34) | 3.14 (3.21) | 4.81 (5.04) | 4.53 (4.38) | 2.35 (2.48) |
| $\omega_e$ ($\text{cm}^{-1}$) | 345 (350) | 505 (511) | 760 (781) | 717 (726) | 546 (560) |
| SOC[b] (eV) | −0.01 | −0.03 | −0.00 | −0.05 | −0.07 |

[a] From ref 17. [b] Effect of spin−orbit coupling on the bond energy.

**TABLE 9: Spectroscopic Constants for the Third-Row Diatomics (Experimental Values within Parenthesis[a])**

| | $Ga_2(^3\Pi_u)$ | $Ge_2(^1\Sigma_g^+)$ | $As_2(^1\Sigma_g^+)$ | $Se_2(^3\Sigma_g^-)$ | $Br_2(^1\Sigma_g^+)$ |
|---|---|---|---|---|---|
| $R_e$ (Å) | 2.697 (−) | 2.362 (2.368) | 2.133 (2.103) | 2.180 (2.166) | 2.298 (2.281) |
| $D_0$ (eV) | 1.13 (1.15) | 2.67 (2.71) | 3.77 (3.93) | 3.43 (3.41) | 1.80 (1.96) |
| $\omega_e$ (cm$^{-1}$) | 191 (−) | 287 (−) | 413 (430) | 384 (385) | 317 (325) |
| SOC[b] (eV) | −0.10 | −0.10 | −0.00 | −0.21 | −0.28 |

[a] From ref 17. For $Ga_2$;[20] for $Ge_2$.[19] [b] Effect of spin−orbit coupling on the bond energy.

**TABLE 10: Spectroscopic Constants for the Fourth-Row Diatomics (Experimental Values in Parenthesis[a])**

| | $In_2(^3\Pi_u)$ | $Sn_2(^1\Sigma_g^+)$ | $Sb_2(^1\Sigma_g^+)$ | $Te_2(^3\Sigma_g^-)$ | $I_2(^1\Sigma_g^+)$ |
|---|---|---|---|---|---|
| $R_e$ (Å) | 2.970 (−) | 2.738 (−) | 2.497 (−) | 2.554 (2.557) | 2.662 (2.666) |
| $D_0$ (eV) | 0.83 (0.77) | 1.70 (1.90) | 2.75 (3.07) | 2.67 (2.64) | 1.53 (1.53) |
| $\omega_e$ (cm$^{-1}$) | 120 (−) | 190 (−) | 265 (−) | 241 (247) | 217 (215) |
| SOC[b] (eV) | −0.28 | −0.49 | −0.10 | −0.45 | −0.58 |

[a] From ref 17. [b] Effect of spin−orbit coupling on the bond energy.

**TABLE 11: Spectroscopic Constants for the Rare Gas Dimers (Experimental Values within Parenthesis[a])**

| | $Ne_2$ | $Ar_2$ | $Kr_2$ | $Xe_2$ |
|---|---|---|---|---|
| $R_e$ (Å) | 3.20 (3.09) | 3.81 (3.77) | 4.03 (4.04) | 4.29 (4.42) |
| $D_0$ (eV) | 0.0012 (0.0027) | 0.0091 (0.0110) | 0.017 (0.016) | 0.031 (0.023) |
| $\Delta G_{1/2}$ (cm$^{-1}$) | 9 (14) | 28 (26) | 23 (22) | 23 (20) |

[a] Experminental data for Ne from ref 26. Experminental data for Ar, Kr, Xe from ref 25 (see text for details).

Gingerich and co-workers.[19,20] $D_0$ is reported to be 1.14 ± 0.07 eV for $Ga_2$[20] and 2.71 eV for $Ge_2$.[19] A value of 2.368 Å is reported for the bond distance in the latter molecule. These results agree nicely with the values computed here, as presented in Table 9.

For the other molecules we see the same trends as for the lighter atoms. The bond distance in $As_2$ is 0.03 Å longer than experiment and the bond energy is 0.16 eV too small. The bond energy in $Se_2$ is slightly too large whereas the other $D_0$ values are on the low side. The effect of spin−orbit coupling is now appreciable. For $Br_2$ it amounts to 0.28 eV. All of this is due to the stabilization of the atoms because the effect is almost totally quenched in the molecule.

**4.4. Fourth-Row Diatomics.** With this row we enter into a more problematic region of the periodic table. The results are presented in Table 10. First, there are much less reliable experimental data to compare with. Second, the effect of spin−orbit coupling is now so large that it is doubtful that the correction to the bond energy can be obtained by just subtracting the atomic contribution. For $In_2$ there is a first-order effect also in the $^3\Pi_u$ ground state. The stabilization of the total energy at equilibrium is 0.07 eV is compared to the effect at the asymptotic limit, 0.35 eV. The SOC contribution at equilibrium is small for the other diatomics and almost all effects arises at the asymptotic limit.

Bond distances are only known for $Te_2$ and $I_2$ with good agreement with computed values. Bond energies are within 0.3 eV of the somewhat uncertain experimental values. The value for $In_2$ is from the compilation of Kontradiev from 1974.[21] The value for $Sb_2$ is from 1973[22] and that for $Sn_2$ is from 1988.[23]

**4.5. Rare Gas Dimers.** We finally present the results obtained for the rare gas dimers. They have been obtained using the same active space, thus reducing the method to standard Møller−Plesset perturbation theory. So, the results are more a test of the accuracy of this approach combined with the present basis set. As can be seen in Table 10, the binding energy is underestimated for the lighter dimers whereas it is too large for $Xe_2$, which shows that $MP_2$ here leads to an overestimate of the binding energy. We checked this by performing CCSD(T) calculation for this molecules using the same basis set. The CC code in MOLCAS was used.[24] The resulting binding energy is 0.020 eV, only 0.003 eV smaller than the experimental value.[25] For the neon dimer we compare the present result to the recent experimental results by Wiiest and Merkt, which were obtained from high-resolution spectroscopic measurements of the $\Pi 0_u^+ \leftarrow X0_g^+$ transition.[26] It is most likely that the too weak bonding obtained in the present work is in part due to the limited basis set used and in part to the MP2 method. For the heavier dimers we use the experimental data quoted in the recent paper by Slavliek et al.[25]

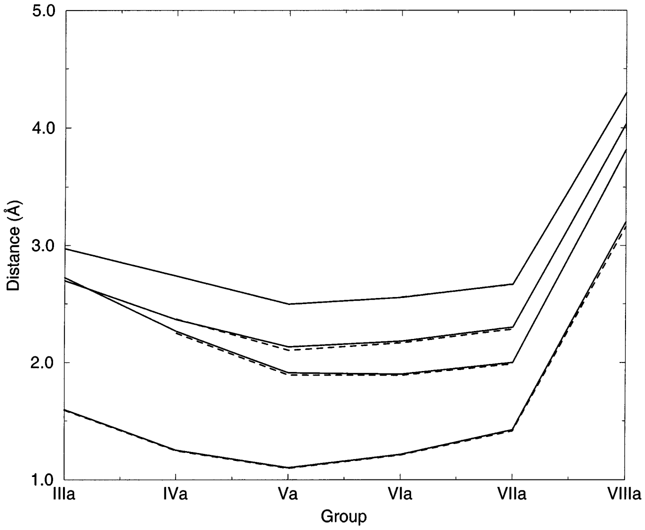

**Figure 4.** Bond distances (Å) for the main group dimers: solid lines, this work; dashed lines, experiment. From bottom up: rows 1−4.

**4.6. Summary of the Results for the Diatomics.** The result presented above for the homonuclear diatomics of the main group elements is an illustration of the type of accuracy that can be achieved with the new basis set in connection with the CASSCF/CASPT2 quantum chemical method. Figure 4 shows the general agreement between theory and experiment for the equilibrium distance. The error is smaller than 0.75% except for the triple-bonded systems $P_2$ (0.90%) and $As_2$ (1.43%). These are the cases that put the highest demands on the basis set and also have the largest systematic methodological errors. In general, we can conclude from the bond distances and the

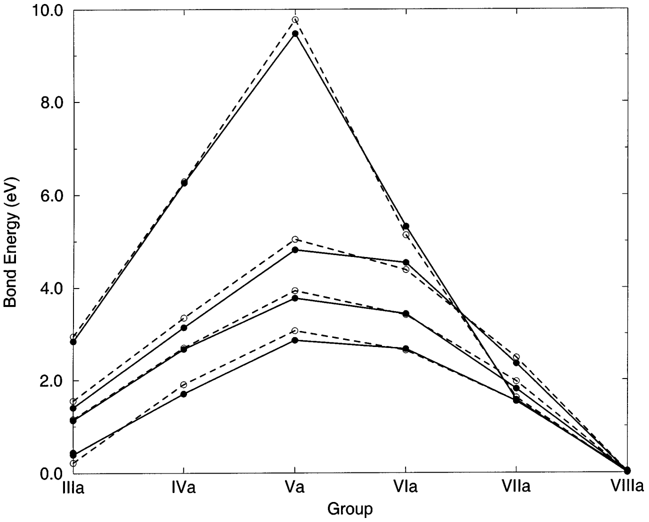

**Figure 5.** Bond energies ($D_0$) (eV) for the main group dimers: solid lines, this work; dashed lines, experiment. From top down: rows 1−4.

computed $\omega_e$ values that the potential curves are well described around the equilibrium geometry.

The situation is slightly different for the bond energies. Here, the errors are more scattered, varying between +3.4 and −8.2%. Even if the largest absolute errors expected occur for the triple-bonded dimers, the largest relative errors are found for the halogens $Cl_2$ and $Br_2$. We have excluded the fourth-row dimers, because the experimental values are here more in doubt, at least for the In and Sn dimers (a recent DFT study of tin clusters yielded a bond energy for $Sn_2$ of 2.74 eV, which is clearly too large[27]). We present a plot of the $D_0$ values in Figure 5. The abnormality of the $F_2$ chemical bonds is a striking feature of this picture.

The effect of spin−orbit coupling on the bond energies is nonnegligible for atoms heavier than sulfur and amounts to about one-third of the bond energy for the fourth-row dimers. Just subtracting the atomic stabilization from the bond energy is questionable already here and is likely the cause of the somewhat large errors for $Sn_2$ and $Sb_2$. The approach is clearly not applicable for the fifth-row dimers, which have to be treated with explicit inclusion of SOC. Results for these dimers will be presented in a forthcoming publication.

All the results presented have been obtained using the full counterpoise approach to correct for basis set superposition errors (BSSE). It might be of some interest to see how large the BSSE is. It is an additional measure of the accuracy of the basis set. The effect on the bond distance for the main group dimers varies between 0.0008 ($B_2$) and 0.011 Å ($In_2$) with an average value of 0.003 Å. The BSSE for the bond energies varies between 0.01 ($B_2$) and 0.06 eV ($Te_2$) with an average of 0.03 eV. For the rare gas dimers the effect on the bond distance is between 0.02 and 0.05 Å with the largest error for $Xe_2$. The effect on the bond energy is also largest for this molecule, 0.009 eV.

## 5. Conclusions

We have in this report described a new basis set of the ANO type, devised to include scalar relativistic effect through the use of a Douglas−Kroll Hamiltonian and correlation of semicore electrons. These basis sets aim to cover the whole periodic system and replace the ANO-L basis set in the MOLCAS software.[3−5] With this publication we have reported the basis sets for groups Ia−VIIIa. The quality has been tested by calculations on spectroscopic and other properties of the atoms and the corresponding homonuclear diatomics. Because the CASSCF/CASPT2 method has been used to obtain the ANOs, the results reflect both the quality of the basis sets and the accuracy of the computational approach. This is not completely satisfactory, but we do not know of any other method that would be equally generally applicable and give the same accuracy. The basis set is flexible enough to yield excitation energies, ionization potentials, and electron affinities for the atoms with good accuracy. Also the spectroscopic constants of the diatomic molecules are reproduced with the accuracy that is expected from the present quantum chemical method. For the triple-bonded molecules and the lighter rare gas dimers even larger basis sets are needed to stabilize the computed properties. It is well-known that it is necessary to include SOC in calculations of relative energies (bond energies, excitation energies, etc.) in compounds containing atoms heavier than Cl. Here we have used the RASSI-SO method to demonstrate this. This approach works well for at least rows 1−4 but becomes more troublesome for the heaviest elements because of the need to include all terms arising from the given electronic configuration. Recent studies on PbO (ref 29) and $Pb_2$ (ref 30) seem to indicate, however, that also for these system accurate results can be obtained for ground- and excited-state properties. Future work will include the transition metals, the lanthanides, and the actinide elements.

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