New Medium-size Basis Sets for Rare-gas Atoms

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Abstract: New medium-size basis sets are constructed for rare-gas (Rg) atoms and tested on their dimers Rg_2. The main part of the these bases contains the standard aug-cc-pVTZ basis set modified and extended by the *g*- and *h*-polarization functions. Their optimization allows accurate calculations of the dispersion interaction without the involvement of the bond functions. A new convenient analytical potential function is invented to fit accurately the interaction energy. The potentials derived for Rg dimers predict the vibrational transition energies and rotational constants to accuracy of 1%.

Graphical abstract: New medium-size basis sets without the involvement of bond functions are constructed for rare-gas atoms and tested on their dimers.

Key words: *ab initio* calculations, basis sets, interaction energy, optimized polarization functions, rare gas clusters, spectroscopic parameters

I. INTRODUCTION

Molecular clusters composed of a single molecule complexed by several rare-gas (Rg) atoms have been a subject of intense experimental and theoretical investigations. Such clusters bound mainly by the dispersion interaction appeared to be most difficult to treat theoretically, since the dispersion energy arises solely from the interelectron correlation. Nevertheless, a good number of benchmark calculations employing sophisticated *ab initio* methods have been reported for Rg dimers [1-15].

A major problem in these methods is the proper choice of the one-particle basis sets. A good description of dispersion needs extensive polarization and diffuse functions in these basis sets. Recently, very accurate interaction potentials for a series of Rg dimers have been calculated by employing large correlation consistent Dunning's basis sets aug-cc-pVXZ [16, 17] up to $X = 5$ and 6, supplemented with the diffuse bond functions located in the middle of the Rg_2 bond [12, 14, 15]. However, the size of such extended basis sets makes the calculations on large Rg clusters unfeasible. An additional problem appears with the bond functions because it is not clear how they should be located in the space between the nuclei.

The goal of this work is to design moderate basis sets without the bond functions that could provide highly accurate results for the clusters containing Rg atoms. The lack of the bond functions can be compensated by the interaction-optimized polarization functions. To test the efficiency of the new basis sets, the interaction potentials for the Rg dimers will be calculated and expressed by a new convenient analytical form.

II. METHOD

The main source of errors in the calculated interaction energy is the incompleteness of the one-particle basis sets. Very large bases are necessary to achieve the complete basis set (CBS) limit. The basis size can be significantly reduced by optimizing the Gaussian parameters of the basis functions. The optimization is a difficult problem, so until now it has been performed only for He_2 [2, 6], Ne_2 [10] and HeNe [11] clusters.

A common practice is the optimization of only a small fraction of the basis functions from the total basis set. For example, Cybulski and coworkers [12, 15] constructed the basis sets for Rg dimers for Rg = He, Ne Ar and Kr from the

standard aug-cc-pVXZ bases (further abbreviated by avxz) supplemented by bond functions of the type proposed by Tao and Pan [18]. Only the bond functions located in the middle of the Rg-Rg bond were optimized in their bases.

We applied a similar method; however, we have not used the bond functions. To reduce significantly the basis size and simultaneously to conserve its flexibility, we have chosen the avtz basis as the main part. However, for He the larger avqz basis was selected because its structure is analogous to the avtz basis for heavier Rg atoms. These bases were modified by removing some tight polarization functions and by adding the *g*- and *h*-functions. Our tests calculations for He_2 and Ne_2 indicated that the tight *d*-type functions with the highest exponent were insignificant in the bonding region, thus they were removed. However, they were conserved for Ar and Kr. The *s*- and *p*-type functions in the avtz and avqz bases were unchanged. As a consequence, the following structure of the basis sets was established: *s*- and *p*-orbitals were taken from the original basis sets mentioned above, the three sets (four for Kr) of *d*-, two sets of *f*-, one set of *g*- and *h*-type functions were included into the desired basis sets. This basis structure will be abbreviated further by avqz(spd')211 for He, avtz(spd')211 for Ne, and avtz(spd)211 for Ar and Kr.

III. RESULTS AND DISCUSSION

III. 1. *Ab initio* interaction energy

The interaction energy of the Rg dimers has been calculated using the coupled cluster singles and doubles including the connected triples theory [CCSD(T)] [19] in the framework of the supermolecular method, by employing the GAUSSIAN03 program package [20]. The basis set superposition error was eliminated by employing the usual counterpoise procedure [21]. As the core correlation has a small influence on the interaction energy, only the valence orbitals were involved in the correlation. Indeed, the core corrections at the equilibrium bond length r_e, for Ne_2 [13], Ar_2 and Kr_2 [14] were estimated to be about 0.2, 1 and 3 cm^{-1}, respectively. The exponents of the polarization functions were optimized at the equilibrium bond length $r = r_e$ because they depended weakly on r.

Table 1 presents the optimum exponents of the polarization functions. The optimum *d*-functions were established in different ways for different Rg atoms. For the Ne atom, the tightest set of *d*-functions was removed from the original avtz basis. Instead, one additional set of the diffuse *d*-functions with the exponent $\zeta = 0.15$ was

added. The two remaining *d*-sets were taken without a modification from the avtz basis. The *d*-functions for He were derived in an analogous way from the avqz basis. The three (four) *d*-sets for Ar (Kr) were left unchanged in the avtz basis. The tightest fourth contracted *d*-orbital of Kr is not presented in Table 1 for shortness. The *f*-functions obtained from the optimization appeared to be much more diffuse than those contained in the original basis sets. The same refers to the additional *g*- and *h*-functions.

The obtained basis sets are not larger for Rg dimers, except for He, than the avtz + 33221 basis sets with the bond functions $3s3p2d2f1g$ [12, 15]. The size of the basis avtz + 33221 quickly grows for the larger clusters Rg_n because the number of the bond functions located in the points placed between the nuclei grows as $n(n+1)/2$. Our basis without the bond functions is more efficient. Nevertheless, it provides the accuracy comparable to that yielded by the larger avtz + 33221 basis set.

Table 1. Orbital exponents ζ of the avqz(spd')211 and atz(spd')211 basis sets optimized for the Rg dimers

ζ	He	Ne	Ar	Kr
d_1	0.15	0.15	0.169[a]	0.1257[a]
d_2	0.351[b]	0.386[a]	0.410[a]	0.3006[a]
d_3	1.223[b]	1.096[a]	1.254[a]	0.8084[a]
f_1	0.25	0.25	0.20	0.15
f_2	0.75	0.75	0.60	0.45
g, h	0.30	0.40	0.25	0.20

[a] *d*– function from the standard avtz basis set
[b] *d* – function from the standard avqz basis set

The interaction energy $E(r)$ calculated in this work in a wide range of the internuclear distance r is compared in Tables 2-5 to the corresponding values calculated with the avtz + 33221 and av5z + 33221 bases [12, 15]. The latter basis set provides the results close to the CBS limit within the frozen core approximation. Indeed, the errors $\Delta E(r)$ in the interaction energy calculated near the potential minimum by employing the basis av5z + 33221 are less than 0.1 μE_h for He_2 and Ne_2, and about 1 μE_h for Ar_2 and Kr_2 [12, 14]

Our results are less accurate in the repulsion region where $E(r) > 0$. This is a consequence of the lack of the tight polarization functions in our bases. However, this drawback is not essential when the bound states of the clusters are considered, because the wave functions of such states are localized mainly in the bonding region where $E(r) < 0$.

Table 2. Comparison of the interaction energies (μE_h) of He$_2$ calculated at the bond length r (Å), using the avqz(spd')21, avtz + 33221 and av5z + 33221 basis sets

r	avqz(spd')21[a] 110[c]	avtz + 33221[b] 91[c]	av5z + 33221[b] 205[c]
1.75	5784.47	5769.68	5721.72
2.000	1743.19	1734.72	1716.26
2.250	454.30	449.81	443.24
2.500	75.36	73.16	71.00
2.750	−19.37	−20.38	−21.08
2.950	−32.79	−33.34	−33.58
2.975	−32.97	−33.48	−33.68
3.000	−32.96	−33.44	−33.61
3.025	−32.79	−33.23	−33.37
3.250	−27.33	−27.54	−27.53
3.50	−19.55	−19.60	−19.57
4.000	−9.15	−9.10	−9.09
5.000	−2.28	−2.27	−2.26

[a]This work
[b]Ref [12]
[c]Dimension of the basis set

Table 3. Comparison of the interaction energies (μE_h) of Ne$_2$ calculated at the bond length r (Å), using the avtz(spd')211, avtz+33221 and av5z+33221 basis sets

r	avtz(spd')211[a] 118[c]	avtz+33221[b] 137[c]	av5z+33221[b] 299[c]
2.25	3670.73	3527.67	3444.36
2.500	817.92	770.84	746.73
2.750	42.74	26.76	23.99
3.000	−121.02	−125.56	−123.67
3.075	−129.68	−132.05	−129.96
3.100	−130.60	−132.33	−130.44
3.125	−130.77	−131.92	−130.13
3.250	−123.74	−122.75	−121.23
3.500	−94.18	−92.29	−90.91
3.750	−65.71	−64.98	−63.24
4.000	−44.74	−44.66	−42.83
4.500	−21.20	−20.83	−20.61
5.000	−10.80	−10.47	−10.54

[a]This work
[b]Ref. [12]
[c]Dimension of the basis set

Table 4. Comparison of the interaction energies (μE_h) of Ar$_2$ calculated at the bond length r (Å), using the avtz(spd)211, avtz + 33221 and av5z + 33221 basis sets

r	avtz (spd)211[a] 140[c]	avtz + 33221[b] 145[c]	av5z + 33221[b] 307[c]
3.000	3330.30	3175.30	3054.98
3.250	628.64	557.65	518.11
3.500	−239.38	−276.99	−278.98
3.750	−429.88	−451.80	−440.82
3.775	−432.56	−453.26	−441.87
3.800	−433.42	−453.03	−441.32
3.850	−430.76	−448.30	−436.21
4.000	−398.84	−411.42	−399.60
4.250	−314.76	−322.75	−313.12
4.500	−233.62	−239.45	−232.30
5.000	−122.88	−123.19	−122.96
6.000	−37.66	−37.81	−37.77
7.000	−14.02	−14.01	−14.03

[a]This work
[b]Ref. [12]
[c]Dimension of the basis set

Table 5. Comparison of the interaction energies (μE_h) of Kr$_2$ calculated at the bond length r (Å), using the avtz(spd)211, avtz + 33221 and av5z + 33221 basis sets

r	avtz(spd)211[a] 158[c]	avtz + 33221[b] 163[c]	av5z + 33221[b] 325[c]
3.250	3866.9	3691.62	3579.74
3.500	764.0	671.39	643.47
3.750	−317.6	−369.74	−361.52
4.000	−588.1	−617.24	−599.07
4.025	−593.9	−621.50	−603.08
4.050	−597.6	−623.46	−604.86
4.075	−598.8	−623.38	−604.69
4.250	−566.8	−583.32	−565.19
4.500	−463.7	−473.40	−458.24
4.750	−355.3	−360.56	−349.83
5.000	−265.1	−267.23	−260.72
6.000	−82.2	−81.82	−81.21
8.000	−12.8	−12.48	−12.62

[a]This work
[b]Ref. [15]
[c]Dimension of the basis set

The errors calculated for He$_2$ using our avqz(spd')21 basis are well below 1 μE_h in a large domain of the bonding region, for $r > r_e$. The additional set of the h-functions reduces the error in this region to less than 0.3 μE_h, so the h-functions are excluded from the presented basis set.

For Ne$_2$, our basis avtz(spd')211, slightly smaller than the avtz + 33221 basis [12] yields more accurate $E(r)$ values near the potential minimum. Both basis sets show a similar behavior at large internuclear distances.

Table 6. Potential parameters determined for the Rg dimers, using our (I) and av5z+33221 (II) basis sets

Parameter	He_2		Ne_2		Ar_2		Kr_2	
	I	II[a]	I	II[a]	I	II[a]	I	II[b]
r_e (Å)	2.9852	2.9755	3.1167	3.0993	3.8009	3.7784	4.0808	4.0601
r_e (Å)[c]		2.9764		3.0988		3.7785		4.0592
a_0	6.2046	6.2081	6.3641	6.3864	6.4062	6.3757	6.3878	6.3799
a_1	−1.2585	−1.2234	−1.4472	−1.4557	−0.8901	−0.8508	−0.7302	−0.7241
a_2	−1.7753	−1.7476	−1.1845	−1.3464	−1.7838	−1.4465	−1.6771	−1.6091
β	1.0000[d]	1.0000[d]	1.0000[d]	1.0000[d]	1.0530	1.2046	1.1508	1.1956
D_e (μE_h)	33.01	33.70	130.89	130.41	433.40	441.88	598.98	605.02
D_e (μE_h)[c]		33.67		130.33		441.90		604.89

[a]Ref. [12]
[b]Ref. [15]
[c]Parameter determined for He_2, Ne_2, Ar_2 in Ref. [12], and for Kr_2 in Ref. [15]
[d]Parameter constrained

The errors $\Delta E(r)$ produced by avtz(spd)211 and avtz+33221 basis sets for Ar_2 are comparable in magnitude $(\approx 10\,\mu E_h)$ near the equilibrium, but their signs are the opposite. For $r > r_e$ the avtz(spd)211 basis provides more accurate results. A similar situation takes place for Kr_2, however $\Delta E(r)$ calculated for avtz + 33221 basis sets are about twice larger than for Ar_2.

III. 2. Analytical potential energy curves

To derive the measurable molecular parameters from the single-point energy values they should be converted to the analytical potential energy curve $V(r)$. Usually, $V(r)$ is composed of a short-range repulsive V_+ and a long-range attractive V_- parts. The attractive potential can be represented by the damped dispersion series containing the dispersion coefficients C_{2n} [22]. The repulsive potential can be well approximated, according to the Born-Mayer model, by the exponential function $V_+ = A\exp(-br)$ or by its modified form $\tilde{V}_+ = A\exp(-br + cr^2)$ [5]. From the potential parameters A, b, c and C_{2n}, one can determine the binding energy D_e and the equilibrium bond length r_e that characterize the potential $V(r)$. However, as noticed by Tang and Toennies [22], the potential parameters A and b are extremely sensitive to D_e and r_e.

Thus, it would be desirable to find the analytical form of $V(r)$ parametrized directly by D_e and r_e. The commonly known Morse potential

$$V_M(r) = D_e\left[y^2(r) - 1\right] \qquad (1)$$

where $y(r) = 1 - \exp(-ax)$ and $x = (r - r_e)/r_e$ fulfils this condition; however, it is not accurate in a long-range domain. This deficiency can be repaired by including the damped dispersion terms into (1) or by modifying the original potential $V_M(r)$ in a different way.

We have found that $V_M(r)$ can be significantly improved by treating the parameter a in (1) as a function of r in the following form

$$a(r) = a_0 + a_1\tanh(\beta x) + a_2\tanh^2(\beta x) \qquad (2)$$

with the adjustable parameter β. Such a modified Morse potential conserves the advantages of the original one and simultaneously allows an accurate fit of the *ab initio* energy values in a large domain of r to a high accuracy, even without additional dispersion terms. Moreover, we have found that the function $a(r)$ in the form (2) remains to work properly also for covalently bound molecules.

The potential parameters D_e, r_e, and a_k fitted to the energy values given in Tables 2-5 are collected in Table 6. The energy values calculated using the av5z + 33221 basis set [12, 15] were fitted with the standard errors of about $0.05\ \mu E_h$ for all the considered dimers. The differences in the binding energies D_e determined in Refs. [12, 15] and in this work are also of the same order of magnitude. Only for Kr_2, this difference is slightly larger (0.13 μE_h). The differences in r_e are less than 0.001 Å. These test results demonstrate that the modified Morse potential is competitive to the standard $V_+ + V_-$ representation.

The potential functions derived for our basis sets are less accurate. The potential minima are shifted by about 0.02 Å (0.01 Å for He_2) towards larger distances, and the binding energies D_e calculated using our basis sets deviate from the corresponding D_e (av5z + 33221) values by about $(-0.1, +0.1, -1.9, -1.3)$ cm^{-1} for He, Ne, Ar, and Kr, respectively. Such errors are comparable to the core corrections, usually neglected in the calculations of the interaction energies.

Table 7. Vibrational transition frequencies (cm^{-1}) and rotational constants B_0 (cm^{-1}) calculated for the Rg dimers, using our (I) and av5z + 33221 (II) basis sets

Dimer	$v' - v''$	I[a]	II[b]
Ne$_2$	1-0	13.56	13.46
	B_0	0.1532	0.1547
Ar$_2$	1-0	24.99	25.27
	2-1	19.87	20.11
	3-2	14.92	15.15
	B_0	0.05641	0.05708
Kr$_2$	1-0	20.61	20.78
	2-1	18.48	18.60
	3-2	16.37	16.45
	4-3	14.29	14.33
	5-4	12.24	12.27
	B_0	0.02369	0.02390

[a]This work
[b]Calculated for Ne$_2$ and Ar$_2$ in Ref. [12], and for Kr$_2$ in Ref. [15]

The quality of the potentials presented was tested from the spectroscopic point of view. Table 7 collects the frequencies of the vibrational transitions as well as the ground-state rotational constants B_0 of the dimers Rg$_2$, except for He$_2$ for which no bound states were found. These quantities were calculated by solving numerically the Schrödinger equation for the nuclear motion. A comparison of the results derived for the avtz(spd)211 and av5z + 33221 basis sets shows that the vibrational frequencies obtained for our basis set deviate by about 1% or less from more accurate values reported [12, 15] for the latter basis set. The same refers for the rotational constants. This shows that our basis sets allow us to generate the potentials useful for spectroscopic purposes.

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