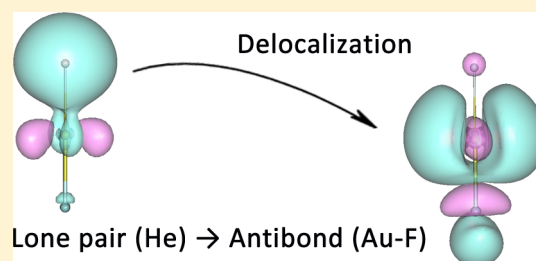


# On the Covalent Character of Rare Gas Bonding Interactions: A New Kind of Weak Interaction

Wenli Zou,<sup>\*,†,§</sup> Davood Nori-Shargh,<sup>†,‡</sup> and James E. Boggs<sup>\*,†</sup><sup>†</sup>Institute for Theoretical Chemistry, Chemistry and Biochemistry Department, The University of Texas at Austin, Austin, Texas 78712-0165, United States<sup>‡</sup>Department of Chemistry, Arak Branch, Islamic Azad University, Arak, Iran**S** Supporting Information

**ABSTRACT:** At the averaged quadratic coupled-cluster (AQCC) level, a number of selected rare gas (Rg) containing systems have been studied using the quantum theory of atoms in molecules (QTAIM), natural bond orbital (NBO), and several other analysis methods. According to the criteria for a covalent bond, most of the Rg–M (Rg = He, Ne, Ar, Kr, Xe; M = Be, Cu, Ag, Au, Pt) bonds in this study are assigned to weak interactions instead of van der Waals or covalent ones. Our results indicate that the rare gas bond is a new kind of weak interaction, like the hydrogen bond for example.

**■ INTRODUCTION**

Since xenon hexafluoroplatinate was discovered by Bartlett in 1962,<sup>1</sup> more and more neutral rare gas compounds have been found (for example, see refs 2–4). In addition to a few krypton and radon compounds, most of them are xenon compounds. Not until 2000 was the first compound of argon, HArF, reported.<sup>5,6</sup> More recently, a class of triatomic rare gas compounds RgMX (Rg = Ar, Kr, Xe; M = Cu, Ag, Au; X = F, Cl) with covalent interactions between the Rg and M atoms has been studied both experimentally and theoretically.<sup>7–20</sup> Although the compounds of helium and neon are still unknown experimentally, a number of theoretical studies show the existence of some metastable helium-containing systems and indicate the possibility of a chemical bond occurring between helium and other atoms.<sup>19,21–38</sup> While the present paper was being written, NeAuF was detected experimentally for the first time,<sup>30</sup> which offers a ray of hope for discovering the helium-containing complex HeMF. An important open question remains: are they real covalent compounds of helium? The same question also exists in other rare gas containing systems.

To answer this question, the topological analysis of the electron density distribution based on the quantum theory of atoms in molecules (QTAIM)<sup>39</sup> may be applied. According to the traditional topological criterion, the covalent (or shared) interaction should have a negative Laplacian of electron density ( $\nabla^2\rho(r_c) < 0$ ) at the bond critical point  $r_c$ .<sup>39</sup> However, this criterion is not sufficient in the case of 3d and heavier atoms,<sup>40</sup> and even for some classic covalent compounds (for example, CO and F<sub>2</sub>; see ref 39, pp 312–314). Cremer and Kraka<sup>41</sup> suggested use of the criterion  $H(r_c) < 0$  as the indicator of a covalent bond, where  $H(r_c) = G(r_c) + V(r_c)$  is the local energy density, and  $G(r_c)$  and  $V(r_c)$  are local kinetic energy density and local potential energy density, respectively. This criterion was then complemented by a condition  $G(r_c)/\rho(r_c) < 1$ .<sup>40</sup> In

addition, some other criteria have also been suggested and summarized in the literature.<sup>42–47</sup>

In Table 1, we show some diatomic molecules calculated at their equilibrium bond lengths,<sup>48–50</sup> which are covalent bonds in the classical outlook of chemists. The empirical covalent bond lengths ( $R_{\text{cov}}$ , i.e. the sums of covalent atomic radii  $R_{\text{cov}} = \sum r_{\text{cov}}$ )<sup>51,52</sup> are also given for comparison. Details of the computational methods will be described in the next section. The covalent bonds in Table 1 can be grouped into four types.

- Type A.  $\nabla^2\rho(r_c) < 0$ , and  $\rho(r_c)$  is large (here we take a threshold of 0.1 au).
- Type B.  $H(r_c) < 0$ , and  $\rho(r_c)$  is large (again with a threshold of 0.1 au).
- Type C.  $H(r_c) < 0$  and  $G(r_c)/\rho(r_c) < 1$ .
- Type D.  $|H(r_c)|$  is small ( $< 0.005$  au is taken) and  $G(r_c)/\rho(r_c) < 1$ .

Type C is also called partial covalent bond in literature.<sup>43,44</sup> In general, although type A can be looked on as a subset of type B and/or C, it is still listed above separately to be consistent with the traditional criteria.

In addition to the above criteria, the covalent bonds are also confirmed by the agreement between the bond lengths and the empirical covalent bond lengths. It should be noted that the alkali dimers have sometimes been looked on as van der Waals (vdW) molecules because of their long bond lengths and small dissociation energies. From the topological point of view, however, they are totally different from vdW bonds and have to be strictly distinguished from them. On the other hand, a few weak bonding interactions (hydrogen bonds, lithium bonds, halogen bonds, and so on, as summarized in ref 53) may also

Received: October 22, 2012

Revised: December 13, 2012

Published: December 14, 2012

Table 1. Bond Lengths (Å) and Topological Properties (au) of Some Covalent Diatomic Molecules

molecule	bond type	$R_c^a$	$R_{cov}^b$	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$H(r_c)$	$G(r_c)/\rho(r_c)$
CO	B	1.128	1.24	0.509	0.633	-1.026	2.326
F <sub>2</sub>	B	1.412	1.28, 1.44 <sup>c</sup>	0.283	0.548	-0.175	1.104
IF	B	1.910	1.97	0.140	0.397	-0.075	1.241
Cl <sub>2</sub>	A, B, C	1.988	1.98	0.168	-0.094	-0.106	0.493
Br <sub>2</sub>	A, B, C	2.281	2.28	0.114	-0.015	-0.055	0.450
I <sub>2</sub>	C	2.666	2.66	0.080	-0.006	-0.031	0.367
At <sub>2</sub>	C	2.862 <sup>d</sup>	2.94	0.064	0.013	-0.021	0.383
ClF	A, B, C	1.628	1.63	0.222	-0.234	-0.232	0.781
IBr	C	2.469	2.47	0.094	0.004	-0.041	0.046
HF	A, B, C	0.917	0.96	0.381	-3.719	-1.033	0.272
Li <sub>2</sub>	C, D	2.673	2.66	0.014	-0.013	-0.004	0.035
Na <sub>2</sub>	C, D	3.079	3.10	0.009	-0.003	-0.002	0.098
K <sub>2</sub>	D	3.905	3.92	0.005	0.002	-0.0004 <sup>f</sup>	0.145
Rb <sub>2</sub>	D	4.210 <sup>e</sup>	4.20	0.005	0.001	-0.0004 <sup>f</sup>	0.148
Cs <sub>2</sub>	D	4.47	4.64	0.005	0.003	-0.0002 <sup>f</sup>	0.212
NaLi	C, D	2.813	2.88	0.012	-0.002	-0.002	0.151

<sup>a</sup>Reference 48. <sup>b</sup>Pyykkö's covalent radii from ref 51. <sup>c</sup>Sandersen's covalent radii from ref 52. <sup>d</sup>Reference 49. Theoretical value. <sup>e</sup>Reference 50. <sup>f</sup>It may be a tiny positive value by other theoretical methods.

Table 2. Bond Length (Å), QTAIM Topological Properties (au), Natural Charge (Q) and WBI, and MBO of Some Rare Gas Bonds

no.	molecule	bond	$R_c$	$R_{cov}$	$R_{vdw}$	QTAIM				NBO			type <sup>a</sup>
						$\rho(r_c)$	$\nabla^2\rho(r_c)$	$H(r_c)$	$G(r_c)/\rho(r_c)$	Q(Rg)	WBI	MBO	
1a	FHeO <sup>-</sup>	He-O	1.100	1.09	2.03	0.324	0.274	-0.335	1.244	0.509	0.667	0.701	B
1b		He-F	1.621	1.10	2.04	0.079	0.346	-0.007	1.192	0.509	0.063	0.162	W <sup>c</sup>
2a	HHeF	He-H	0.818	0.78	1.72	0.256	-1.704	-0.478	0.202	0.314	0.425	0.446	A,B,C
2b		He-F	1.418	1.10	2.04	0.141	0.537	-0.043	1.258	0.314	0.115	0.374	W <sup>c</sup>
3a	HArF	Ar-H	1.329	1.28	2.20	0.228	-0.693	-0.240	0.294	0.513	0.642	0.790	A,B,C
3b		Ar-F	1.967	1.60	2.52	0.103	0.320	-0.028	1.045	0.513	0.193	0.386	W <sup>c</sup>
4	HeCuF	He-Cu	1.659	1.58	2.33	0.072	0.570	-0.012	2.148	0.037	0.081	0.144	W <sup>c</sup>
5	HeAgF	He-Ag	2.143	1.74	2.61	0.031	0.184	0.0004	1.478	0.011	0.023	0.036	W <sup>n</sup>
6	HeAuF	He-Au	1.841	1.70	2.77	0.073	0.499	-0.011	1.853	0.054	0.102	0.157	W <sup>c</sup>
7	NeCuF	Ne-Cu	2.172	1.79	2.48	0.029	0.241	0.002	2.020	0.019	0.030	0.063	W <sup>n</sup>
8	NeAgF	Ne-Ag	2.700	1.95	2.76	0.013	0.080	0.002	1.386	0.004	0.006	0.023	W <sup>n</sup>
9	NeAuF	Ne-Au	2.444	1.91	2.92	0.026	0.172	0.001	1.648	0.019	0.028	0.062	W <sup>n</sup>
10	ArCuF	Ar-Cu	2.219	2.08	2.81	0.063	0.328	-0.014	1.538	0.065	0.133	0.280	W <sup>c</sup>
11	ArAgF	Ar-Ag	2.558	2.24	3.09	0.042	0.181	-0.005	1.206	0.036	0.068	0.150	W <sup>c</sup>
12	ArAuF	Ar-Au	2.391	2.20	3.25	0.068	0.289	-0.016	1.306	0.102	0.176	0.319	W <sup>c</sup>
13	KrCuF	Kr-Cu	2.316	2.29	2.93	0.064	0.267	-0.017	1.319	0.085	0.169	0.356	W <sup>c</sup>
14	KrAgF	Kr-Ag	2.594	2.45	3.21	0.049	0.175	-0.010	1.078	0.057	0.108	0.228	W <sup>c</sup>
15	KrAuF	Kr-Au	2.460	2.41	3.37	0.074	0.242	-0.022	1.120	0.141	0.237	0.418	W <sup>c</sup>
16	XeCuF	Xe-Cu	2.430	2.43	3.11	0.067	0.198	-0.022	1.064	0.116	0.227	0.458	W <sup>c</sup>
17	XeAgF	Xe-Ag	2.666	2.59	3.39	0.057	0.146	-0.015	0.908	0.092	0.172	0.343	C
18	XeAuF	Xe-Au	2.543	2.55	3.55	0.082	0.171	-0.031	0.899	0.200	0.331	0.532	C
19a	HePtF	<sup>2</sup> Σ <sup>+</sup> He-Pt	1.828	1.69	2.64	0.066	0.580	-0.003	2.247	0.058	0.105	0.177	W <sup>c</sup>
19b		<sup>2</sup> Π He-Pt	1.860	1.69	2.64	0.070	0.457	-0.010	1.777	0.060	0.111	0.149	W <sup>c</sup>
19c		<sup>2</sup> Δ He-Pt	1.798	1.69	2.64	0.080	0.601	-0.011	2.012	0.068	0.128	0.193	W <sup>c</sup>
20a	HePtXe	He-Pt	1.818	1.69	2.63	0.077	0.539	-0.012	1.905	0.075	0.139	0.180	W <sup>c</sup>
20b		Xe-Pt	2.509	2.54	3.41	0.087	0.180	-0.035	0.918	0.223	0.420	0.616	C
21	HeB(CH <sub>3</sub> ) <sub>3</sub>	He-B	1.355	1.19	2.13	0.061	0.647	-0.010	2.818	0.249	0.387	0.277	W <sup>c</sup>
22	HeBeO	He-Be	1.522	1.48	2.13	0.030	0.307	0.012	2.176	0.036	0.068	0.084	W <sup>n</sup>
23	NeBeO	Ne-Be	1.798	1.69	2.28	0.025	0.259	0.009	2.242	0.034	0.052	0.146	W <sup>n</sup>
24	ArBeO	Ar-Be	2.076	1.98	2.61	0.033	0.213	0.001	1.605	0.082	0.133	0.315	W <sup>n</sup>
25	KrBeO	Kr-Be	2.211	2.19	2.73	0.032	0.178	-0.002	1.435	0.102	0.165	0.366	W <sup>c</sup>
26	XeBeO	Xe-Be	2.385	2.33	2.91	0.033	0.133	-0.006	1.197	0.134	0.215	0.412	W <sup>c</sup>

<sup>a</sup>A, B, C: types A, B, and C of covalent bond. W<sup>c</sup>, W<sup>n</sup>: weak bonding interaction with some covalent or noncovalent (electrostatic) properties. See the text.

show some covalent character (large  $\rho(r_c)$ , or negative  $H(r_c)$ ) and may be confused with covalent bonds (for example, see refs 43–46, and 54–59), but the bond lengths are much larger (at least 0.2 Å larger) than the empirical covalent bond lengths.

To reveal the nature of rare gas compounds (or complexes), the QTAIM topological data of some rare gas bonds are calculated in this paper, and analyzed using the above criteria for covalent interactions. In addition, natural bond orbital (NBO)<sup>60</sup> and some other widely used analysis techniques have also been performed.

## ■ COMPUTATIONAL METHODS

In addition to the rare gas compounds and complexes mentioned above (RgMF, RgBeO, and so on), the anion FHeO<sup>-61</sup> and unstable HHeF<sup>62,63</sup> were also calculated for comparison. At their equilibrium structures summarized in Table S1 (Supporting Information), the averaged quadratic coupled-cluster (AQCC) method<sup>64</sup> as contained in the MOLPRO program package<sup>65</sup> was used throughout this paper, and was combined with the one-electron second-order Douglas–Kroll–Hess (DKH2)<sup>66,67</sup> approach for the scalar relativistic effects. AQCC has an accuracy similar to that of CCSD, but its natural orbital and electron density are much cheaper to calculate. After the reference wave function was generated by the restricted Hartree–Fock method, all the  $(n-1)d$  [or  $(n-1)s$  and  $(n-1)p$  for alkali atoms],  $ns$ , and  $np$  electrons were correlated at the AQCC level, whereas for the open-shell system HePtF, AQCC was implemented in the multireference (MR) frame (i.e., MR-AQCC; see ref 31 for details). The basis set used in the calculations is the DKH2 relativistic contracted correlation-consistent atomic natural orbital (ANO-RCC) basis functions<sup>68</sup> of quadruple- $\zeta$  quality, in which all the  $h$ -functions are eliminated.

After the wave function at the AQCC level was saved in a Molden<sup>69</sup> file, the format was converted using our Molden2AIM program, and the QTAIM analysis was then carried out using a modified version of Bader's AIMPAC program.<sup>70</sup> The NBO 3.0 program<sup>71</sup> was adopted for the NBO analysis via our interface program MOLBO written for MOLPRO, and the generated orbital files were plotted using GABEDIT<sup>72</sup> with the help of our NBO2Molden program. In addition, the electron localization function (ELF)<sup>73</sup> and the localized orbital locator (LOL)<sup>74</sup> were also calculated using MULTIWFN.<sup>75</sup> The utilities Molden2AIM, MOLBO, and NBO2Molden can be obtained from the Supporting Information.

## ■ RESULTS AND DISCUSSION

The calculated QTAIM topological properties, natural charges of natural population analysis (NPA)<sup>76</sup> and Wiberg bond indices (WBIs)<sup>77</sup> (see also Supporting Information about natural charge and WBI), and Mayer bond orders (MBOs)<sup>78</sup> of the rare gas bonds are summarized in Table 2. In addition, the  $R_{\text{cov}}$  value and the lower limit of the vdW bond length ( $R_{\text{vdw}}$ ) are also shown. The latter can be estimated by

$$R_{\text{vdw}}(\text{Rg}-\text{M}) = r_{\text{vdw}}(\text{Rg}) + r_{\text{ion}}(\text{M}^+)$$

for ionic M–F bonds in RgMF or

$$R_{\text{vdw}}(\text{Rg}-\text{M}) = r_{\text{vdw}}(\text{Rg}) + r_{\text{cov}}(\text{M})$$

for covalent M–X bonds in other molecules, where the covalent atomic radii ( $r_{\text{cov}}$ ) and vdW atomic radii ( $r_{\text{vdw}}$ ) were

respectively given by Pyykkö,<sup>51,79</sup> and the ionic atomic radii ( $r_{\text{ion}}$ ) were proposed by Quill.<sup>80</sup>

The QTAIM analysis indicates covalent He–O, He–H, and Ar–H bonds in FHeO<sup>-</sup>, HHeF, and HArF, respectively (nos. 1–3 in Table 2). These chemical bonds are also supported by the considerable WBI and MBO values. It suggests that the He–O bonds in CsFHeO, NMe<sub>4</sub>FHeO, and more recently studied HeO(LiF)<sub>2</sub><sup>34</sup> may also be covalent ones of type B. According to the sign of the  $H(r_c)$  value, the interaction between F and Rg atoms has more covalent properties in these molecules. The He–F bond in FHeO<sup>-</sup> does not belong to the known covalent bonds. Because it is much larger than the corresponding  $R_{\text{cov}}$  but smaller than  $R_{\text{vdw}}$ , it can be assigned to weak interactions with some covalent properties (bond type of W<sup>c</sup>). The Rg–F bonds in HHeF and HArF may be assigned to covalent bonds of type B. By comparing their bond lengths with  $R_{\text{cov}}$ , however, we find they are W<sup>c</sup> instead. This conflict may indicate that the two Rg–F bonds are a transition type from covalent to W<sup>c</sup> ones. Note that our results of the Ar–F bond are completely different from the ones of Lein et al.,<sup>81</sup> where the Ziegler's energy decomposition analysis (EDA)<sup>82</sup> was performed. It is known that the EDA method has a strong dependence on the choices of molecular fragments, which may introduce some uncertainty into the results. The natural charge of  $-0.73e$  on the F atom indicates that HArF is an intermediate between the extreme cases HAr<sup>+</sup> + F<sup>-</sup> (electrostatic Ar–F<sup>81</sup>) and HAr + F (covalent Ar–F<sup>81</sup>), so it is crude to take either of the choices of the fragments. In the case of polar systems, the other EDA-like methods may also have the same defects, unless fractional charges are used.

Turning to the results of RgMF (M = Cu, Ag, Au, Pt; nos. 4–19 in Table 2), it can be seen that all the RgMF species have positive  $\nabla^2\rho(r_c)$  values, but they do not lead to noncovalent interactions as pointed out above. In the literature, the QTAIM analyses of KrAuF,<sup>10</sup> HePtF,<sup>31</sup> and other RgMF systems<sup>11,26</sup> were misled by the use of  $\nabla^2\rho(r_c)$  and should be re-evaluated.

Because the Rg–M bonds in HeAgF and NeMF have positive local energy densities and large  $G(r_c)/\rho(r_c)$  ratios, they cannot be covalent interactions. On the other hand, however, they are not vdW bonds because their bond lengths are much shorter than  $R_{\text{vdw}}$ . By combining the two points, these Rg–M bonds can be assigned to weak interactions with some noncovalent (electrostatic) properties (bond type W<sup>b</sup>).

All the other Rg–M bonds have negative  $H(r_c)$  parameters, meaning that the covalent interaction is dominant. According to the criteria for a covalent bond given in the Introduction, the Rg–M bonds in XeAgF and XeAuF are covalent (type C) because they have negative  $H(r_c)$  values and small  $G(r_c)/\rho(r_c)$  ratios, whereas the other ones are W<sup>c</sup> type of bonds. However, comparison of the Rg–M bond lengths with the empirical covalent radii suggests that KrCuF, KrAuF, and XeCuF may also have covalent Rg–M bonds, as suggested by Gerry and co-workers,<sup>9,10</sup> and supported by sizable bond orders. This indicates that these three Rg–M bonds may lie on the junction between covalent and weak interactions.

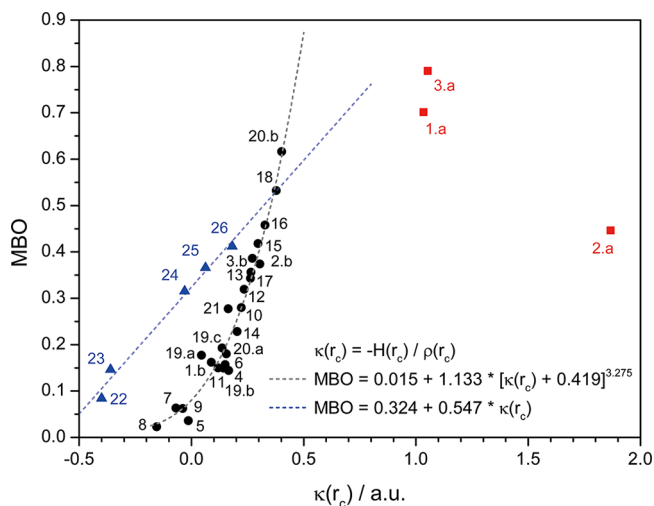
It should be noted that the three widely used analysis methods (EDA, ELF, and LOL) fail to explain the Rg–M bonds. For example, there is no doubt that the Xe–Au bond in XeAuF is covalent (see above analysis, and also ref 7). However, EDA, ELF, and LOL analyses support ionic Xe–Au bond because of strong electrostatic interactions being obtained. The quantitatively wrong results were also reported in the literature (for example, Table 4 in ref 18, and ref 11). It

seems that QTAIM is more robust to analyze the strange and extraordinary bonds.

HePtXe (no. 20) and HeB(CH)<sub>3</sub> (no. 21) are different types of systems from RgMF because the Pt and B atoms are in a covalent environment instead of an ionic one. Using the same criteria for a covalent bond, one can see that the He–Pt and He–B bonds belong to weak interactions ( $W^c$ ), whereas the Xe–Pt bond is covalent, as also supported by the bond lengths and bond orders.

The last group of systems to be analyzed is RgBeO (nos. 22–26 in Table 2). For the lighter three rare gas elements, the Rg–Be bonds can be assigned to the bond type of  $W^n$  because of positive local energy densities and shorter bond lengths than  $R_{vdw}$ , whereas the heavier two elements are  $W^c$  bonds, in spite of considerable bond orders in the Xe–Be bond. The electrostatic character of the He–Be bond also agrees with the previous analyses.<sup>15,22,23</sup>

By comparing  $H(r_c)$  of the two groups RgMF and RgBeO, it seems that they may have different trends in the rare-gas bonds from He to Xe, which may indicate different bonding mechanisms. To examine this idea, we have plotted MBO vs  $\kappa(r_c) = -H(r_c)/\rho(r_c)$  in Figure 1. It can be seen that MBO

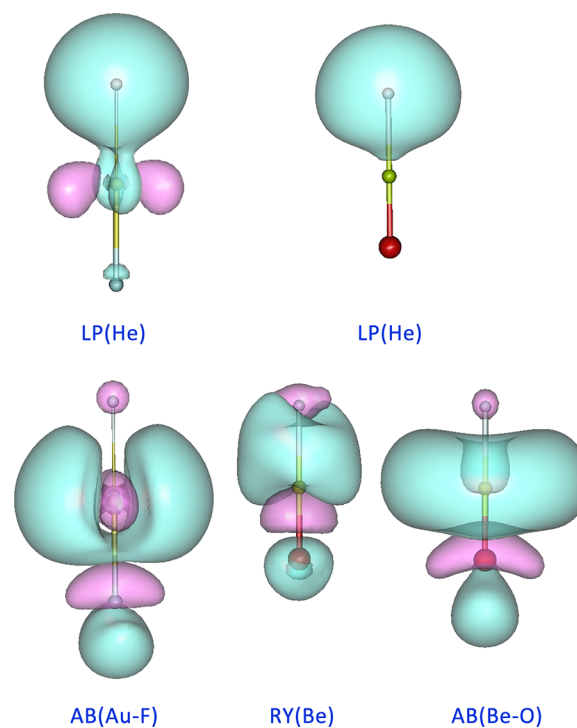


**Figure 1.** Relationship between MBO and  $\kappa(r_c) = -H(r_c)/\rho(r_c)$  with the root-mean-square deviations of 0.032 and 0.015, respectively. See Table 2 for the bond numbers.

(instead of the WBI of NBO) is related to  $\kappa(r_c)$  for both Rg–Be and other rare gas bonds, but with different functions. Note that the function between MBO and  $\kappa(r_c)$  exists only for the covalent bonds of type C and weak interaction bonds. For the He–O (no. 1a), He–H (no. 2a), and Ar–H (no. 3a) bonds, which are covalent bonds of type A and/or B, a simple function cannot be found. In the literature the ratio of  $H(r_c)/\rho(r_c)$  has been called the bond degree (BD).<sup>43</sup> Figure 1 shows that  $\kappa(r_c) = -BD$  is proportional to MBO, at least for the bond types of C,  $W^n$ , and  $W^c$ .

Second-order perturbation theory analysis,<sup>60</sup> which evaluates the donor–acceptor interaction, can help us to understand the origin of stabilization. It was found that the donor is always the rare-gas lone pair (LP) NBO, mainly 1s of He or  $np_z$  of other Rg atoms, but the acceptors are different. The acceptor of RgAuF is the unoccupied valence Au–F antibond (AB), and the donor–acceptor interaction  $LP(Rg) \rightarrow AB(Au-F)$  gives the strongest stabilization energy ( $E_2$ ). For RgBeO there is also

an unoccupied Rydberg (RY) NBO of Be in addition to the Be–O antibond, and the  $E_2$  ratio of the donor–acceptor interactions  $LP(Rg) \rightarrow RY(Be)$  and  $LP(Rg) \rightarrow AB(Be-O)$  is approximately 2:1. So the bonding mechanism of RgBeO is different from that of RgAuF, which may explain the two trend curves in Figure 1. The donor and acceptor NBOs of HeAuF and HeBeO are plotted in Figure 2. It is seen that a small



**Figure 2.** Donor (upper panel) and acceptor (lower panel) NBOs of HeAuF (left panel) and HeBeO (right panel). From top to bottom, the atoms are He, Au, or Be and F or O, respectively. Isovalue = 0.02 (donor) or 0.04 (acceptor).

overlap in the LP(He) of HeAuF exists between He and Au that cannot be found in the LP(He) of HeBeO, so the He–Au bond has more covalent interactions than that in the He–Be one.

From He to Xe (but except Ne), the  $E_2$  value becomes larger and larger, meaning that the RgAuF and RgBeO systems are more and more stable. By checking each term of the formula of  $E_2$  (see eq 1.24 of ref 60), we find that the stabilization strengthening results mainly from the lowering of the donor–acceptor energy gap, whereas the other terms are nearly constants. Although only RgBeO and RgAuF are discussed here, the cases of other species are similar.

## CONCLUSIONS

In this work a number of rare gas bonds, which range from covalent to weak interactions, have been studied at the high-accuracy relativistic AQCC level of theory, mainly by QTAIM with more comprehensive criteria and NBO. The results show that QTAIM (but not including its derivatives, such as QTAIM charge, QTAIM bond order, and so on) is a powerful utility and is universal for the unusual rare gas bonds. In addition, the second-order perturbation theory analysis based on NBO reveals that RgMF and RgBeO have different bonding mechanism.



It was found that most of the Rg–M (M = Cu, Ag, Au, Pt) bonds and all the Rg–Be bonds belong to weak interactions instead of covalent or vdW ones. Our analyses also suggest that, in addition to the known hydrogen bonds, lithium bonds, and halogen bonds,<sup>53</sup> rare gas bonds may be a new kind of weak bonding interaction.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Equilibrium geometries used in this research and the utilities Molden2AIM, MOLBO, and NBO2Molden are available free of charge via the Internet at <http://pubs.acs.org>. Users may modify the source codes, distribute them, or incorporate them (in whole or in part) in their own programs without informing the authors. For questions and bug reports, please send them to the author (W.Z.).

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: W.Z., [wzou@mail.smu.edu](mailto:wzou@mail.smu.edu); J.E.B., [james.boggs@mail.utexas.edu](mailto:james.boggs@mail.utexas.edu).

### Present Address

<sup>§</sup>Department of Chemistry, Southern Methodist University, Dallas, Texas 75275-0314, USA.

### Notes

The authors declare no competing financial interest.

## ■ REFERENCES

- (1) Bartlett, N. *Proc. Chem. Soc.* **1962**, 218–218.
- (2) Atwood, D. A. Noble Gases: Inorganic Chemistry. In *Encyclopedia of Inorganic Chemistry*, 2nd ed.; King, R. B., Eds.; J. Wiley & Sons, Inc.: England, 2005; Vol. VI.
- (3) (a) Schrobilgen, G. J.; Brock, D. S. *Annu. Rep. Prog. Chem. A* **2011**, *107*, 135–141. (b) Schrobilgen, G. J.; Brock, D. S. *Annu. Rep. Prog. Chem. A* **2012**, *108*, 138–145.
- (4) Seidel, S.; Seppelt, K. *Science* **2000**, *290*, 117–118.
- (5) Khriachtchev, L.; Pettersson, M.; Runeberg, N.; Lundell, J.; Räsänen, M. *Nature* **2000**, *406*, 874–876.
- (6) Runeberg, N.; Pettersson, M.; Khriachtchev, L.; Lundell, J.; Räsänen, M. *J. Chem. Phys.* **2001**, *114*, 836–841.
- (7) Cooke, S. A.; Gerry, M. C. L. *J. Am. Chem. Soc.* **2004**, *126*, 17000–17008.
- (8) Cooke, S. A.; Gerry, M. C. L. *Phys. Chem. Chem. Phys.* **2004**, *6*, 3248–3256.
- (9) Michaud, J. M.; Gerry, M. C. L. *J. Am. Chem. Soc.* **2006**, *128*, 7613–7621.
- (10) Thomas, J. M.; Walker, N. R.; Cooke, S. A.; Gerry, M. C. L. *J. Am. Chem. Soc.* **2004**, *126*, 1235–1246.
- (11) Michaud, J. M.; Cooke, S. A.; Gerry, M. C. L. *Inorg. Chem.* **2004**, *43*, 3871–3881.
- (12) Evans, C. J.; Gerry, M. C. L. *J. Chem. Phys.* **2000**, *112*, 9363–9374.
- (13) Evans, C. J.; Gerry, M. C. L. *J. Chem. Phys.* **2000**, *112*, 1321–1329.
- (14) Evans, C. J.; Rubinoff, D. S.; Gerry, M. C. L. *Phys. Chem. Chem. Phys.* **2000**, *2*, 3943–3948.
- (15) Evans, C. J.; Wright, T. G.; Gardner, A. M. *J. Phys. Chem. A* **2010**, *114*, 4446–4454.
- (16) Mou, C.-H.; Witek, H. A. *J. Chem. Phys.* **2008**, *129*, 244310–1–11.
- (17) Lovallo, C. C.; Klobukowski, M. *Chem. Phys. Lett.* **2003**, *368*, 589–593.
- (18) Fang, H.; Zhang, X.-G. *Theor. Chem. Acc.* **2009**, *123*, 443–453.
- (19) Lai, T.-Y.; Yang, C.-Y.; Lin, H.-J.; Yang, C.-Y.; Hu, W.-P. *J. Chem. Phys.* **2011**, *134*, 244110–1–8.
- (20) Belpassi, L.; Infante, I.; Tarantelli, F.; Visscher, L. *J. Am. Chem. Soc.* **2008**, *130*, 1048–1060.
- (21) Koch, W.; Collins, J. R.; Frenking, G. *Chem. Phys. Lett.* **1986**, *132*, 330–333.
- (22) Koch, W.; Frenking, G.; Gauss, J.; Cremer, D.; Collins, J. R. *J. Am. Chem. Soc.* **1987**, *109*, 5917–5934.
- (23) Frenking, G.; Koch, W.; Gauss, J.; Cremer, D. *J. Am. Chem. Soc.* **1988**, *110*, 8007–8016.
- (24) Borocci, S.; Bronzolino, N.; Grandinetti, F. *Chem. Phys. Lett.* **2005**, *406*, 179–183.
- (25) Takayanagi, T.; Motegi, H.; Taketsugu, Y.; Taketsugu, T. *Chem. Phys. Lett.* **2008**, *454*, 1–6.
- (26) Zou, W.; Liu, Y.; Boggs, J. E. *Chem. Phys. Lett.* **2009**, *482*, 207–210.
- (27) Chen, R.; Zhu, H.; Xie, D.; Yan, G. *Sci. China B: Chem.* **2009**, *52*, 1987–1990.
- (28) Evans, C. J.; Wright, T. G.; Gardner, A. M. *J. Phys. Chem. A* **2010**, *114*, 4446–4454.
- (29) Rodrigues, E. F. F.; de Sá, E. L.; Haiduke, R. L. A. *J. Phys. Chem. A* **2010**, *114*, 5222–5229.
- (30) (a) Wang, X.; Andrews, L.; Brosi, F.; Riedel, S. *Chem. Eur. J.* **2012**, DOI: 10.1002/chem.201203306. (b) Wang, X.; Andrews, L.; Willmann, K.; Brosi, F.; Riedel, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 10628.
- (31) Zou, W.; Liu, Y.; Boggs, J. E. *Dalton Trans.* **2010**, *39*, 2023–2026.
- (32) Rzepa, H. S. *Nat. Chem.* **2010**, *2*, 390–393.
- (33) Taketsugu, Y.; Taketsugu, T.; Noro, T. *J. Chem. Phys.* **2006**, *125*, 154308–1–10.
- (34) (a) Grochala, W. *Pol. J. Chem.* **2009**, *83*, 87–122. (b) Grochala, W. *Phys. Chem. Chem. Phys.* **2012**, *14*, 14860–14868.
- (35) Ono, Y.; Taketsugu, T. *J. Chem. Phys.* **2004**, *120*, 6035–6040.
- (36) Ono, Y.; Taketsugu, T. *Monatsh. Chem.* **2005**, *136*, 1087–1106.
- (37) (a) Kobayashi, T.; Seki, K.; Takayanagi, T. *Chem. Phys. Lett.* **2010**, *498*, 235–239. (b) Kobayashi, T.; Kohno, Y.; Takayanagi, T.; Seki, K.; Ueda, K. *Comput. Theor. Chem.* **2012**, *991*, 48–55.
- (38) Tanaka, T.; Takayanagi, T.; Taketsugu, T.; Ono, Y. *Chem. Phys. Lett.* **2012**, *539–540*, 15–18.
- (39) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, U.K., 1990.
- (40) (a) Macchi, P.; Proserpio, D. M.; Sironi, A. *J. Am. Chem. Soc.* **1998**, *120*, 13429–13435. (b) Macchi, P.; Garlaschelli, L.; Martinengo, S.; Sironi, A. *J. Am. Chem. Soc.* **1999**, *121*, 10428–10429. (c) Novozhilova, I. V.; Volkov, A. V.; Coppens, P. *J. Am. Chem. Soc.* **2003**, *125*, 1079–1087. (d) Farrugia, L. J.; Senn, H. M. *J. Phys. Chem. A* **2010**, *114*, 13418–13433.
- (41) Cremer, D.; Kraka, E. *Angew. Chem., Int. Ed.* **1984**, *23*, 627–628.
- (42) Koritsanszky, T. S.; Coppens, P. *Chem. Rev.* **2001**, *101*, 1583–1627.
- (43) Espinosa, E.; Alkorta, I.; Elguero, J.; Molins, E. *J. Chem. Phys.* **2002**, *117*, 5529–5542.
- (44) Gervasio, G.; Bianchi, R.; Marabello, D. *Chem. Phys. Lett.* **2004**, *387*, 481–484.
- (45) Nakanishi, W.; Hayashi, S.; Narahara, K. *J. Phys. Chem. A* **2009**, *113*, 10050–10057.
- (46) Grabowski, S. J. *Chem. Rev.* **2011**, *111*, 2597–2625.
- (47) Koch, U.; Popelier, P. L. A. *J. Phys. Chem.* **1995**, *99*, 9747–9754.
- (48) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules*; Van Nostrand Reinhold: New York, 1979.
- (49) Peterson, K. A.; Figgen, D.; Goll, E.; Stoll, H.; Dolg, M. *J. Chem. Phys.* **2003**, *119*, 11113–11123.
- (50) Amiot, C.; Crozet, P.; Vergès, J. *Chem. Phys. Lett.* **1985**, *121*, 390–394.
- (51) Pyykkö, P.; Atsumi, M. *Chem.—Eur. J.* **2009**, *15*, 12770–12779.
- (52) Sanderson, B. T. *Chemical Bonds and bond energy*; Academic Press: New York, 1976.
- (53) Li, Z.; Shi, X.; Tang, H.; Zhang, J. *Sci. China Chem.* **2010**, *53*, 216–225.

- (54) Huang, Z.; Yu, L.; Dai, Y. *Struct. Chem.* **2010**, *21*, 565–572.
- (55) Fuster, F.; Grabowski, S. J. *J. Phys. Chem. A* **2011**, *115*, 10078–10086.
- (56) Zhao, J.; Khalizov, A.; Zhang, R.; McGraw, R. *J. Phys. Chem. A* **2009**, *113*, 680–689.
- (57) Bianchi, R.; Forni, A.; Pilati, T. *Chem.—Eur. J.* **2003**, *9*, 1631–1638.
- (58) Lu, Y.-X.; Zou, J.-W.; Wang, Y.-H.; Yu, Q.-S. *J. Mol. Struct. THEOCHEM* **2006**, *776*, 83–87.
- (59) Zhang, X.; Zeng, Y.; Li, X.; Meng, L.; Zheng, S. *Struct. Chem.* **2011**, *22*, 567–576.
- (60) Weinhold, F.; Landis, C. R. *Valency and bonding: a natural bond orbital donor-acceptor perspective*; Cambridge University Press: New York, 2005.
- (61) Li, T.-H.; Mou, C.-H.; Chen, H.-R.; Hu, W.-P. *J. Am. Chem. Soc.* **2005**, *127*, 9241–9245.
- (62) Wong, M. W. *J. Am. Chem. Soc.* **2000**, *122*, 6289–6290.
- (63) Takayanagi, T.; Wada, A. *Chem. Phys. Lett.* **2002**, *352*, 91–98.
- (64) Szalay, P. G.; Bartlett, R. J. *Chem. Phys. Lett.* **1993**, *214*, 481–488.
- (65) Werner, H.-J.; Knowles, P. J.; Lindh, R.; Manby, F. R.; Schütz, M.; Celani, P.; Korona, T.; Mitrushenkov, A.; Rauhut, G.; Adler, T. B.; Amos, R. D.; Bernhardsson, A.; Berning, A.; Cooper, D. L.; Deegan, M. J. O.; Dobbyn, A. J.; Eckert, F.; Goll, E.; Hampel, C.; Hetzer, G.; Hrenar, T.; Knizia, G.; Köppl, C.; Liu, Y.; Lloyd, A. W.; Mata, R. A.; May, A. J.; McNicholas, S. J.; Meyer, W.; Mura, M. E.; Nicklass, A.; Palmieri, P.; Pflüger, K.; Pitzer, R.; Reiher, M.; Schumann, U.; Stoll, H.; Stone, A. J.; Tarroni, R.; Thorsteinsson, T.; Wang, M.; Wolf, A. *MOLPRO*, version 2009.1, a package of ab initio programs; 2009. <http://www.molpro.net>.
- (66) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89–155.
- (67) Hess, B. A. *Phys. Rev. A* **1986**, *33*, 3742–3748.
- (68) Roos, B. O.; Lindh, R.; Malmqvist, P.-Å.; Veryazov, V.; Widmark, P.-O. *J. Phys. Chem. A* **2005**, *109*, 6575–6579.
- (69) Schaftenaar, G. *MOLDEN* version 5.0, a pre- and post processing program of molecular and electronic structure, 2010. <http://www.cmbi.ru.nl/molden/molden.html>.
- (70) Bader, R. F. W. *AIMPAC*, 1994. <http://www.chemistry.mcmaster.ca/aimpac/>; the source codes were a little modified to use the g basis functions.
- (71) Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO* version 3.0, 1994. <http://www.ccl.net/cca/software/SOURCES/FORTRAN/nbo/index.shtml>.
- (72) Allouche, A. R. *J. Comput. Chem.* **2011**, *32*, 174–182.
- (73) Savin, A.; Silvi, B.; Colonna, F. *Can. J. Chem.* **1996**, *74*, 1088–1096.
- (74) Schmider, H. L.; Becke, A. D. *J. Mol. Struct. THEOCHEM* **2000**, *527*, 51–61.
- (75) Lu, T.; Chen, F. *J. Comput. Chem.* **2012**, *33*, 580592; <http://multiwfn.codeplex.com/>
- (76) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735–746.
- (77) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083–1096.
- (78) Mayer, I. *Int. J. Quantum Chem.* **1986**, *29*, 477–483.
- (79) Pyykkö, P. *Chem. Rev.* **1997**, *97*, 597–636.
- (80) Chen, N.; Lu, W.; Yang, J.; Li, G. *Support Vector Machine in Chemistry*; World Scientific: Singapore, 2004.
- (81) Lein, M.; Frunzke, J.; Frenking, G. *Struct. Bonding (Berlin)* **2004**, *106*, 181–191.
- (82) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1–10.