Closed-Shell Interactions in Heavy-Element Chemistry

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The title subject arises from correlation effects and is influenced by relativistic effects for the heavier main-group molecules or for the d^8, d^{10} and s^2 metal cations. They all show attractions in the energy range of 0.1 – 0.4 eV per pair, below normal covalent or metal-ligand bond energies, but at the upper limit of the van der Waals ones. This attraction arises between closed-shell monomers of the same charge, in the absence of binding valence electrons. The available structural and energetic evidence was reviewed in [1]. Theoretical ab initio calculations recover this attraction, with the right range and energy, at the correlated level. A substantial body of work now exists on monovalent coinage metals, notably Au(I). The latest papers are [2-3]. Ongoing work reveals attractions between Au(I) and Pd(II) or between Au(I) and an aromatic ring. Both classical dispersion and ionic excitations contribute. We furthermore have reconsidered cyclopentadienyls of In and Tl [4].

1. P. Pyykkö, "Strong closed-shell interactions in inorganic chemistry", *Chem. Rev.* **97** (1997) 597.
2. P. Pyykkö and T. Tamm, *Organometallics* **17** (1998) 4842.
3. P. Pyykkö and T. Tamm, *Theor. Chem. Acc.* (1999).
4. P. Pyykkö, M. Straka and T. Tamm, *PCCP* (1999) 3441.

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