

# Theory of d 10 - d 10 Closed-Shell Attraction. III. Rings

Pyykkö, Pekka

Mendizabal, Fernando

We study the dependence of the intramolecular M I-M I interaction on electron correlation effects in eight-membered rings of type  $[M_2(PH_2CH_2PH_2)_2]^{2+}$ ,  $[M_2(NHCHNH)_2]$ ,  $[M_2(SCHS)_2]$  ( $M = Au, Ag, Cu$ ),  $[Au_2(PH_2CH_2PH_2)_2]Cl_2$ , halogenometal(I)  $[M_2X_4]^{2-}$  ( $M = Au, Ag, Cu$ ;  $X = Cl, Br, I$ ), and  $[Au_2Te_4]^{2-}$  at the quasirelativistic pseudopotential ab initio MP2 and Hartree-Fock levels. The intramolecular M I-M I distances,  $R$ , at the MP2 level fall in the same range as the experimental ones. The  $R$  values are reduced from HF to MP2 level. All the calculations suggest that correlation effects are essential. The reduction of  $R$  depends on the particular M-L combination ( $L =$  ligand). In the rings, short Cu I-Cu I distances are recovered for the first time. The explicit inclusion of the counterions is unimportant for M I and essential for M II, as shown by a study of the oxidative addition of  $Cl_2$  to the model  $[Au_2(CH_2PH_2CH_2)_2]^-$ . The Au(I) is then oxidized to Au(II), and the Au-Au dis