Unexpected features of correlation effects involving 3d-electrons

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Two pairs of basis set sequences that systematically converge to the complete basis set (CBS) limit have been employed in the calculations of various components of the electron correlation energies of Zn^{2+} and Zn by several state-of-the-art *ab initio* techniques [1].

The correlation energies have been determined with second-order Møller-Plesset perturbation theory (MP2) and several single-reference coupled cluster (CC) methods [CCD, CCSD, CCSD(T), CCSDT, CCSDT(Q)]. The CC results represent the most accurate post-MP2 correlation energies ever obtained for closed-shell atoms including 3d-electrons .

Our results indicate that for the systems considered, the magnitudes of the MP2 correlation energies overestimate the magnitudes of the CC values for all electrons correlated as well as of their various subsets. For the all-electron correlation energies of the Zn atom, our result confirms the finding of McCarthy and Thakkar [2] obtained by means of non-*ab initio* approaches for all heavy closed-shell atoms. We have shown that both for Zn^{2+} and Zn this overestimation is directly caused by the presence of the $3d^{10}$ electron configuration.

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[1] K. Jankowski and K. A. Peterson, Phys. Rev. A **86**, 022526 (2012).

[2] V. McCarthy and A. J. Thakkar, J. Chem. Phys. **134**, 044102 (2011).