Dimer-based atomic basis sets from coupled-cluster theory

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A new concept in the construction of atomic basis sets is presented, in which they are not generated from atomic calculations, but rather from calculations on the corresponding dimers. These new sets are obtained according to the atomic natural procedure (ANO),[1-3] from CCSD(T) density matrices using the primitive Gaussians in the correlation consistent series (cc-pVXZ, X=D, T, Q),[4] calculated for the dimers of the atoms in the first and second rows of the periodic table, at the experimental bond lengths and in the respective ground states. This approach alleviates the bias toward the atoms in comparison with molecular species and provides a superior alternative to the usual recipe of basis set development. Results show significant improvement over the cc-pVXZ sets as well as in comparison with our ANO-VT-XZ[basis sets for the total energy calculations in the neutral species of the Gaussian-1[5] and Gaussian-2[6] test sets.

References

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