Tightening the screws: The importance of diffuse and tight d functions in post-CCSD(T) calculations

Amir Karton[1,2]

[1]*School of Science and Technology, University of New England, Armidale, NSW 2351, Australia*
[2]*School of Molecular Sciences, The University of Western Australia, Perth, WA 6009, Australia*

E-mails: amir.karton@une.edu.au; amir.karton@uwa.edu.au

High-level composite ab initio methods that include contributions beyond the CCSDT(Q) level can obtain thermochemical data with confident sub-kJ/mol accuracy. Apart from obtaining highly accurate thermochemical and kinetic properties, these methods are essential for generating large and diverse databases for the parameterization and validation of CCSD(T)-based composite ab initio procedures and double-hybrid density functional theory methods.[1] This talk will focus on the basis set convergence of post-CCSD(T) contributions for a diverse set of first- and second-row molecules.[2,3] This set covers many possible bonding situations and electronic structures, including pseudohypervalent, multireference, and open-shell species. We consider the correlation-consistent cc-pV*n*Z, aug-cc-pV*n*Z, and cc-pV(*n*+d)Z basis sets (*n* = D, T, Q, 5, 6). We show that the effect of diffuse functions diminishes for higher cluster expansion terms (i.e., in the order T–(T) > (Q) > Q–(Q)) and with the size of the basis set. Importantly, we find that diffuse functions tend to systematically reduce the T–(T) contribution but increase the (Q) contribution.[2] Thus, using the cc-pV*n*Z basis sets benefits from a certain degree of error cancellation between these two components. The addition of high-exponent d functions on second-row elements can affect the overall post-CCSD(T) contributions to total atomization energies by up to 0.1 kcal mol^{-1} for pseudohypervalent species such as $HClO_4$ and ClF_5.

References:

[1] A. Karton, N. Sylvetsky, J. M. L. Martin, *J. Comput. Chem.* **2017**, 38, 2063.

[2] A. Karton, *J. Chem. Phys.* **2018**, 149, 034102.

[3] A. Karton. *J. Chem. Phys.* **2020**, 153, 024102.