Chemically-accurate excited- state energies and properties for molecules

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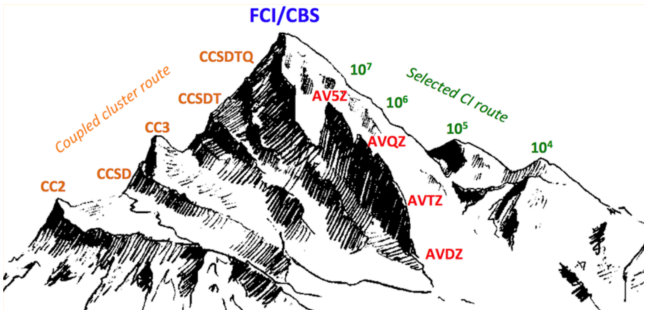
During this seminar, I will describe efforts made to create a large database of ultra-accurate reference values for electronic excited states, the so-called QUEST database. The database encompasses vertical transition energies,[1] oscillator strengths,[2] dipole moments,[2] and geometries[3] for a large set of small and medium-sized molecules. Excited states of various nature (π-π *, n- π *, double excitation, Rydberg, singlet, doublet, triplet…) have been considered. These values have been obtained using an incremental strategy which consists in combining high-order coupled cluster and selected configuration interaction calculations using increasingly large diffuse basis sets in order to reach high accuracy. This allowed producing theoretical best estimates (TBEs) with the *aug*-cc-pVTZ basis set for each of these transitions, as well as basis set corrected TBEs (i.e., near the complete basis set limit) for some of them. It should be noted that the QUEST database does not rely on any experimental values, avoiding potential biases inherently linked to experiments and facilitating theoretical cross comparisons. In a second part of the talk, I will show how the TBEs/*aug*-cc-pVTZ have been employed to benchmark a large number of (lower-order) wave function methods such as CIS(D), ADC(2), CC2, STEOM-CCSD, CCSD, CCSDR(3), CCSD(T)(a)*, CCSDT-3, ADC(3), CC3, CASPT2, NEVPT2, and so on (including spin-scaled variants). The performances of CC4[4] and the specific case of double excitations[5] will be discussed as well.



[1] M. Véril et al. *WIREs Comp. Mol. Sc*. **11** (2021) e1517
[2] A. Chrayteh, A. Blondel, P. F. Loos and D. Jacquemin *J. Chem. Theory Comput*. **17** (2021) 416
[3] S. Budzak, G. Sclamani and D. Jacquemin *J. Chem. Theory Comput*. **13** (2017) 6237.
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Excited states; Benchmarks; Selected CI; Coupled-Cluster