Searching for Super-Accuracy in Excited-State Calculations

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I will summarize recent efforts devoted to the definition of very accurate values for electronic excited states. For vertical transition energies, for which no comparisons with experimental data are available, I will show how high-level coupled cluster (CC) calculations (up to CCSDTQP) and selected configuration interaction (sCI) calculations (up to several millions of determinants) can provide very consistent estimates, of Full CI quality, for more than 100 states in compact compounds [1]. These reference data can be further used to benchmark several wave function methods in a very reliable way [1], including excited states presenting a strong double excitation character [2] Next, I will turn to comparisons with experimental data, and, more precisely 0-0 energies, for which I will show that chemical accuracy (errors smaller than 0.05 eV) can be reached almost systematically, even when geometries that are not extremely accurate are used [3,4]. Finally, I will discuss the quality of the excited state geometrical parameters that can be attained with various theoretical approaches [5,6], as well as their influence on the vertical fluorescence energies [7].

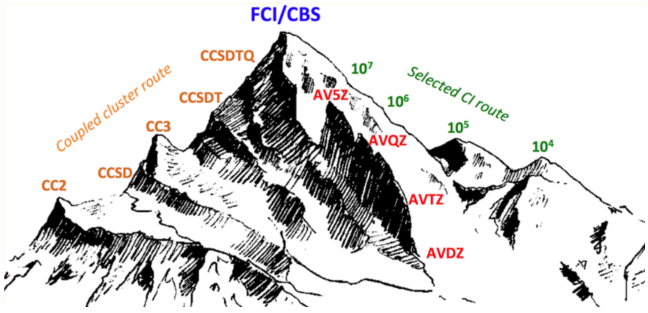

Figure 1: Illustration of the approach followed.

References

1. P. F. Loos, A. Scemana, A. Blondel, Y. Garniron, M. Caffarel and D. Jacquemin, *J. Chem. Theory Comput.* **14** (2018), 4360.
2. P. F. Loos, M. Boggio-Pasqua, A. Scemana, M. Caffarel and D. Jacquemin, *J. Chem. Theory Comput.* **15** (2019), 1939.
3. P. F. Loos, N. Galland and D. Jacquemin, *J. Phys. Chem. Lett.* **9** (2018), 4646.
4. P. F. Loos and D. Jacquemin, *J. Chem. Theory Comput.* (2019), 10.1021/acs.jctc.8b01103.
5. S. Budzak, G. Scalmani and D. Jacquemin, *J. Chem. Theory Comput.* **13** (2017), 6237.
6. E. Bremond, M. Savarese, C. Adamo and D. Jacquemin, *J. Chem. Theory Comput.* **14** (2018), 3715.
7. D. Jacquemin, *J. Chem. Theory Comput.* **14** (2018), 1534.