Computational Studies

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Excellent, Valuable, and Entertaining

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I very much enjoyed reading this essay by three of the most prominent computational chemists,[1] who touch upon very important and long-standing issues.

The term "stability" is indeed used with different definitions, which are usually implicitly taken for granted within the corresponding communities but which often lead to misunderstandings if used in front of a more general, mixed audience. As the authors correctly describe, for a computational chemist (but not exclusively for those; many gas-phase chemists behave similarly) a molecule or ion is stable if it resides in a (usually local) minimum with barriers exceeding the zero-point energy of the corresponding vibrations. In experimental terms, this translates into stability in perfect vacuum at $T = 0$ K, not a very common situation. This has nothing to do with the "you can fill it in a bottle" criterion which our experimental friends usually employ and which more or less corresponds to "viable" molecules/ions as defined by the authors. Here, let me mention one critical comment which I ask the authors to consider: The authors admit that their HOMO–LUMO criterion is biased towards organic species, since it does not apply to extended inorganic structures with metallic character. To be frank, in my opinion this disqualifies the whole criterion.

The domain of "fleeting" molecules is the true domain of computational chemistry and its experimental ally, gas-phase chemistry. However, I do not completely agree with the authors' criterion that is it sufficient to have calculated only real frequencies. A species with only real frequencies (which are computed in the harmonic approximation!) can still be unstable (in the fleeting sense) if the zero-point vibrational energy of a particular mode is higher than the barrier in the electronic energy along this coordinate (i.e. if the potential in that dimension is not deep enough to accommodate at least the $v = 0$ vibration).

The discussion of accuracy and precision is enjoyable and instructive reading. Unfortunately, the problem of the lack of precision (or the reproducibility of numerical results using the same level of theory but different programs, in particular with approximate DFT) is not common knowledge. Let me also here note a small inaccuracy in the discussion: While B3LYP is indeed based on Becke's three-parameter hybrid approach, the explicit form of the functional is not from Becke but from Stephens et al. Hence, Becke never "intended" anything with B3LYP. Nevertheless, the basic statement, namely that there are different implementations of the B3LYP functional (which differ in the VWN component of the local correlation contribution) is correct.

Nothing to comment on the part on "significant figures". This indeed is an annoying problem. Inexperienced users uncritically believe everything the programs tell them and mix up the numerical accuracy of the machine with the inherent accuracy of the chosen level of approximation. Although this is, in principal, a trivial point, it is worth repeating.

One final comment: I am a great believer in calibration when it comes to applying in particular approximate DFT to new problems. I wonder whether the authors share this view and would add a corresponding recommendation.

To sum up: This is an excellent contribution, nice and even entertaining to read but nevertheless full of very valuable insights and recommendations. The paper should be published in *Angewandte Chemie*, but I ask the authors to consider my minor comments given above.

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