

On carbon clusters: A general purpose wave function-based method for calculation and automated location of multiple structural isomers

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Carbon clusters have fascinated chemists and physicists throughout the years. The smaller C_n clusters play a key role in the chemistry of carbon stars, comets, and interstellar molecular clouds, while acting as building blocks for the formation of complex carbon-containing compounds. Added to such a vast astrophysical significance, carbon chains can act as intermediates in chemical vapor deposition systems for production of carbon-rich thin films, and be predominant species in terrestrial sooting flames. All the above stems from their physico-chemical properties, which find a justification on the exceptional bonding flexibility of carbon as demonstrated by its unique ability to form single, double, and triple (even quadruple for C_2 ($X^1\Sigma_g^+$) [1]) bonds; the field has been much reviewed, and hence we address the reader to our recent papers [2, 3] for references. Naturally, the elucidation of the possible mechanisms that lead to formation of such aggregates is only attainable once the properties of the smaller ones have been clarified [4]. It turns out that the existence of nearly isoenergetic isomers, a high-density of low-lying singlet/triplet electronic states, and a significant multi-reference character, makes their study theoretically challenging [2, 3].

Density functional theory (DFT) is commonly regarded as the leading first-principles method in computing electronic structures and properties in molecular science, particularly when dealing with large-sized molecules [4, 7]. Of concern here is its mainstream: Kohn-Sham [6] (KS) DFT. Although offering an exact formulation of quantum mechanical electronic structure theory, KS DFT relies on approximate exchange-correlation functionals: were these known, and it would fully account for all complex many-body effects at a cost characteristic of mean-field approximations. As a result, one meets a proliferation of DFT functionals, with the best for one application being often not the best for another. Recently [8], we have found that second-order Moller-Plesset perturbation theoretic results extrapolated from the first steps of the

hierarchical staircase to the complete basis set limit, MP2/CBS(d, t), can rival DFT/M06-2X [7], both in time and accuracy. Such findings extend to other popular functionals.

After introducing the various involved issues, we show that by combining second-order Møller-Plesset perturbation theoretic calculations with extrapolation of the energy to the complete basis set limit, a fully ab initio approach emerges capable of rivaling with KS DFT both in accuracy and cost-effectiveness. In fact, spin-scaling may even be used to give the calculated energies couple-cluster-like quality: first to the MP2/*VDZ* and MP2MP2/*VTZ* energies, then to the MP2/CBS(d, t) ones. The results are shown to compare well with the much more expensive CCSD(T)/CBS(d, t) energies, which are considered the golden rule of quantum chemistry.

By further combining the approach with a stimulated breakup of the molecule, the present wave function based method is shown to offer a near automated tool for locating all structural isomers at a high level of theory. Further adaptations suggest themselves for locating unstable intermediates.

References

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