Development of a two point extrapolated energy based on the B3LYP/cc-pVDZ and cc-pVTZ energies, aiming a CBS method

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INTRODUCTION

Considering the current performance of computers along with the constant and growing need for general accurate data, a single configuration and small basis set do not represent an appropriate methodology for obtaining accurate molecular properties for large systems. On the other hand, reliable and accurate methods like MRCI are computationally expensive and prohibitive for large molecules. Composite methods such as CBS (Complete Basis Set) present an alternative based on suitable extrapolation of properties considering a sequence of calculations from an hierarchical basis set (ANO Almlöf, Dunning Correlation-Consistent Basis Set,[1] pc-n and others) and an appropriate correlated level of theory. On the other hand, the low cost of density functional calculation recommend its use as a source of reliable information for large molecules. The present work combines both perspectives, it describes the development of an extrapolation method based on a two points energies formula at the B3LYP/cc-pV(n)Z (n = D and T) level of theory.

METHODS

A set of 26 open and closed shell molecules, 14 atoms, 21 cationic and 19 anionic species were selected as test set. B3LYP/6-31G(d) was chosen to define the equilibrium geometry and B3LYP/cc-pV(n)Z (n = D, T, Q and 5) single-point energies was used to interpolate the energies according to the expression: E_{CBS}: $E_n = E_{CBS} + B\exp(-n/t)$.[2] The same procedure was done using the inverse cubic extrapolation formula with cc-pVDZ and cc-pVTZ basis, including one additional term in the extrapolation formula in two different forms, resulting in the following forms: $E_n = E_{CBS} + A(n + b)^{-3}$ and $E_n = E_{CBS} + An^{-3b}$, "b" was obtained by minimizing the sum of squared differences between the energies calculated by the exponential and the modify inverse cubic formula.

RESULTS AND DISCUSSION

The exponential model for extrapolation to the CBS limit showed an excellent agreement with respect to the calculated energies (n = 2, 3, 4 and 5) and it was used to adjust the "b" parameter in the modified inverse cubic function. The calculated OLS for the modified inverse cubic form ($E_n = E_{CBS} + An^{-3b}$) compared with B3LYP/cc-pV(n)Z energies presented the largest deviation (about 0.44 kcal.mol^{-1}) for ionized atoms. The OLS differences estimated between both models are greater for ionic molecules (0.31 kcal.mol^{-1}).

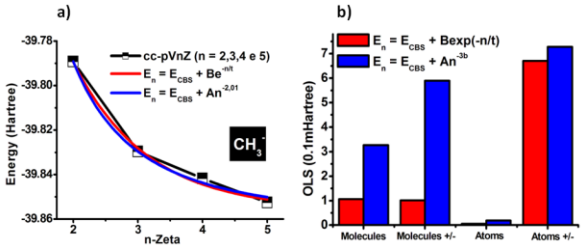

Figure 1: a) Single-point energies for modified inverse cubic and exponential extrapolated curves, b) OLS energies estimated between both forms.

CONCLUSIONS

The two modify formulas $E_n = E_{CBS} + A(n + b)^{-3}$ and $E_n = E_{CBS} + An^{-3b}$ related in this work, with the b parameter based on exponential extrapolation method present an excellent alternative to estimate E_∞ on CBS methodologies by using B3LYP calculations.

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