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Assessing Dunning's basis set along with the G3(MP2)//B3 theory for ionization energies

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Abstract: Combinations of ab initio calculations at distinct levels to produce accurate results are known as composite methods. Its use has been often made to estimate different properties with high accuracy, mainly controlling basis functions and electron correlation effects [1]. Among these methods, Gaussian-n (n = 1, 2, 3, 4) developed by Pople, Curtiss et al [2] stands out in the literature. Different versions of the G3 theory with reduced computational costs have been developed more recently as for example: G3(MP2)//B3 [3] e G3(MP2)//B3-CEP [1]. In all Gaussian-n composite methods the use of Pople basis functions is predominant. In this work, we evaluated the effectiveness of Dunning basis sets, cc-pVnZ and aug-cc-pVnZ with n = 2, 3, 4 and 5, in the reduced order theory G3(MP2)//B3 for ionization energy calculations of atoms from the 1st, 2nd and 3rd period of the periodic table. The original version uses the 6-31G(d) double-zeta basis sets for the optimization of geometry, harmonic frequencies, both at the B3LYP level, and electronic correlation effects at QCSID(T). For the purpose of comparison, the mean absolute error (MAD) and standard deviations (Std.) were used. All calculations were performed with Gaussian software 09W [4].
From the calculation of first ionization energies it was observed a reduction of MAD from 1.6 kcal mol^{-1} to 0.8 kcal mol^{-1} when the cc-pVdZ and cc-pV5Z basis set were used along with G3(MP2)//B3. The results with the largest basis set show that the modified G3(MP2)//B3 achieves lower MAD than the original method (MAD = 1.7 kcal mol^{-1}) and the respective version using pseudopotential, G3(MP2)//B3-CEP (MAD = 2.3 kcal mol^{-1}). The inclusion of diffuse functions reduces the error from 1.4 kcal mol^{-1} to 1.0 kcal.mol^{-1}.
Therefore, the results show that the search for better accuracy in calculations involving ionization energy and the G3(MP2)//B3 composite method is convenient to consider the correlation-consistent basis set instead of the traditional Pople's bases.

Key-words: ionization energy, compound methods, Dunning basis set.
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