XIX SBQT
Simpósio Brasileiro de Química Teórica 2017
12 a 17/Nov, 2017, Águas de Lindóia/SP, Brasil

Study of Dimers via Quantum Monte Carlo

Authors: Cassius Marcellus Costa Carvalho, José Roberto dos Santos Politi.

Address: Universidade de Brasília, Instituto de Química, Laboratório de Química Computacional, CP 04478, Brasília, DF, 70904-970.

Abstract: Monte Carlo method is a statistical method used to calculate integrals by means of random samplings. When this method is applied to calculate quantum properties of atomic and molecular systems, it is called Quantum Monte Carlo (QMC) [1]. The two most commonly used QMC methods are: Variational Monte Carlo and Diffusion Monte Carlo [2]. In this work, QMC was used for the calculation of interaction energy of dimers, specifically dimers of CH_4 that have an expressive van der Waals interactions contribution. The studied dimers were: CH_4-CH_4, CH_4-HF, CH_4-H_2O. These dimers have great importance in astrophysical and spectroscopic applications [3,4,5,6]. Thus, the main objective of this work is to evaluate the QMC method to calculate the interaction energy of van der Waals dimers. To perform the calculations, it was used wave functions generated by two *ab initio* methods - Hartree Fock (HF) and DFT – in order to analyze the quality of the wave functions to be used as guide function in QMC. The Gaussian09 program was used to perform the HF and DFT calculations and the two wave functions were used as input of QMC method in Casino software. By analyzing the results of the energies of the molecules and the dimers, it was observed that all of them were in line with the referential values. Also, it was confirmed that the effects included in the DFT did not impact the wave function when it was used in QMC and the same basis set did not induce the same proportional energy improvement in the dimer and in separated molecules. In other words, the quality of the wave function is not equal for the dimer and for the molecules that composed it. Another important characteristic observed was that the deviations of the interaction energy increase with the number of electrons difference between the two molecules that formed the dimer. Finally, it was observed that the quality of the results generated by QMC does not depend on the nature of the interaction.

Key-words: Monte Carlo, dimers, van der Waals interactions
Support: This work has been supported by CNPq, FAPDF and CAPES.

References:

[1] J. R. S. Politi, R. Custódio, N. H. Morgon, K. Coutinho, "Métodos de Química Teórica e Modelagem Molecular" (2007), Editora Livraria da Física, São Paulo, Brazil.
[2] W. F. D. Angelotti, A. L. d. Fonseca, G. B. Torres, R. Custodio, Química Nova., 31, 433 (2008).
[3] I. Buryak, Y. Kalugina, A. Vigasin, Journal of Molecular Spectroscopy., 291, 102 (2013).
[4] Y. N. Kalugina, S. E. Lokshtanov, V. N. Cherepanov, A. A. Vigasin, The Journal of chemical physics., 144, 054304 (2016).
[5] A. C. Legon, B. P. Roberts, A. L. Wallwork, Chem. Phys. Lett., 173, 107 (1990).
[6] Z. Cao, J. W. Tester, B. L. Trout, The Journal of chemical physics., 115, 2550 (2001)