Stereoelectronic Contributions to ^{1}H-^{1}H Coupling Constants

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Abstract: The effect of stereoelectronic interactions on coupling constants is shown. The analysis is done with a new approach in which a selected interaction is deleted and the effect over the couplings is analyzed. ^{1}H-^{1}H magnetic couplings three and four bonds apart in hydrocarbons are shown.

Introduction

Coupling constants have been widely used to carry out conformational analysis in molecules. In these studies the relationship between structural parameters (dihedral angles) and experimental data (magnetic coupling constants) are provided. For this reason it is interesting to analyze the intramolecular interactions that produce Karplus-like curves.

Results and Discussion

The methodology presented here implies, as a first step, a Natural Bond Order [1] (NBO) localization, followed by the deletion of selected Fock matrix elements (written in the NBO basis) representative of the interaction between selected orbitals. The next step is to recalculate the density matrix in the AO basis using the modified Fock matrix and then calculate the electronic polarization propagator [2]. With this propagator it is possible to determine several second order properties, like magnetic couplings, which are of interest in this work. The magnitude calculated in this way is then compared with the magnitude obtained without deletions and so it is possible to evaluate the effect of the interactions corresponding to the deletions considered. The computations were done with Gaussian 98 (geometry optimizations and NBO analysis) and SYSMO (magnetic properties).

Using the present formalism we analyzed coupling constants between protons three and four bonds apart. In the former, the main contributions to the angle dependence of the coupling constants came from the vicinal interactions between the C-H bonds and antibonds corresponding to the coupled protons. The geminal interactions between C-H and C-C bonds and antibonds along the way of the coupled protons are also important, but of less magnitude.

In the case of $^4J_{HH}$, three model compounds were considered, in order to analyze magnetic couplings transmitted through sigma, pi and cyclopropane bonds:

Propane (**1**)   Propene (**2**)   Ethylcyclopropane (**3**)
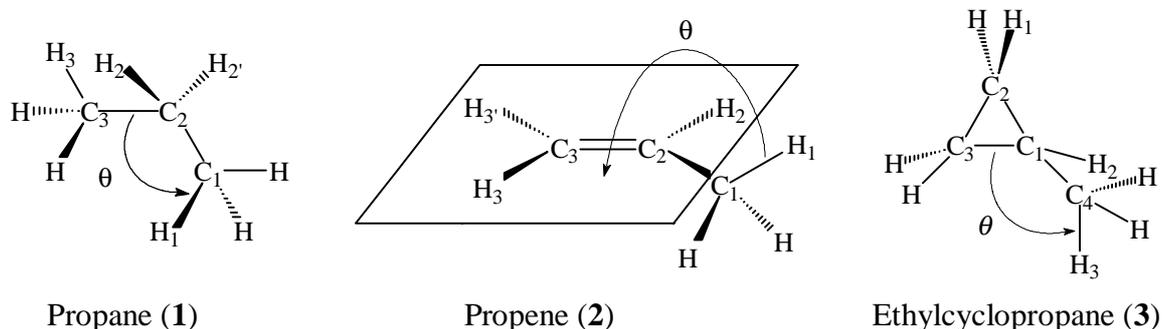
In the first case **1** the main interactions came from the vicinal interactions {The following abbreviation is consider for the stereoelectronic interactions: $\alpha(A_i\text{-}A_j)\leftrightarrow\beta(A_k\text{-}A_l)$ is the same as $\alpha(A_i\text{-}A_j)\rightarrow\beta^*(A_k\text{-}A_l) + \beta(A_k\text{-}A_l)\rightarrow\alpha^*(A_i\text{-}A_j)$, where α, β indicate σ or π orbitals, and A_i stands for atom i, etc.} $\sigma(C_1\text{-}C_2)\leftrightarrow\sigma^*(C_3\text{-}H_3)$, $\sigma(C_2\text{-}C_3)\leftrightarrow\sigma^*(C_1\text{-}H_1)$ and the direct interaction $\sigma(C_1\text{-}H_1)\leftrightarrow\sigma^*(C_3\text{-}H_3)$. A detailed analysis of the two kinds of interactions shows that the vicinal ones are more important in the θ interval between $0°$ and $120°$, while the four bond apart interaction is more important between $120°$ and $180°$, being the last one the so called "W" conformation, which usually gives rise to "visible" $^4J_{HH}$ couplings.

In the case of **2**, the most important interactions are those whose localized orbitals correspond to the mobile $C_1\text{-}H_1$ and the double bond $C_2\text{=}C_3$: $\sigma(C_1\text{-}H_1)\leftrightarrow\sigma^*(C_2\text{=}C_3) + \sigma(C_1\text{-}H_1)\leftrightarrow\pi^*(C_2\text{=}C_3)$. Among these, the most important is the $\pi(C_2\text{=}C_3)\rightarrow\sigma^*(C_1\text{-}H_1)$.

In the last case considered **3**, it is necessary to take account a larger quantity of stereoelectronic interactions than in the previous ones, in order to take into account the angular dependence of the couplings: $\sigma(C_1\text{-}C_2)\leftrightarrow\sigma(C_4\text{-}H_3) + \sigma(C_1\text{-}H_2)\leftrightarrow\sigma(C_4\text{-}H_3) + \sigma(C_1\text{-}C_3)\leftrightarrow\sigma(C_4\text{-}H_3) + \sigma(C_1\text{-}C_4)\leftrightarrow\sigma(C_4\text{-}H_3) + \sigma(C_1\text{-}C_2)\leftrightarrow\sigma(C_1\text{-}C_4) + \sigma(C_1\text{-}C_2)\leftrightarrow\sigma(C_2\text{-}H_1) + \sigma(C_2\text{-}H_1)\leftrightarrow\sigma(C_1\text{-}H_2) + \sigma(C_1\text{-}C_4)\leftrightarrow\sigma(C_2\text{-}H_1) + \sigma(C_1\text{-}C_3)\leftrightarrow\sigma(C_2\text{-}H_1) + \sigma(C_2\text{-}H_1)\leftrightarrow\sigma(C_4\text{-}H_3)$. The most important interaction is the vicinal $\sigma(C_1\text{-}C_2)\leftrightarrow\sigma(C_4\text{-}H_2)$.

In **1** and **2** a few interactions contribute to the couplings, while in **3** there are no main contributions. From a general point of view, the methodology proposed here is rigorous and is approximately additive. One of the drawbacks is the necessity of testing all possible interactions in order to know which are the most important.

References

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2. Jörgensen, P.; Simons, J. *Second Quantization Based Methods in Quantum Chemistry*; Academic Press: New York, 1981.