INTRODUCTION

It is a known fact that to get accurate results for calculations of some molecular properties, like the indirect spin-spin coupling constant for medium and large-size molecules is a very demanding task, specially when the computational resources are limited. In this concerned, models are attempt to overtake such a difficulty. One promising model was recently developed [1], and it is based upon a good description of the basis set in the region where coupling is going to be calculated. Such a consideration let one to have the possibility of increasing the number of atoms in the molecule under study and the inclusion of electronic correlation.

In this work we present all coupling constant in ethane with two convention of basis sets sad-J [2] and Sadlej [3,4] at second order polarization propagator approach (SOPPA), \{'it i.e.,\, basis set sad-j for the atoms in which we calculate the coupling constant and either sad-J and Sadlej for the others.

THEORY

Ramsey [5] formulated the non-relativistic theory of the indirect spin-spin coupling constant between two nuclei M and N proposing for it four contributions. It arises by means of two mechanisms, whereby one nucleus perturbs the electrons surrounding it and the induced electronic currents produce a magnetic field at the site of the other nucleus. If the nucleus interacts with the spin of the electrons the Fermi-contact (FC) and spin-dipolar (SD) contributions arise, whereas the interactions with the orbital angular moment of the electrons is given by the orbital paramagnetic (OP) and orbital diamagnetic (OD) contributions.

The first three contributions depend on the first order wavefunction and are thus given as sum-over-states expressions

\[
J_{MN}^A = \frac{2 \gamma_M \gamma_M}{3} \frac{\hbar}{h} \sum_{\alpha=x,y,z} \sum_{n \neq 0} \left\langle 0 \left| \hat{O}_M^A \right| n \right\rangle \left\langle n \left| \hat{O}_N^A \right| 0 \right\rangle \frac{E_n - E_M}{E_0 - E_M}
\]

where A can be OP, FC, SD and the corresponding operators are defined as

\[
\left( \hat{O}_M^{OP} \right)_\alpha = \left( \mu_0 \frac{e \hbar}{4\pi m_e} \right) \sum_{l} \left( \frac{\bar{l}}{l} \right)_\alpha \left( \frac{\bar{r}}{l} \right)_M
\]

\[
\left( \hat{O}_M^{FC} \right)_\alpha = \left( \mu_0 \frac{4\pi g_e \hbar}{3m_e} \right) \sum_{l} \left( \frac{\bar{r}}{l} \right)_\alpha \left( \delta_{\bar{r}M} \right)
\]
\[
\left( Q_{M}^{SD}\right) _{\alpha } = \left( \frac{\mu _{0}}{4\pi } \right) \left( \frac{g_{e} e \hbar }{2m_{e}} \right) \sum _{i} \frac{3\left( \vec{\sigma }_{i} \cdot \vec{r}_{iM} \right) \left( \vec{r}_{iM} \right) _{\alpha } - r_{iM}^{2} \left( \vec{\sigma }_{i} \right) _{\alpha }}{r_{iM}^{5}}
\]

The magnetogyric ratio of nucleus \( M \) is \( \gamma _{M} \), \( \vec{r}_{iM} = \vec{r}_{i} - \vec{r}_{M} \) is the difference of the position vectors of electron \( i \) and nucleus \( M \), \( \vec{\sigma }_{i} \) is the spin angular momentum operator and \( \vec{r}_{i} \) the orbital angular momentum operator of electron \( i \) in units \( J/s \), \( \delta (x) \) the Dirac delta function and all other symbols have their usual meaning [6].

The orbital diamagnetic term, on the other hand, is a ground state average value, but it can also be expressed as a sum-over-states [7].

## RESULTS

Bases set sad-J is based upon Sadlej [3,4] basis set. It was performed for a proper description of the Fermi contact term [1,8,9]. This J-shaped basis set were made by adding four tight s-type function on hydrogen, carbon and re-contracting the most heaviest s-type function for H and s- and p-type functions for C and N with their own SCF MO coefficients.

All the calculation presented here were performed with version 1.2 of the Dalton [8] program package and using experimental equilibrium geometries for the molecule. The results are presented in Tables 1, 2 and 3.

For one-bond couplings (see Table 1 and 2), we find that \( ^{1}J_{C,C} \) the changes are under 0.1 Hz and are due to enteraly to the change in the Fermi contact term. However, the \( ^{1}J_{C,H} \) coupling present almost no changes because of the differences in the orbital paramagnetic and Fermi contact contributions compensate each other.

Table 1: \( \text{H}_{3}\text{C-CH}_{3} \) : \(^{1}J_{C,C} \) dependence on the basis sets on hydrogen

<table>
<thead>
<tr>
<th>C</th>
<th>H</th>
<th>( J^{\text{OD}} )</th>
<th>( J^{\text{OP}} )</th>
<th>( J^{\text{SD}} )</th>
<th>( J^{\text{FC}} )</th>
<th>( J )</th>
</tr>
</thead>
<tbody>
<tr>
<td>sad-J</td>
<td>sad-J</td>
<td>0.11</td>
<td>0.25</td>
<td>1.07</td>
<td>34.81</td>
<td>36.24</td>
</tr>
<tr>
<td>sad-J</td>
<td>sadlej</td>
<td>0.11</td>
<td>0.25</td>
<td>1.08</td>
<td>34.69</td>
<td>36.13</td>
</tr>
</tbody>
</table>

Table 2: \( \text{H}_{3}\text{C-CH}_{3} \) : \(^{1}J_{C,H} \) dependence on the basis sets on carbon and hydrogen in the other CH\(_{3}\) group of the molecule

<table>
<thead>
<tr>
<th>Coupled CH(_{3})</th>
<th>other CH(_{3})</th>
<th>( J^{\text{OD}} )</th>
<th>( J^{\text{OP}} )</th>
<th>( J^{\text{SD}} )</th>
<th>( J^{\text{FC}} )</th>
<th>( J )</th>
</tr>
</thead>
<tbody>
<tr>
<td>sad-J</td>
<td>sad-J</td>
<td>0.49</td>
<td>1.11</td>
<td>-0.07</td>
<td>127.26</td>
<td>128.80</td>
</tr>
<tr>
<td>sad-J</td>
<td>sadlej</td>
<td>0.49</td>
<td>1.18</td>
<td>-0.07</td>
<td>127.20</td>
<td>128.80</td>
</tr>
</tbody>
</table>

Tables 3 and 4 present two cases for establishing a local dense basis set for the geminal coupling \(^{2}J_{H,H} \). The former analysis is done considering the basis set sad-J only for the hydrogens involved in the coupling and basis set sadlej for the others. Here, all contributions change in the same direction, but the orbital diamagnetic. Moreover, the marked changes are in the orbital paramagnetic and the total couplings present a difference of ~ 1 Hz. However, the latter considers the basis set sad-J also including the carbon bonded to the hydrogens involved in the coupling. In this case changes are much smaller for all contributions, but for the orbital diamagnetic, and the changes of the total coupling depend mostly from the orbital paramagnetic.

Table 3: \( \text{H}_{3}\text{C-CH}_{3} \) : \(^{2}J_{H,H} \) dependence on the basis sets on carbon

<table>
<thead>
<tr>
<th>C</th>
<th>H</th>
<th>( J^{\text{OD}} )</th>
<th>( J^{\text{OP}} )</th>
<th>( J^{\text{SD}} )</th>
<th>( J^{\text{FC}} )</th>
<th>( J )</th>
</tr>
</thead>
<tbody>
<tr>
<td>sad-J</td>
<td>sad-J</td>
<td>-2.93</td>
<td>2.98</td>
<td>0.41</td>
<td>-16.42</td>
<td>-15.96</td>
</tr>
<tr>
<td>sadlej</td>
<td>sad-J</td>
<td>-2.91</td>
<td>2.37</td>
<td>0.38</td>
<td>-16.76</td>
<td>-16.92</td>
</tr>
</tbody>
</table>
Table 4: \( ^3 \text{J}_{\text{H-H}} \) dependence on the basis sets on carbon and hydrogen in the other \( \text{CH}_3 \) group of the molecule

<table>
<thead>
<tr>
<th>Coupled ( \text{CH}_3 )</th>
<th>other ( \text{CH}_3 )</th>
<th>( ^3 \text{J} \text{OD} )</th>
<th>( ^3 \text{J} \text{OP} )</th>
<th>( ^3 \text{J} \text{SD} )</th>
<th>( ^3 \text{J} \text{FC} )</th>
<th>( \text{J} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>sad-J</td>
<td>sad-J</td>
<td>-2.93</td>
<td>2.98</td>
<td>0.41</td>
<td>-16.42</td>
<td>-15.96</td>
</tr>
<tr>
<td>sad-J</td>
<td>Sadlej</td>
<td>-2.93</td>
<td>3.05</td>
<td>0.40</td>
<td>-16.43</td>
<td>-15.91</td>
</tr>
</tbody>
</table>

The vesinal coupling \( ^3 \text{J}_{\text{H-H}} \) shows larger differences of the orbital paramagnetic term respect to the spin dipolar and the Fermi contact which in part are compensated by these two last. Although, this behavior exposes the character of through bond of such a coupling, change are lower than 0.2Hz approximately.

Table 5: \( ^3 \text{J}_{\text{H-H}} \) dependence on the basis sets on carbon

<table>
<thead>
<tr>
<th>C</th>
<th>H</th>
<th>( ^3 \text{J} \text{OD} )</th>
<th>( ^3 \text{J} \text{OP} )</th>
<th>( ^3 \text{J} \text{SD} )</th>
<th>( ^3 \text{J} \text{FC} )</th>
<th>( \text{J} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>sad-J</td>
<td>sad-J</td>
<td>-1.63</td>
<td>1.54</td>
<td>0.05</td>
<td>8.00</td>
<td>7.95</td>
</tr>
<tr>
<td>sadlej</td>
<td>sad-J</td>
<td>-1.63</td>
<td>1.22</td>
<td>0.06</td>
<td>8.07</td>
<td>7.72</td>
</tr>
</tbody>
</table>

**CONCLUSION**

This investigation thus shows that using locally dense basis sets, i.e., using basis sets optimized for the calculation of spin-spin coupling constants only on the atoms of interest, is a real possibility for reducing the basis set size, if an error of about 0.2 Hz in the total coupling constant is acceptable.

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**BIBLIOGRAPHY**