Natural Orbital Functional Theory Applied to Biologically relevant systems

J. M. Matxain\textsuperscript{1}, X. Lopez\textsuperscript{1}, F. Ruipérez\textsuperscript{1}, J. M. Ugalde\textsuperscript{1}, M. Piris\textsuperscript{1,2}, E. Matito\textsuperscript{3}

\textsuperscript{1}Euskal Herriko Unibertsitatea / University of the Basque Country  
\textsuperscript{2}IKERBASQUE, Basque Foundation for Science  
\textsuperscript{3}University of Girona

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Molecular electronic structure program within Natural Orbital Functional Theory

Developed by Prof. Mario Piris (Ikerbasque R. P.)

Arina (one processor)

H Abstraction and C–C and O–O Homolytic Bond Cleavage

<table>
<thead>
<tr>
<th>Reaction</th>
<th>PNOF5</th>
<th>CASSCF(2,2)</th>
<th>CASPT2(2,2)</th>
<th>exptl</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CH_4 \rightarrow \cdot CH_3 + \cdot H$</td>
<td>98.9</td>
<td>98.0</td>
<td>109.6</td>
<td>113.0</td>
</tr>
<tr>
<td>$NH_3 \rightarrow \cdot NH_2 + \cdot H$</td>
<td>97.9</td>
<td>93.3</td>
<td>111.5</td>
<td>115.9</td>
</tr>
<tr>
<td>$H_2O \rightarrow \cdot OH + \cdot H$</td>
<td>106.1</td>
<td>92.9</td>
<td>122.8</td>
<td>126.0</td>
</tr>
<tr>
<td>$C_2H_6 \rightarrow \cdot C_2H_5 + \cdot H$</td>
<td>98.9</td>
<td>89.2</td>
<td>106.0</td>
<td>109.4</td>
</tr>
<tr>
<td>$H_2O_2 \rightarrow \cdot OOH + \cdot H$</td>
<td>86.6</td>
<td>81.3</td>
<td>91.0</td>
<td>92.7</td>
</tr>
<tr>
<td>$C_2H_6 \rightarrow 2 \cdot CH_3$</td>
<td>83.1</td>
<td>74.2</td>
<td>96.6</td>
<td>96.6</td>
</tr>
<tr>
<td>$H_2O_2 \rightarrow 2 \cdot OH$</td>
<td>32.6</td>
<td>19.4</td>
<td>53.7</td>
<td>55.1</td>
</tr>
</tbody>
</table>

- **PNOF5 results between CASSCF and CASPT2**
- Non-dynamical correlation like CASSCF, and part of dynamical correlation
ROS (Reactive Oxygen Species): abundant among radical species (RNS, RCS, RSS)
- \( \cdot OH, \cdot OOH, \cdot O_2^-, ^1O_2 \).

Biomacromolecular targets:
- Proteins, cell membrane phospholipids, DNA, RNA...

Attack may cause...
- Alteration of the function (function loss) of cell macromolecules
- If not controlled, cell death

Diseases
- Alzheimer, Parkinson etc...
- Among others, \( \cdot OH \) Attack to proteins
Based on success on the study of radical mediated reactions, want to study radical reactions with larger systems: proteins.
Parallelization of PNOFID program carried out by E. Matito
Tests on Arina (Supercomputer at UPV/EHU) Successfull
Possible to jump to larger systems? Let us try!
Very Challenging in NOFT!!
Project to carry out at BSC Mare Nostrum supercomputer

- QCM-2012-2-0011: PNOF theory: Towards biological applications (Feb - June 2012)
- QCM-2012-1-0019: PNOF theory: Towards biological applications (July - October 2012)
- Total hours: 800,000
Model: Tripeptide model, R only at the central amino acid.
Transition Metals

- Transition Metal chemistry also challenging within Natural Orbital Functional Theory
- $\text{Cr}_2, \text{Mo}_2, \text{W}_2$
  

![Graph showing orbital energies and bond lengths.](image-url)
Transition Metals in Biology

- $Fe_xS_y$ clusters metallic part of proteins (interaction with cys)

Two projects at MN:
- QCM-2012-3-0004: Transition metal chemistry with PNOF5 (Nov 2012 - Feb 2013)
- QCM-2013-1-0007: Transition metal chemistry with PNOF5. (March 2013 - June 2013)
- Total hours: 820.000

- New MN: recompilation
- Not fast task (longer calculation periods desirable)
Concluding Remarks

- Parallelization good. It could be improved.
- Desirable longer periods in MN.
- Possible to study large systems with PNOF5.
- Results in between CASSCF and CASPT2.
- Three publications (in production)
- A step forward in Natural Orbital Functional Theory
Acknowledgments

Theoretical Chemistry Group

Supercomputing Resources

- The SGI/IZO–SGIker (UPV/EHU)
  - Arina supercomputer
- BSC
  - Mare Nostrum supercomputer

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