

DP4+ App

<https://github.com/Sarotti-Lab/DP4plus-App>

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Example Manual - HALO-DP4+

Overview

The DP4+ App provides a robust framework for correlating experimental NMR chemical shifts with DFT-calculated magnetic shielding tensors. This manual illustrates the use of the HALO-DP4+ module to perform probabilistic structural assignments, using output files from single-point Gaussian NMR calculations. All necessary data—including shielding tensors, SCF energies, and the halogen-sensitive correlation matrix—are extracted directly from these files. By following this guide, users will be able to efficiently apply the HALO-DP4+ methodology to halogen-containing molecules.

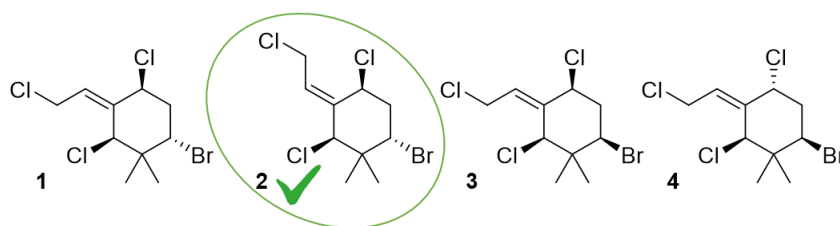
Procedure

The “*example_HALO*” includes all files required for this demonstration:

- *Gaussian calculations*: Fourteen *.log* files corresponding to NMR computations for several candidate isomers. These were optimized at the B3LYP/6-31G* level and subsequently evaluated with the following Gaussian09 command:

```
# mPW1PW91/6-31+G** scrf=(PCM,solvent=chloroform) nmr
```

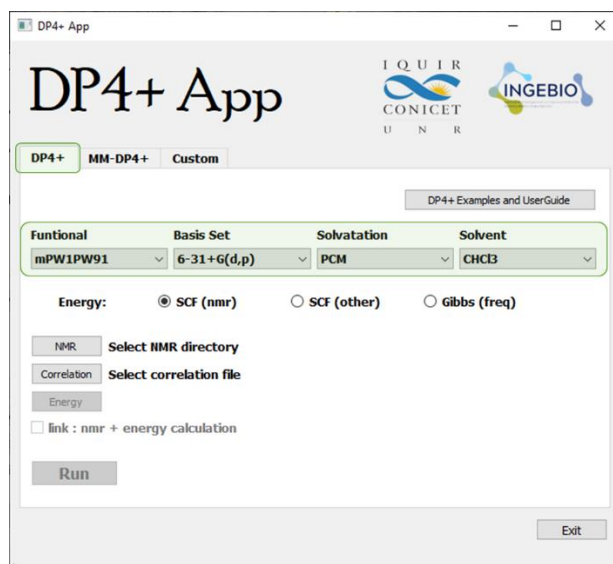
- *Correlation spreadsheet*: *02_SSSZ_Correlation.xlsx* contains experimental chemical shift data for isomer 02_SSSZ (the correct structure), along with correlation labels that link experimental and theoretical assignments.



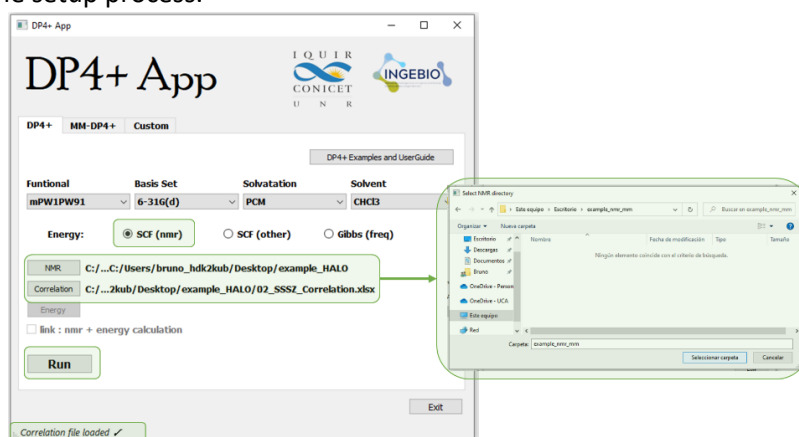
Procedure

To begin the analysis, navigate to the **DP4+** tab and configure the parameters as follows:

- **Functional:** mPW1PW91
- **Basis set:** 6-31+G (d,p)
- **Solvation:** SMD
- **Solvent:** CHCl₃



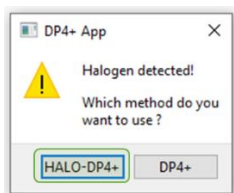
Use the folder selection buttons located beneath the theory level panel to upload the required Gaussian and Excel files. The application will automatically validate the input structure and correlation file format. For further details regarding input requirements, refer to the *Warnings and Input Control* section of the full User Manual. The status bar will provide feedback throughout the setup process.



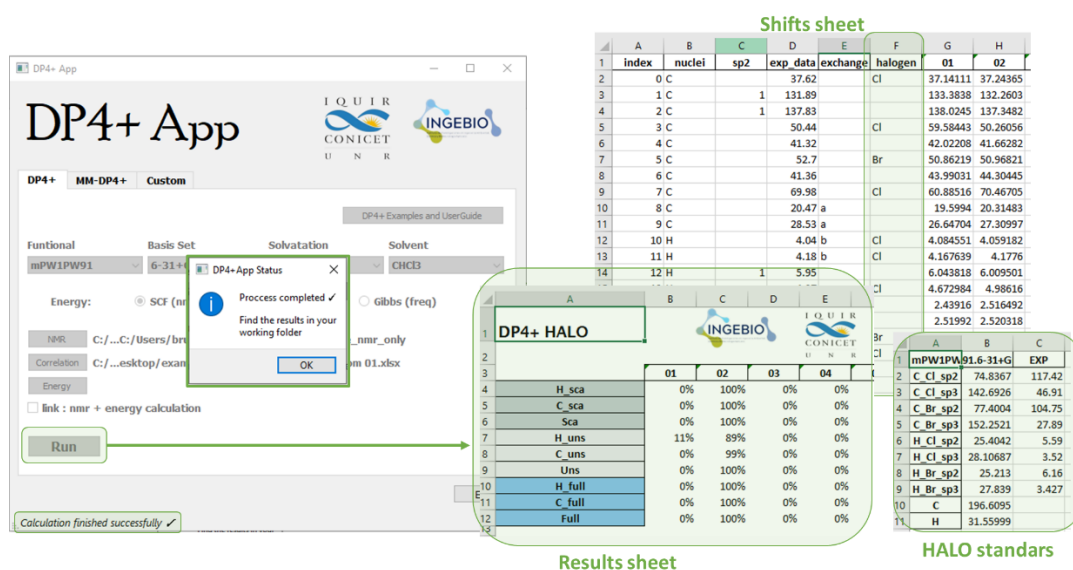
To simulate potential input errors, corrupted files labeled '*brk*' have been introduced. These files are designed to trigger alerts related to structural mismatches or failed calculations. When such files are detected, DP4+App will isolate them automatically to prevent disruption of the main workflow. In routine use, these files should be corrected or removed, but for this example, the warnings can be ignored.

Once all required inputs have been loaded and validated, the **Run** button will be enabled. Execution begins with a consistency check between the selected theory level and the Gaussian command line. If any discrepancies are detected, a warning message will be issued, allowing the user to proceed at their discretion or return to correct the settings.

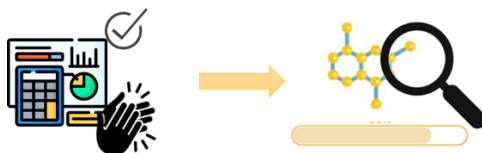
Cause candidate structures contain **halogen atoms—chlorine (Cl) and bromine (Br)**—the application will prompt to select between performing a standard DP4+ calculation or activating **HALO-DP4+ mode**. Choose HALO-DP4+, as this mode applies a specialized multi-standard referencing protocol. In this configuration, carbon and hydrogen atoms bonded to halogens are referenced using calibrated tensors appropriate for their electronic environment, resulting in improved chemical shift accuracy.



Upon completion, the results sheet will include a dedicated column identifying the nuclei treated with the multi-standard correction, and the parameters sheet will report the specific tensors and chemical shifts used in this adjustment.



Once the process is finished, a pop-up will signal the successful termination of the DP4+ calculation, and the results will be automatically displayed. The output spreadsheet will include a column labeled **"halogen"** in the **results** sheet, indicating the nuclei for which HALO-specific corrections were applied. In addition, the **parameters** sheet will provide the shielding tensors and chemical shift values used in the HALO adjustment, including both standard (TMS-based) and HALO-corrected references.



Disclaimer



This example is provided for educational purposes only to illustrate the application's capabilities. The analysis is not based on real-world data. To simplify distribution, not all conformations within a 10 kcal/mol energy window are included in this example. Therefore, replicating this study may produce varying outcomes.