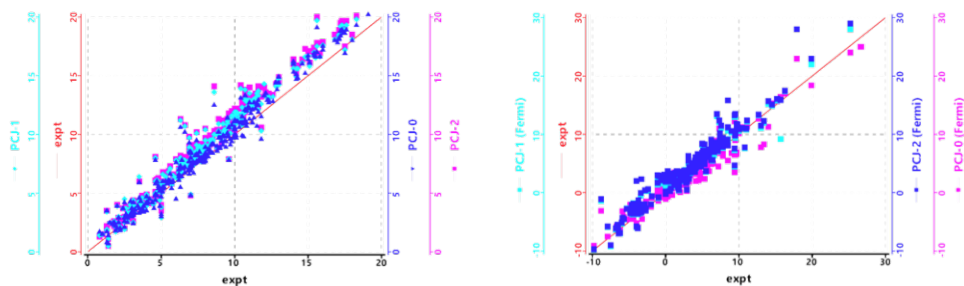# CALCULATING HH AND CH COUPLING CONSTANTS

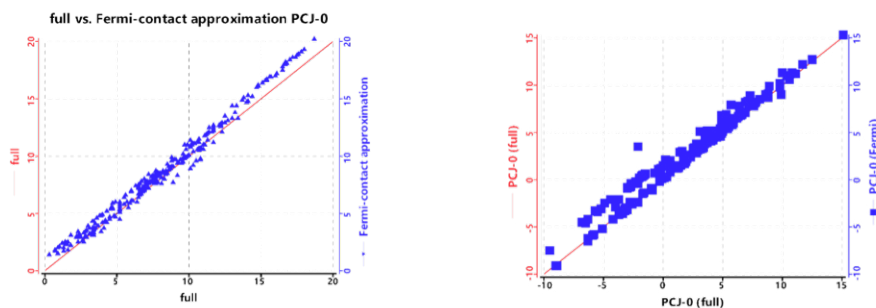Coupling constants may be calculated, either "exactly" or within the so-called Fermi-contact approximation. The latter approach is significantly the less demanding both in terms of computation time and memory required. 3-bond HH coupling constants may be estimated using the Karplus relationship [reference]. A parameterized variation on Karplus have long been provided in **Spartan**, and with **Spartan'20**, has been extended this to estimate both 2 and 3-bond CH coupling constants.

So-called "range-separated-hybrid" functionals such as ωB97X-D used for determining geometry and chemical shifts are not presently available in Spartan for coupling constant calculations. The popular B3LYP "global hybrid" functional has instead been used. In addition, the 6-31G* basis set used for chemical shift calculations has been replaced by one of a series of basis sets that have been expressly developed for coupling constant calculations. The smallest of these is PCJ-0, which is similar in construction to 6-31G* and readily applicable to molecules of comparable size. PCJ-1 and PCJ-2 basis sets are larger and therefore more limited in their practical range of application.

The first comparison relates coupling constants calculated within the Fermi-contact approximation and using the PCJ-0, PCJ-1 and PCJ-2 basis sets with experimental data for two sets of small molecules taken from the Reich web site [reference]. Data for 3-bond HH coupling constants with ~300 comparisons, and (combined together) 2 and 3-bond CH coupling constants with ~200 comparisons are shown below at the left and right, respectively. HH coupling constants range from roughly 0 to 20 Hz and are almost entirely positive. (The few small negative values have been excluded from the plot as have HH coupling constants larger than 20 Hz.) The overall range of CH coupling constants is similar although there are a significant number of negative values, almost entirely for 2-bond coupling. It should be noted that the sign of measured coupling constants is rarely reported and the experimental data from the Reich web site is almost entirely unsigned. We have adjusted the sign on experimental coupling constants to be in accord with the calculated values.

The second comparison examines the effect of the Fermi-contact approximation on coupling constants obtained using the PCJ-0 basis set. Results for 3-bond HH (left) and (combined together) 2 and 3-bond CH (right) coupling constants are shown below where the "full" calculations act as reference. The RMS deviations here, x.x and y.y for HH and CH coupling constants, respectively, are smaller than the previously mentioned RMS errors referenced to experiment.

Given that the primary objective for calculating coupling constants is to identify couplings between pairs of hydrogens that are large enough to be observed in a COSY spectrum and those between carbon and hydrogen that are large enough to be observed in an HMBC spectrum, it is likely conclude that calculations within the framework of the Fermi approximation using the PCJ-0 basis set are adequate.[*] As previously mentioned, current generation personal computers allow application to molecules with molecular weights on the order of 500 amu.

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[*] It is also likely that empirically derived HH and CH coupling constants will be adequate for construction of COSY and HMBC spectra.