A Quantum Monte Carlo and CIPSI case study: Magnetic Coupling of a meta-xylylene diradical.

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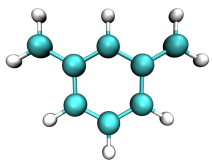
Calculating accurate magnetic couplings has been, and is, a difficult and challenging endeavor [1]. Even so, successful strategies for calculating diradical conjugated hydrocarbons have been devised in previous works using CASSCF level calculations [2].

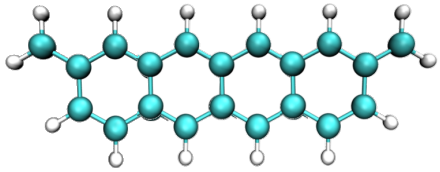
Our work intends to conceive such a strategy for a meta-xylylene diradical *(Fig. a)* under a Quantum Monte Carlo framework, and eventually to be able to treat bigger and more general magnetic systems *(Fig. b)*. Due to the intrinsic multiconfigurational character of the wavefunction and the weakness of the magnetic coupling magnitude, good correlation energy is paramount to provide a precise account of this phenomena.

Starting from Hartree Fock we build a multiconfigurational wavefunction by selecting configuration interactions according to a perturbative criteria. This is done with the CIPSI algorithm [3]. Many parameter were explored to devise the best approach: Number of Determinants, stoping criteria, use of Dressed CI [4]) and type of orbitals (fock, natural, localized), among others.

The resulting wavefunction is then treated with Fixed-Node Diffusion Monte Carlo with the QMC=CHEM [5] software. As a result we have designed a perturbation based stoping criteria that provides accurate results for this system.



(a)



(b)

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