Ab initio MO studies of nuclear spin–spin coupling constants in CH$_4$, SiH$_4$, AlH$_4$ and GeH$_4$ systems

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Summary. Ab initio molecular orbital calculations of electron coupled nuclear spin–spin coupling constants are performed for CH$_4$, SiH$_4$, AlH$_4$ and GeH$_4$ systems using the SCF perturbation theory. Basis set dependence of the major contributing terms such as orbital diamagnetic, orbital paramagnetic, spin dipolar and Fermi contact terms are studied. The study also illustrates the relative importance of bond centred functions and nuclear centred polarization functions in predicting the directly bonded and geminal couplings in the systems selected. Basis sets having uncontracted core s functions and augmented with bond functions seem to predict most of these couplings fairly satisfactorily when compared to the experimental values.

Key words: Ab initio – Spin–spin coupling constants – Bond centred functions

Introduction

Electron coupled nuclear spin–spin coupling constant is one of the important molecular parameters observed in high resolution NMR spectroscopy of fluids and is a measure of the energy of interaction between two magnetic nuclei in different parts of the same molecule. After the first theoretical explanation by Ramsey [1], different theoretical approaches at various levels of approximation as well as at ab initio level have been employed by many workers in the past to compute this second order property. Good reviews of these studies are written by Kowalewski [2], Fukui [3] and Oddershede [4]. Ditchfield and Snyder [5] evaluated all the four major contributing terms to nuclear spin couplings in CH$_3$F by employing the ab initio SCF perturbation theory. Kowalewski and coworkers [6–10] performed non empirical calculations of Fermi contact contributions to nuclear spin couplings in a number of systems. Guest et al. [11], Guest and Overill [12] and Overill and Guest [13] carried out extensive calculations of nuclear spin coupling constants for a series of molecules. Also, there exist other methods such as first order polarization propagator approach (FOPPA) by Lazzeretti et al. [14], the equations of motion (EOM) method at ab initio level by Fronzoni and Galasso [15, 16] and Galasso [17], second order polarization propagator approach (SOPPA) by Geertsen et al. [18] and the coupled cluster polarization propagator approach...
(CCPPA) by Geertsen [19] for the evaluation of indirect nuclear spin–spin Couplings, coupled cluster singles and doubles polarization propagator approach (CCSDPMPA) has been employed by Scuseria and coworkers [20, 21] to have a better estimate of correlation contribution to spin–spin couplings, than was available in earlier methods. Fukui et al. [22] have employed many body perturbation theory (MBPT) to calculate the electron correlation contribution to Fermi contact term. All these calculations are restricted to small molecules. Recently Malkin et al. [23] have employed a density functional approach to calculate coupling constants in large molecules with encouraging results.

The present study is concerned with the basis set dependence of the coupling constants at ab initio level by employing the SCF perturbation theory put forward by Blizzard and Santry [24]. It also illustrates the relative importance of bond centred functions and polarization functions in predicting different couplings. The basis set dependence of different contributing mechanisms to spin couplings namely, orbital diamagnetic (OD), orbital paramagnetic (OP), spin dipolar (SD), and Fermi contact (FC), has also been examined. The molecular systems studied include CH₄, SiH₄, AlH₄ and GeH₄.

Theoretical methods

According to Ramsey [1], the nuclear spin dependent terms in the Hamiltonian for the interaction of a molecule with electromagnetic field are as under,

\[ H_1^a = \frac{1}{2c^2} \sum_k \sum_N \gamma_N \gamma_{N'} \left( \frac{I_N \times r_{kN}}{r_{kN}^3} \right) \left( \frac{I_N' \times r_{kN'}}{r_{kN'}^3} \right), \]

\[ H_1^b = \frac{1}{c^2} \sum_k \sum_N \gamma_N \frac{I_N L_{kN}}{r_{kN}^3}, \]

\[ H_2 = \frac{1}{c} \sum_k \sum_N \gamma_N \left[ \frac{3(S_k r_{kN})(I_N r_{kN})}{r_{kN}^5} - \frac{S_k I_N}{r_{kN}^3} \right], \]

\[ H_3 = \frac{8\pi}{3c} \sum_k \sum_N \gamma_N \delta(r_{kN}) s_k I_N, \]

\( H_1^a \) corresponds to the orbital diamagnetic interaction, \( H_1^b \) corresponds to the orbital paramagnetic interaction, \( H_2 \) represents the spin dipolar interaction and \( H_3 \) is the Hamiltonian for the Fermi contact interaction.

Here, \( \gamma_N \) represents the magnetogyric ratio of the nucleus \( N \), \( I_N \) the spin angular momentum of nucleus \( N \), \( L_{kN} \) the orbital angular momentum of the \( k \)th electron about nucleus \( N \), \( S_k \) the spin angular momentum of the electron \( k \), \( r_{kN} \) is the radius vector from the \( N \)th nucleus to the \( k \)th electron and \( \delta(r_{kN}) \) is the Dirac delta function which picks up values at \( r_{kN} = 0 \).

The theoretical treatment of these contributing mechanisms at ab initio level by employing the SCF perturbation theory [24, 25] is discussed in detail elsewhere [26, 27]. Following these methods, the four major contributions to indirect nuclear