Molecular Orbital Theory of Nuclear Spin-coupling Constants: Implications for Fluorine Couplings

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Summary By using a more efficient theory, often neglected contributions to nuclear spin coupling constants can readily be calculated and are shown to be important in fluorine couplings.

A SELF-CONSISTENT field theory of nuclear spin coupling constants has recently been developed by Pople, McIver, and Ostlund.[1] According to this theory, the nuclear spin coupling constant, J_{AB}, between a nucleus A with gyromagnetic ratio γ_A and magnetic moment μ_A, and a nucleus B is given by an expression of the form

$$J_{AB} = \frac{\hbar\gamma_A\gamma_B}{2\pi}\sum_{\sigma,\lambda}\left(\frac{\partial \boldsymbol{P}_{\sigma\lambda}}{\partial\mu_A}\right)_{\mu_A=0}\left(\frac{\partial \boldsymbol{H}_{\sigma\lambda}}{\partial\mu_B}\right) \qquad (1)$$

where $\boldsymbol{P}_{\sigma\lambda}$ is the bond-order, or spin density, matrix element between atomic orbitals σ and λ and $\boldsymbol{H}_{\sigma\lambda}$ is the corresponding element of the Hamiltonian for the electron–nuclear interaction. In the Pople, McIver, and Ostlund theory[1] $\boldsymbol{H}$ was approximated to the contact Hamiltonian, so that both the orbital and direct dipolar terms were neglected. These workers suggested a numerical method for calculating the differential of the bond-order matrix based on the Newton–Stirling formula. In practice, this method turns out to be very time-consuming, and often impractical for large molecules because of slow convergence.

We present a more efficient method for calculating $\partial\boldsymbol{P}/\partial\mu_A$ by replacing matrix diagonalization by matrix multiplication, and show that orbital contributions to coupling constants are not negligible.

By definition, the first-order change in the bond-order is

$$\left(\frac{\partial \boldsymbol{P}\sigma\lambda}{\partial_{\mu A}}\right)_{\mu_A=0} = \boldsymbol{P}^{(1)}_{\sigma\lambda} = 2\sum_{i}^{\text{occ}}\left(\boldsymbol{C}^{(0)*}_{\sigma j}\,\boldsymbol{C}^{(1)}_{\lambda j} + \boldsymbol{C}^{(1)*}_{\sigma j}\,\boldsymbol{C}^{(0)}_{\lambda j}\right). \qquad (2)$$

For perturbations which lead to spin polarization, such as the contact interaction, the method of separate orbitals for separate spins will be used. In such cases the factor 2 is omitted from Equation 2 and the spin bond order matrices are written as $\boldsymbol{P}^{(1)\alpha}_{\sigma\lambda}$ and $\boldsymbol{P}^{(1)\beta}_{\sigma\lambda}$. Using conventional perturbation theory it is easily shown that

$$\boldsymbol{C}^{(1)}_{j} = -\left[\sum_{l}^{\text{vacant}}\left(\epsilon^{(0)}_{l} - \epsilon^{(0)}_{j}\right)^{-1}\boldsymbol{C}^{(0)}_{l}\widetilde{\boldsymbol{C}}^{(0}_{l}\right]\boldsymbol{F}^{(1)}\,\boldsymbol{C}^{(0}_{j} \qquad (3)$$

where C is the first-order change in the column vector corresponding to the jth MO, $\boldsymbol{F}^{(1)}$ is the first-order change

F–F *Nuclear spin coupling constants in Hz*

Molecule[a]	Contact[b]	Orbital [b,c]	Contact + orbital	Experiment[d]	
CHF_3	9·48	76·05	85·53	±[150—270]	*gem*
1,1-$C_2H_2F_2$	− 4·09	64·89	60·87	(+) 36·4	*gem*
C_2HF_3	1·42	90·60	92·02	(+) 87	*gem*
cis-$C_2H_2F_2$	− 3·51	− 29·15	− 32·66	(+) 18·7	*vic*
cis-C_2HF_3	− 4·06	− 17·81	− 21·87	(+) 33	*vic*
trans-$C_2H_2F_2$	−10·44	−108·45	−118·89	(−)124·8	*vic*
trans-C_2HF_3	−11·03	−104·37	−115·40	(−)119	*vic*

[a] For geometry see ref. 5; [b] $S_A{}^2(0)$ and $\langle r^{-3}\rangle_A$ were taken from ref. 6; [c] orbital term was averaged over x, y, and z directions; [d] the experimental value for CHF_3 was quoted in ref. 3. The remaining values are from ref. 7.

in the Fock matrix, $C_j^{(1)}$ are the unperturbed virtual molecular orbitals and $\epsilon_j^{(0)}$ are the corresponding zero-order orbital energies. As $F^{(1)}$ is a function of $C_j^{(1)}$ through the first-order bond-order, this equation is most easily solved iteratively. Note that Equation 3 involves only multiplication of a column vector by two matrices rather than a matrix diagonalization as required in the method of Pople *et al.*[1] Furthermore, the matrix in square brackets need only be calculated once for a given set of MO's and need not be re-calculated for each iteration. Finally, since this is a *direct* calculation of the change in the MO's, it is not subject to the same kind of rounding errors as the Pople[1] method.

$F^{(1)}$ may be expressed as the sum of the first-order change, $H^{(1)}$, in the Hamiltonian for the electron–nucleus interaction and the corresponding first-order change, $G^{(1)}$, in the electron repulsion energy. In the present communication

$$F^{(1)} = H^{(1)} + G^{(1)} \qquad (4)$$

we develop $H^{(1)}$ and $G^{(1)}$ for the contact and orbital contributions only. The theory for the dipolar term has been developed and applied to several molecules. However, as this contribution was found to be small, the presentation of the rather complicated equations will be delayed for a subsequent fuller publication.

In the following, the nuclear spin is centred on A and is taken to lie along the z-direction. The electron-repulsion matrix, $G^{(1)}$, is developed in terms of the INDO[2] approximation.

The formula for $H^{(1)\alpha}$ has already been given:[1]

$$H_{ss}^{(1)\alpha} = \frac{8\pi}{3}\beta\mu_A S_A^2(0) \qquad (5)$$

where the subscript s labels the valence shell orbital of atom A, $S_A{}^2(0)$ is the density of the valence shell s-electron at the nucleus, and the remaining symbols have their conventional meaning. All other $H^{(1)\alpha}$ matrix elements are assumed to be zero. In general the operator $G^{(1)\alpha}$ will have matrix elements between all atomic orbitals whether or not they are on centre A. These elements are given, in the notation of ref. 2, by:

$$G_{\mu\mu}^{(1)\alpha} = -\sum_{\lambda} P_{\lambda\lambda}^{(1)\alpha}\langle\mu\lambda|\mu\lambda\rangle \quad \text{where } \mu \text{ and } \lambda \text{ are on the same atom} \qquad (6)$$

$$G_{\mu\nu}^{(1)\alpha} = -P_{\mu\nu}^{(1)\alpha}\left[\langle\mu\nu|\mu\nu\rangle + \langle\mu\mu|\nu\nu\rangle\right] \qquad (7)$$

where μ and ν are on the same atom but $\mu \neq \nu$

$$G_{\mu\nu}^{(1)\alpha} = -P_{\mu\nu}^{(1)\alpha}\langle\mu\mu|\nu\nu\rangle \quad \mu \text{ and } \nu \text{ on different atoms and } \mu \neq \nu. \qquad (8)$$

(2) Orbital Term.

As this perturbation is pure imaginary,

$$P_{\mu\nu}^{(1)} = -P_{\nu\mu}^{(1)}. \qquad (9)$$

In the present approximation we assume that $H^{(1)}$ has matrix elements between valence shell p-orbitals on atom A only. These elements are given by:

$$H_{xy}^{(1)} = -2\beta\mu_A\langle r^{-3}\rangle_A i \qquad (10)$$

where x and y label the valence shell p_x and p_y orbitals.

The matrix elements of the $G^{(1)}$ operator are given by:

$$G_{\mu\mu}^{(1)} = 0 \qquad (11)$$

$$G_{\mu\nu}^{(1)} = -\tfrac{1}{2}P_{\nu\mu}^{(1)}\left(\langle\mu\mu|\nu\nu\rangle - \langle\mu\nu|\mu\nu\rangle\right) \qquad (12)$$

μ and ν on the same atom, $\mu \neq \nu$

$$G_{\mu\nu}^{(1)} = -\tfrac{1}{2}P_{\nu\mu}^{(1)}\langle\mu\mu|\nu\nu\rangle \quad \mu \text{ and } \nu \text{ on different atoms, } \mu \neq \nu. \qquad (13)$$

In the accompanying Table we have collected sample calculations of fluorine–fluorine coupling constants for different chemical environments. Although other workers have suggested that the orbital contribution to coupling constants can be significant in the case of fluorine,[3,4] it was not suspected that it could be larger than the contact term as shown by our results. Furthermore it should be noticed that the inclusion of the orbital term improves the performance of the theory so that it is no longer necessary to scale the $S^2(0)$ values in order to achieve reasonable agreement between theory and experiment for F–F couplings.

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