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Commentationes

N. M. R. Coupling Constants

I. The Molecular Orbital Approach

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Approximate *ab-initio* calculations of NMR coupling constants are reported, for a number of small molecules. The agreement with experiment is erratic, and is shown to depend critically on the form of the excited state wavefunctions. This suggests that the use of an "average energy" approximation is far from valid.

NMR Kopplungskonstanten werden für eine Anzahl von kleinen Molekülen mitgeteilt, wobei sich keine rechte Übereinstimmung mit dem Experiment ergibt. Es zeigt sich, daß die Werte kritisch von der Form der Wellenfunktion für die angeregten Zustände abhängen. Das läßt vermuten, daß die Verwendung eines mittleren Energienenners nicht zu empfehlen ist.

Calculs *ab-initio* approchés des constantes de couplage NMR d'un certain nombre de petites molécules. L'accord avec l'expérience est erratique et dépend d'une façon critique de la forme des fonctions d'onde excitées. Ceci suggère que l'emploi d'une approximation d'«énergie moyenne» est loin d'être valable.

Introduction

In a previous publication [1], results of calculations of EPR hyperfine coupling constants were reported. Molecular wavefunctions were computed using a non-empirical method utilizing both Slater and Gaussian functions [2]. The calculated proton coupling constants were in overall good agreement with experiment, but the results were poor for heavy nuclei. This result is almost certainly due to the very poor description of the core electrons of a heavy atom by a single Slater type function, especially in the region of the nucleus. These calculations provide a useful test of the ability of minimal basis MO calculations to describe the molecular electron density adequately.

The coupling constants observed in NMR experiments are predominantly due to a similar term in the Hamiltonian in a different order of perturbation theory; they depend on two simultaneous transition spin densities.

It has become usual, since early work of Pople and Santry [3], to rationalize these effects in terms of simple semi-empirical MO theory, yet little theoretical work has been done to investigate the validity of this approach. In this paper, we report some non-empirical calculations, within the framework of MO theory, for a selection of small molecules.

Molecular Wavefunctions

All molecular wavefunctions used were LCAO SCF MO wavefunctions, the various molecular integrals for all molecules except HF being calculated by a process outlined in detail in [2]; briefly, the one electron integrals were computed over a basis of Slater type orbitals directly, and the two electron integrals by expansion of the Slater functions as linear combinations of Gaussian functions.

Nuclear Spin-Spin Coupling Constants in the MO *Framework*

It is well known from the work of Ramsey [4] that the dominant term in the molecular Hamiltonian, which gives rise to internuclear coupling, is the Fermi contact interaction between the electron spin and the nuclear spin

$$H' = \frac{8\beta h}{3} \sum_k \sum_n \gamma_n \boldsymbol{S}_k \cdot \boldsymbol{I}_n \delta(r_{kn}) \tag{1}$$

in the usual notation [3].

With this approximation, and regarding H' as a perturbation on the molecular spin-free Hamiltonian, the spin-spin coupling constant $J_{n,n'}$ between nuclei n and n' can be written in the notation of McWeeny [5] as

$$J_{n,n'} = \frac{-2g_n\beta_n g_{n'}\beta_{n'}}{h} \left(\frac{8\pi g\beta}{3}\right)^2 \sum_t \frac{D(0,t\,|\,r_n)\,D^*(0,t\,|\,r_{n'})}{\Delta E(0,t)} \tag{2}$$

where $D(0,t\,|\,r_n)$ is the value of the transition spin density matrix between the singlet ground state Ψ_0 (denoted by 0 in the above equation), and an excited triplet function Ψ_t, (denoted by t), evaluated at the position of nucleus n.

$\Delta E(0,t)$ is the difference in energy between the singlet function Ψ_0 and the triplet function Ψ_t.

If all the states Ψ_0, Ψ_t, are obtained as determinants of molecular orbitals (MO's), then because of the orthogonality of these MO's, the only triplet functions contributing *directly* to $J_{n,n'}$ are the ones in which an electron is promoted from a filled MO Ψ_a into a virtual MO $\Psi_{\bar{a}}$.

Other triplet functions contribute to the effect in an indirect way discussed in the conclusion.

Two sets of calculations were performed, using different forms for the triplet functions.

A. Basic MO *Triplet Functions*

If we take the functions obtained by single electron promotion,

$$\Psi_t \equiv \frac{1}{\sqrt{2}} \{|a\bar{\varkappa}| + |\bar{a}\varkappa|\} \tag{3}$$

in an obvious notation, and use these as the triplet functions in Eq. (2), then since the one-body transition density matrix between the ground state Ψ_0 and excited triplet state Ψ_t is

$$\varrho_1(0,t\,|\,1;1') = \frac{1}{\sqrt{2}} a(1)\,\varkappa^*(1')\,\{\alpha(1)\,\alpha^*(1') - \beta(1)\,\beta^*(1')\} \tag{4}$$

Table

Molecule	n, n'	$J_{nn'}$		EXP.[a]
		A	B	
HF; $\zeta_{H=1.0}$	HF	-530	-470	-609
HF; $\zeta_{H=1.2}$	HF	-659	-535	-609
HF; ζ_{optimal} [7]	HF	-314	-237	-609
H_2O	HH	0.08	$-$ 3.73	
	HO	50.2	37.6	73.5
NH_3	HH	9.76	8.94	
	HN	25.1	42.6	45.8
BH_4^-	HH	2.46	$-$ 0.410	
	HB	38.4	44.6	27.2
CH_4	HH	10.5	9.63	$-$ 12.4
	HC	124	173	125
NH_4^+	HH	7.46	7.18	
	HN	50.8	76.0	49.9
HCC′H′	HC	158	154	294
	CC′	766	911	172
	HC′	$-$ 4.85	13.3	49.2
	HH′	22.1	23.9	9.42

[a] Sign inferred.

we find easily

$$D(0, t \mid r_n) = \frac{1}{\sqrt{2}} \{a(r_n)\, \varkappa^*(r_n) + \varkappa(r_n)\, a^*(r_n)\} \tag{5}$$

where, for example, $a(r_n)$ means the value of the MO "a", $\equiv \Psi_a$ evaluated at position r_n. Also

$$\Delta E(0, t) = \varepsilon_\varkappa - \varepsilon_a - (aa, \varkappa\varkappa) \tag{6}$$

in standard notation (5). Thus, expressing the MO's as linear combinations of the atomic orbital basis functions $\boldsymbol{\Phi} = (\varphi_1 \varphi_2 \ldots \varphi_m)$, the matrix representation of D above is

$$(\boldsymbol{D})_{kl} = \frac{1}{\sqrt{2}} (a_k \varkappa_l^* + \varkappa_k a_l^*) \tag{7}$$

where a_k is the k^{th} coefficient of the MO "a", etc, and denoting by $\boldsymbol{\Phi}(r)$, the value of $\boldsymbol{\Phi}$ above evaluated at position r, Eq. (5) above is evaluated by calculating $\boldsymbol{\Phi}(r)\, \boldsymbol{D} \boldsymbol{\Phi}^+(r)$. All such triplets were taken into account independently in the (i.e. no average energy approximation was made), and the results for the molecules studied are in the column headed "A" of the Table. Detailed discussion is deferred until later, the only general point emerging is that the agreement with experimental values is poor.

B. Configuration Interaction Triplet Functions

A physically more realistic basis of triplet function can be obtained by allowing the basic MO triplet functions Ψ_t to interact, and yield linear combinations which diagonalise the spin-free molecular Hamiltonian. Thus, we take

$$\Psi_T = \sum_t c_{t,T} \Psi_t \tag{8}$$

the Ψ_t being the MO triplets used in calculation A. The result for $J_{nn'}$ is then easily obtained, since if $\varrho_1(0, T|1;1')$ represents the transition density matrix between Ψ_0 and Ψ_T, then

$$\varrho_1(0, T|1;1') = \sum c_{t,T} \varrho_1(0, t|1;1') \tag{9}$$

and hence

$$D(0, T|1;1') = \sum c_{t,T} D(0, t|1;1') \tag{10}$$

$\Delta E(0, T)$ is just the corresponding eigenvalue of the CI matrix.

The results are collected in the column headed "B" of the Table.

Discussion

HF *Molecule*

The molecular integrals for this diatomic molecule were computed exactly, over Slater orbitals, since only two centre integrals are involved. The simplicity of this molecule enabled a limited investigation to be carried out of the effect of changing the minimal basis set orbital exponents. Three different basis sets were used.

(a) All exponents obtained by Slaters rules
($1s_F = 8.7$, $2s_F = 2p_F = 2.6$, $1s_H = 1.0$).

(b) As above except $1s_H = 1.2$.

(c) Best limited LCAO MO [7]
($1s_F = 8.6533$, $2s_F = 2.5551$, $2p_\sigma = 2.6693$, $1s_H = 1.3163$, $2p_\pi = 2.4965$).

The table shows that for both A and B calculations a large variation in computed J_{HF} occurs for these quite small variations in orbital exponent, the "optimum" set yielding results which are the worst of the three sets.

H_2O

Both J_{OH} and $J_{HH'}$ are in poor agreement with experiment, calculations A and B showing a large change on admitting configuration interaction. $J_{HH'}$ actually changes sign on going from A to B.

NH_3

In this case both computed coupling constants are in satisfactory agreement with experiment, improving on going from A to B.

BH_4^-, CH_4 *and* NH_4^+

This isoelectronic series shows surprising differences in computed values of coupling constants. In all cases the X–H coupling constant is in good agreement with experiment in column *A*, worsening on going over to column *B*, in marked disagreement with the trend for J_{NH} in NH_3.

The proton coupling constants have either the wrong sign (CH_4, NH_4^+) or change sign from *A* to *B* (BH_4^-).

C_2H_2

This molecule is by far the worst molecule studied from the point of view of agreement of computed values with experiment. None of the four distinct coupling constants are in satisfactory agreement with the experimental values. This fact is almost certainly due to low lying molecular levels of the system which can bring in terms of third order in perturbation theory which are usually negligible. The effect of systems of NMR coupling constants is under study by the authors. It is disappointing that empirical theories arrive at much better agreement with experiment, thus masking the mechanism of the coupling in these systems.

Conclusions

The work summarised in this paper shows that it is possible to compute the coupling constants $J_{nn'}$ for directly bonded nuclei to a fair degree of accuracy using a minimal basis of Slater functions. However comparison of the two methods *A* and *B* shows that, far from being able to use an average energy approximation in (1), the form of the triplet functions has a marked effect on the computed value. In this context it is worth discussing the effect of inclusion of triplet functions other than those of form (3). Although these functions have no transition spin density with the ground state wave function they will interact with the triplets of form (3) and so appear in the expansion (8) of the excited state wave-function, thus changing the coefficients with which the other triplets appear in (8). Thus inclusion of these triplets will effect the computed coupling constant, in a way which intuitively would be expected to be slight.

The computed proton-proton coupling constants are in general in worse agreement with experiment than the X–H values, not showing the intuitive trends expected in similar molecules (cf. H_2O, NH_3, CH_4, BH_4^-, NH_4^+) and often having the wrong sign. These values also do not show stable behaviour with respect to changing the basis of triplet functions (*A* to *B*) and small changes in orbital exponents and we are sure that the interpretation of proton coupling constants from simple MO wave-functions should be treated with great caution.

The main conclusion is that the minimal basis MO calculation of NMR coupling constants is an unreliable process. Because of the strong "chemical" appeal of the minimal basis, the computation of coupling constants in other formulations of the molecular wave function (Valence Bond, Separate Electron pairs [6]) is being carried out and will be reported elsewhere. It is possible, however, that the main source of error in all calculations of this type is simply the fact that Slater functions are a good basis for description of the "chemical" properties – i.e. bonding regions, whilst they are very poor elsewhere e.g. near the nuclei. Intuitively it seems possible to treat the density at the nucleus as a parameter to study the effects of molecular environment on coupling constants, and this topic is under investigation.

References

1. Cook, D. B., Hinchliffe, A., Palmieri, P.: Chem. Physics Letters **3**, 233 (1969).
2. — Palmieri, P.: Molecular Physics **17**, 271 (1969).
3. Pople, J. A., Santry, D. P.: Molecular Physics **8**, 1 (1964).
4. Ramsey, N. F.: Physic. Rev. **91**, 303 (1953).
5. McWeeny, R.: J. chem. Physics **42**, 1717 (1965).
6. Klessinger, M., McWeeny, R.: J. chem. Physics **42**, 3343 (1965).
7. Ransil, B. J.: Rev. mod. Physics **32**, 245 (1960).

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