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Some Consequences of the Magnetic Interaction of Protons and Electrons

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It is well known that, in a molecule, the magnetic moment of a nucleus interacts with nearby electrons in such a way that they are to a small extent 'unpaired'; that is, the two possible spin wavefunctions of an electron acquire different weights in different parts of the molecule [1—3]. We can see this most clearly in the simplest case, the hydrogen molecule $H_a - H_b$ (or rather, hydrogen deuteride). The magnetic effect of nucleus H_a leads to a mixing of singlet and triplet states and we may expect the lowest of these to be the most important in forming a ground-state wavefunction $|0\rangle_A$ which includes the perturbation [1]. If we form $|0\rangle_A$ from linear combinations of the two lowest states $|0\rangle$, $|1\rangle$ for which $s_z = 0$ we obtain the equation:

$$|0\rangle_A = |0\rangle + \lambda\,|1\rangle \qquad \text{(unnormalised)}\,. \tag{1}$$

In the valence-bond approximation [4] omitting overlap we can rewrite this equation:

$$|0\rangle_A = (1+\lambda)\,|0\rangle + 2\lambda[a\alpha(1)\,b\beta(2) - a\alpha(2)\,b\beta(1)] \tag{2}$$

where:

$$|0\rangle = \tfrac{1}{2}\,(ab+ba)\,(\alpha\beta-\beta\alpha)$$
$$|1\rangle = \tfrac{1}{2}\,(ab-ba)\,(\alpha\beta+\beta\alpha)$$

a, b, are the 'spatial' atomic orbitals of H_a, H_b respectively and α, β the electron spin eigenfunctions. Eq. (2) tells us that according to the sign of λ, either α or β spin will be preferred near to H_a, other things being equal. This equation also shows that the opposite spin would then be associated with the other atomic orbital which goes into the formation of the bond. When we add the interaction of the nucleus H_b with the electrons we again modify the distribution of electron spin and we get two terms for the interaction energy. One is of second order and is of the same type as we have implied for H_a and the other is the first order interaction with the excess spin density induced by H_a. The magnitude of this first order interaction will be determined largely by the values of the atomic orbitals a, b, at their respective nuclei and in the case when the molecule is rotating rapidly and at random, we can write:

$$J_{ab} \sim a_0^2\, b_0^2\,, \tag{3}$$

where J_{ab} = coupling constant

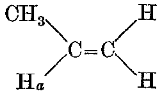
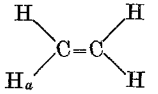
a_0, b_0 = values of a, b, at nuclei H_a, H_b respectively.

This result follows because the dominant term in the Hamiltonian will be the Fermi Contact term [5]. The relation (3) could have been deduced alternatively, but less instructively, by using the 'averaged energy' approximation.

Now suppose that we replace H_b by a hydrocarbon radical fragment R- so that the molecule becomes R–H_a. We might expect the C–H_a bond to be approximately 'isolated' from the rest of the molecule and neglecting differences in electronegativity, we might expect a relationship such as that shown in Eq. (3) still to be applicable. The atomic orbital b would now be the appropriately hybridised orbital on the carbon atom, or more exactly, if we speak in molecular orbital terms, the 'singly occupied MO of the fragment R-' and will be centred mainly on the carbon atom adjacent to H_a. This leads to two implications. The first is that the C^{13}–H coupling constants should be proportional to the 's-character' of the carbon hybrid orbital [6], i.e. we would expect J_{sp}, J_{sp^2}, J_{sp^3} to be in the ratios $\frac{1}{2}:\frac{1}{3}:\frac{1}{4}$ in that order. This agrees very well with the experimental values [6].

The second is that the coupling constants between H_a and the other nuclei should be approximately proportional to the spin densities at those nuclei in the radical R-. Now there are a few radicals which are of σ- rather than π-type and in which we would expect little change in geometry on addition of a hydrogen atom to complete the molecule. In this case the spin distribution around the radical can be measured by the hyperfine splitting of lines in its E.S.R. spectrum. We should therefore expect to find a simple proportionality between the coupling constants in the radical and corresponding proton-proton interactions in the molecule as measured by N.M.R. A glance at table shows that such a relationship does appear to exist, to a certain extent. The correlation for geminal protons is poor; but then the largest alteration in geometry on forming the radical would be expected to be on the α-carbon atom. The difference between the ratios for the different types of molecule may be attributed to structural changes (e.g. lengthening of C=C bond when acetylene loses a hydrogen atom) and/or to differing excitation energies. The experimental results for the olefinic compounds and radicals do however give us some confidence in a method for working out proton spin spin coupling constants in hydrocarbons, i.e. they will be proportional to the spin densities at the nuclei

Table. *Comparison of some hyperfine coupling constants in radicals (electron-proton) and in corresponding molecules (proton-proton)*

molecule	electron-proton coupling constants in radical R-(gauss)	proton-proton coupling constants in molecule RH (c/s)	ratio gauss/(c/s)
	a_{CH_3} = 19.5 [7]	J_{CH_3} = 6.4 [8]	3.0
	a_{trans} = 58.9	J_{trans} = 16.8	3.5
	a_{cis} = 32.9	J_{cis} = 10.0	3.3
	a_{gem} = 15.7 [9]	J_{gem} = 2.9 [6]	5.4
	a_{trans} = 68.5	J_{trans} = 19.0	3.6
	a_{cis} = 34.2	J_{cis} = 11.7	2.9
H_a—C≡C—H	a_H = 16.1 [9]	J_H = 9.1 [6]	1.6
H_a—D	a_D = 78.3	J_D = 43 [10]	1.9

in the appropriate hypothetical radical fragment. The determination of such spin densities is often comparatively easy and so we have another way of approaching the theory of hyperfine interactions in N.M.R. spectra.

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