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Field Theoretical Treatment of the Proton hfs in Aromatic Ion Radicals

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Field theoretical method to estimate the proton hfs in aromatic ion radicals is presented, and applied to explain why the proton hfs of the positive ion is larger than that of the negative ion of the same molecule. Since the Hartree-Fock orbitals of the neutral molecule are adequate for describing the negative ion state of this molecule, but not for the positive ion state, the correlation effect in the latter should be effectively taken into account, so that the particle propagators in the positive ion are renormalized. The hyperfine energy consists of two terms, the hyperfine self-energy term and the pole strength which is interpreted as the existence probability of the state under investigation. The electron correlation affects these differently between positive and negative ions.

It has been observed in aromatic compounds that absolute values of the proton hfs constants of the positive ions are larger than those of the corresponding negative ions.[1] Usually we adopt the simple relation that the hfs constant a_N is proportional to the spin density at the nucleus N;

$$a_N = Q\rho_N, \tag{1}$$

where Q is the proportionality constant, being estimated to be about -23 G. If we estimate ρ_N by means of the Hückel method or the PPP (Pariser-Parr-Pople) method, we can obtain

$$\rho_N^{(+)} = \rho_N^{(-)}. \tag{2}$$

That is, the spin density of the positive ion at the nucleus N, $\rho_N^{(+)}$ is equal to that of the negative ion, $\rho_N^{(-)}$. This relation is one of pairing properties widely found in the alternant hydrocarbons.[2]

Higuchi[3] tried a careful calculation taking into account the excess (shortage) of charge in the negative (positive) ion, and obtain the result reverse to the observation. Bolton[4] treated this problem from a intuitive aspect. His idea is that the orbital exponent of the wave function is larger (in absolute value) in the positive ion than in the negative ion, since there is an excessive nuclear attraction in the former.

It seems true that any theoretical effort to explain this problem would be in vain, so long as symmetrical character be kept in the alternant hydrocarbons. However, we should like to insist that it is preferable to treat both ions with common reference orbitals which are evaluated in the neutral molecule.

General

As is well known, the origin of the proton hfs in aromatic radicals is spin polarization due to the electron correlation at the nucleus in question. A little spin density produces magnetic energy due to the coupling between electron and nuclear spins.

A nice way to take the electron correlation effect into account in the spin polarization was introduced by Cederbaum.[5] This method will be briefly presented in the following.

We note that energy responsible for the proton hfs is a tiny part of the entire electron energy. In this sense, we wish to obtain the electron Green's function of which self-energy part contains the hyperfine energy. The total Hamiltonian of the system in question is written symbolically as

$$H = H_0 + H_V + H_{hf} \tag{3}$$

where H_0 is the HF (Hartree-Fock) Hamiltonian, H_V the electron correlation term and H_{hf} the hyperfine interaction between electron and nuclear spins.

Let us assume that we have already obtained in the HF approximation a set of one-particle orbitals, $\{\phi_n\}$ and that of orbital energies, $\{\varepsilon_n\}$. The Green's function in this approximation is

$$G_{ij}^{\circ}(\omega) = \frac{\delta_{ij}}{\omega - \varepsilon_i + i\eta \operatorname{sign} \varepsilon_i}, \tag{4}$$

where the orbital energy ε_i is counted from the chemical potential which is set at the mid-point between occupied and vacant orbital energies, and η the positive infinitesimal.

The Green's function for the total Hamiltonian (3) is written in matrix form as

$$G(\omega) = [G^0(\omega)^{-1} - \Sigma(\omega)]^{-1}, \tag{5}$$

and that for the first two terms of (3) is

$$G^V(\omega) = [G^0(\omega)^{-1} - \Sigma^V(\omega)]^{-1}, \tag{6}$$

where $\Sigma(\omega)$ and $\Sigma^V(\omega)$ are self-energy terms. It is obvious that

$$\Sigma(\omega) = \Sigma^V(\omega) + \Sigma^{hf}(\omega), \tag{7}$$

in which $\Sigma^{hf}(\omega)$ is the self-energy term concerning to the hyperfine interaction. $\Sigma^{hf}(\omega)$ arises in two ways: If the unpaired electron has finite density at the nucleus in question (the case of s electron), the electron spin directly couples with nuclear spin, while if not (the case of π electron, for example) the coupling takes place indirectly through intermediate states. In the latter case the electron correlation effect is especially important. However, even in the first case, we can show a correlation effect which is not given by current theories, but is given by the following field theoretical treatment.

Using relations (5) and (6) in (7), we obtain

$$G^V(\omega)^{-1} - G(\omega)^{-1} = \Sigma^{hf}(\omega). \tag{8}$$

Let $G^V(\omega)$ is diagonalized in the form

$$G_{ii}^V(\omega) = \frac{p(E_i^V)}{\omega - E_i^V}. \tag{9}$$

In the above, E_i^V is determined from

$$\det|G^V(\omega)| = 0, \tag{10}$$

and $p(E^{V}_{i})$ is called the pole strength which is approximately evaluated as follows. Neglecting the off-diagonal terms in $G^{V}(\omega)$, we obtain

$$G^{V}_{ii}(\omega) = [\omega-\varepsilon_i-\Sigma^{V}_{ii}(\omega)]^{-1}. \tag{11}$$

Then we set

$$\omega - \varepsilon_i - \Sigma^{V}_{ii}(\omega) = (\omega-E^{V}_{i})p(\omega)^{-1} \tag{12}$$

and differentiate both sides with respect to ω, and finally put $\omega=E^{V}_{i}$. Thus it follows that

$$p(E^{V}_{i}) = \left\{1-\left.\frac{\partial\Sigma^{V}_{ii}(\omega)}{\partial\omega}\right|_{\omega=E^{V}_{i}}\right\}^{-1}. \tag{13}$$

Similarly we obtain

$$G_{ii}(\omega) = \frac{p(E_i)}{\omega-E_i}, \tag{14}$$

$$p(E_i) = \left\{1-\left.\frac{\partial\Sigma_{ii}(\omega)}{\partial\omega}\right|_{\omega=E_i}\right\}^{-1}. \tag{15}$$

It should be stressed that the pole strength $p(E_i)$ is the probability that the state with an unpaired electron of which energy is E_i can exist.

The electron energy E_i consists of the energy containing up to the correlation effect, E^{V}_{i} and the hyperfine energy, Δ_i;

$$E_i = E^{V}_{i} + \Delta_i. \tag{16}$$

Using (9) and (14) in (8), we get

$$\frac{\omega-E^{V}_{i}}{p(E^{V}_{i})} - \frac{\omega-E_i}{p(E_i)} = \Sigma^{hf}_{ii}(\omega). \tag{17}$$

Here putting $\omega=E_i$, we have the result,

$$\Delta_i = p(E^{V}_{i})\,\Sigma^{hf}_{ii}(E_i). \tag{18}$$

Considering that $p(\omega)$ and $\Sigma^{hf}_{ii}(\omega)$ are smooth and slowly varying function of energy parameter, we may be allowed to approximate as

$$\Delta_i \simeq p(\varepsilon_i)\,\Sigma^{hf}_{ii}(\varepsilon_i). \tag{19}$$

This result shows us that the hyperfine energy is given by a product of two terms; the first is the pole strength which concerns electronic structure of the whole system, and the second is the hyperfine self-energy term which is determined from a rather local structure giving the hyperfine interaction. Therefore we can say that even if the hyperfine interaction is simple as in the case with an unpaired electron in the s orbital, the correlation effect is taken into account *via* the pole strength.

Case of Aromatic Ion Radicals

In order to discuss the difference of the proton hfs values between aromatic positive and negative ion radicals in terms of the pole strength and the hyperfine self-energy term as in (19), let us define:

$$\delta p = (p^{+}-p^{-})/p^{-},$$
$$\delta\Sigma^{hf} = (\Sigma^{hf+}-\Sigma^{hf-})/\Sigma^{hf-},$$

where $+$ and $-$ are added to clearly indicate positive and negative ions, respectively. Then it is found that

$$\delta\Delta \equiv (\Delta^{+}-\Delta^{-})/\Delta^{-}$$
$$\simeq \delta p + \delta\Sigma^{hf}, \tag{20}$$

neglecting the second order terms with respect to δp and $\delta\Sigma^{hf}$.

Now we evaluate the hyperfine self-energy term. The current treatments in evaluating the hyperfine energy have been carried out under the condition that $p(\varepsilon_i)=1$, so that the hyperfine self-energy term itself is the hyperfine energy. Since the π-orbital with an unpaired electron has a nodal plane on which the proton is, an exchange type interaction shown in Fig. 1a is invoked to cause the spin polarization at the proton. The magnetic interaction represented by a dotted line creates a particle-hole pair, then the hole propagator of it annihilates combined with the incomming particle propagator, i, while the particle propagator of the pair is scattered to i with the electronic interaction. This mechanism is called the σ-π exchange interaction. However, the direct type interaction in Fig. 1b has vanishing result to the spin polarization due to the possibility of arbitrary choice of spin directions of the polarization part.

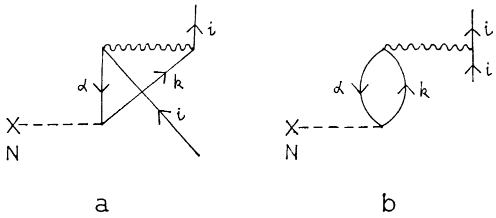


Fig. 1. Hyperfine self-energy terms.
a: Exchange type, b: direct type.

Observing the Fig. 1a, we can immediately obtain

$$\Sigma^{hf-}_{ii}(\varepsilon_i) = -\sum_{k\alpha}(\mathrm{N};\,k\alpha)(ki;\,i\alpha)/\varepsilon_{\alpha k}, \tag{21}$$

$$\varepsilon_{\alpha k} = \varepsilon_{\alpha} - \varepsilon_{k}, \tag{21a}$$

where indices k and α denote the particle and hole states respectively, and

$$(\mathrm{N};\,k\alpha) = \int \mathrm{N}(\boldsymbol{r})\phi_k(\boldsymbol{r})\phi_{\alpha}(\boldsymbol{r})\mathrm{d}\boldsymbol{r}. \tag{22}$$

refering the magnetic interaction, and further

$$(ki;\,i\alpha) = \int \phi_k(\boldsymbol{r}_1)\phi_i(\boldsymbol{r}_1)\frac{1}{r_{12}}\phi_i(\boldsymbol{r}_2)\phi_{\alpha}(\boldsymbol{r}_2)\mathrm{d}\boldsymbol{r}_1\mathrm{d}\boldsymbol{r}_2. \tag{23}$$

In the above, the one-electron orbitals are assumed to be real without loss of generality.

We suppose the expression (21) refers to the negative ion, that is, an unpaired electron is in the lowest vacant orbital i. If we consider the positive ion in which an unpaired electron is in the highest occupied orbital η, we get a similar result,

$$\Sigma^{hf+}_{\eta\eta}(\varepsilon_{\eta}) = -\sum_{k\alpha}(\mathrm{N};\,k\alpha)(k\eta;\,\eta\alpha)/\varepsilon_{\alpha k}. \tag{24}$$

In the corresponding diagram which leads to the above result, the direction of every line in Fig. 1a is reversed (see Fig. 2), and i is replaced by η.

Then using one of the pairing properties of the alternant hydrocarbons

$$(ki;\,i\alpha) = (k\eta;\,\eta\alpha) \tag{25}$$

we get

$$\Sigma_{ii}^{\mathrm{hf}-}(\varepsilon_i) = \Sigma_{\eta\eta}^{\mathrm{hf}+}(\varepsilon_\eta). \tag{26}$$

This is nothing but to reformulate the Mclachlan's result.[2)]

To make steps further, a physical intuition is needed. Remember how to determine the HF orbitals. The HF functions of the particle state are determined for the state in which hole levels are already doubly occupied, then an extra electron is introduced. Therefore we can say that the HF functions are considerably suitable for describing the negative ion state. If we get a same order of approximation to the positive ion, we have to use the HF functions determined in the reference system which is the doubly ionized positive ion. Such consideration makes us use a different basis set for the positive ion from that for the negative ion. This is the Bolton's idea. However in the present treatment, we do not follow this, but want to use the identical basis set for both ions.

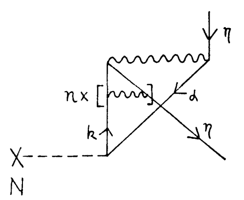


Fig. 2. Renormalization of the particle propagator in the hyperfine self-energy term of the positive ion.

When the basis set determined in the neutral molecule is employed, it is probable that the positive ion is more sensitive to the electron correlation than the negative ion is. An extra positive charge in the positve ion works to decrease the virtual excitation energies, that is, the particle propagator should be renormalized with an extra hole propagator which arises only in the positive ion. To this end, in Fig. 2 the ladder type of particle-hole interactions are inserted n times (n tends to ∞). Combining this diagram and the corresponding exchange one, we can obtain

$$\begin{aligned}\Sigma_{\eta\eta}^{\mathrm{hf}+}(\varepsilon_\eta) &= -\sum_{k\alpha}(\mathrm{N};\, k\alpha)(k\eta;\, \eta\alpha)[\varepsilon_{\alpha k}+(\eta\eta;\, kk)-(\eta k;\, k\eta)]^{-1}\\ &= -\sum_{k\alpha}(\mathrm{N};\, k\alpha)(ki;\, i\alpha)[\varepsilon_{\alpha k}+(ii;\, kk)-(ik;\, ki)]^{-1},\end{aligned} \tag{27}$$

following the Kelly's technique to shift the energy denominator,[6)] and using the pairing property to obtain the second equality. This is same as the expression of (21) for the negative ion except for the energy-shift terms of the denominator.

If we employ the CH fragment to estimate Σ^{hf}, the orbitals α and k are as usual restricted to the CH bonding and anti-bonding orbitals, respectively, so that we can remove the summation symbol. Consequently the second term of (20) becomes

$$\delta\Sigma^{\mathrm{hf}} = \{1+[(ii;\, kk)-(ik;\, ki)]/\varepsilon_{\alpha k}\}^{-1} - 1. \tag{28}$$

Since $\varepsilon_{\alpha k}$ is negative, it is obvious that the sign of (28) is positive, that is, at this stage the hfs value of the positive ion always larger than that of the negative ion.

We turn to evaluation of the pole strength, following

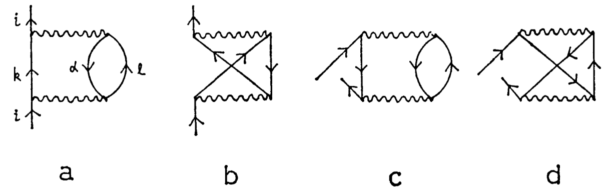


Fig. 3. Second order diagrams for the electron correlation (negative ion).

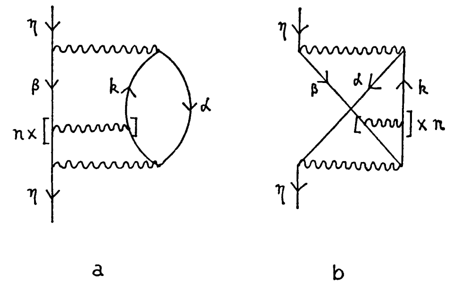


Fig. 4. Renormalization of the particle propagator in the electron correlation diagram (positive ion).

the spirit previously mentioned. To do so, the self-energy terms for the electron correlation will be calculated. Since we are using the HF orbitals, the first order diagrams are already included to infinite order. For the negative ion we are satisfied with an approximation displayed by Fig. 3, but the Fig. 3c and 3d can be neglected due to their small contributions (because of the large energy denominator). Therefore the second order correction in the negative ion becomes

$$\Sigma_{ii}^{\mathrm{V}}(\omega) = \sum_{\alpha kl} g(il;\, l\alpha)/(\omega+\varepsilon_\alpha-\varepsilon_k-\varepsilon_l), \tag{29}$$

$$g(ik;\, la) = 2(ik;\, l\alpha)(ki;\, \alpha l)-(ik;\, l\alpha)(k\alpha;\, li). \tag{29a}$$

In the case of the positive ion, the diagrams shown in Figs. 4a, 4b, and the corresponding exchange diagrams yield

$$\begin{aligned}\Sigma_{\eta\eta}^{\mathrm{V}}(\omega) = \sum_{\alpha\beta l} g(\eta\beta;\, l\alpha)/[\omega+\varepsilon_l-\varepsilon_\alpha-\varepsilon_\beta-(\beta\beta;\, ll)\\ +(\beta l;\, l\beta)].\end{aligned} \tag{30}$$

Then we get

$$\frac{\partial}{\partial\omega}\Sigma_{ii}^{\mathrm{V}}(\omega)\bigg|_{\omega=\varepsilon_i} = -\sum_{\alpha kl} g(ik;\, l\alpha)/(\varepsilon_i+\varepsilon_\alpha-\varepsilon_k-\varepsilon_l)^2, \tag{31}$$

$$\begin{aligned}\frac{\partial}{\partial\omega}\Sigma_{\eta\eta}^{\mathrm{V}}(\omega)\bigg|_{\omega=\varepsilon_\eta} &= -\sum_{\alpha\beta l} g(\eta\beta;\, l\alpha)/[\varepsilon_\eta-\varepsilon_\alpha-\varepsilon_\beta+\varepsilon_l\\ &\quad -(\beta\beta;\, ll)+(\beta l;\, l\beta)]^2\\ &= -\sum_{\alpha kl} g(ik;\, l\alpha)/[\varepsilon_i+\varepsilon_\alpha-\varepsilon_k-\varepsilon_l\\ &\quad +(kk;\, ll)-(kl;\, lk)]^2,\end{aligned} \tag{32}$$

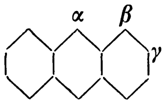
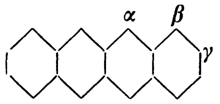
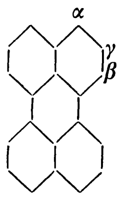
for the negative and positive ions, respectively. In obtaining the second equality of (32), use was made of the pairing properties,

$$\varepsilon_\eta = -\varepsilon_i, \qquad g(\eta\beta;\, l\alpha) = g(ik;\, l\alpha). \tag{33}$$

The expression of (32) is same as that of (31) except for additional terms in the denominator.

Using (31) and (32) in (15), we get δp of (20) as

Table 1. Proton hfs values of aromatic ion radicals. Experimental and theoretical results

		Experimental hf value/G			Theoretical		
		+ion	−ion	$\delta\Delta$	δp	$\delta\sum^{\text{hf}}$	$\delta\Delta$
	α	6.65	5.41	0.23	−0.051	0.340	0.189
	β	3.12	2.76	0.13	−0.051	0.107	0.056
	γ	1.40	1.53	−0.085	−0.051	0.051	0.
	α	5.17	4.25	0.22	−0.060	0.173	0.113
	β	1.72	1.55	0.11	−0.060	0.060	0.
	γ	1.06	1.15	−0.078	−0.060	0.035	−0.025
	α	4.10	3.53	0.16	−0.066	0.121	0.055
	β	3.10	3.08	0.0065	−0.066	0.091	0.025
	γ	0.46	0.46	0.	−0.066	0.013	−0.053

$$\delta p \simeq \left.\frac{\partial\sum^{\text{v}}_{\eta\eta}(\omega)}{\partial\omega}\right|_{\omega=\varepsilon_\eta} - \left.\frac{\partial\sum^{\text{v}}_{ii}(\omega)}{\partial\omega}\right|_{\omega=\varepsilon_i}$$

$$= -\sum_{\alpha kl} g(ik;\, l\alpha)\{[\varepsilon_{i\alpha kl}+(kk;\, ll)-(kl;\, lk)]^{-2}-\varepsilon_{i\alpha kl}^{-2}\} \tag{34}$$

with

$$\varepsilon_{i\alpha kl}=\varepsilon_i+\varepsilon_\alpha-\varepsilon_k-\varepsilon_l. \tag{34a}$$

As $\varepsilon_{i\alpha kl}$ is negative, it is found that δp has the positive sign.

Comming back to (20), we discuss effects of two terms constructing the hyperfine energy difference between positive and negative ions: the first is δp which is negative and relates with the electron correlation of the whole system, and the second is $\delta\sum^{\text{hf}}$ which is positive, strongly depending upon the local situation where the magnetic nucleus under consideration is.

Numerical Results and Discussion

The present theory being semi-qualitative, the numerical procedure is simplified to save computer time. The π electron orbitals which are involved in our calculation are obtained by the Hückel method, and are regarded as the self-consistent HF orbitals in the PPP approximation. Then the electron-electron interactions are introduced with the Nishimoto-Mataga parametrization.[7] Therefore the orbital energies in (34a) are not Hückel ones, but are regarded as the HF orbital energies in the PPP approximation.

In evaluating the hyperfine self-energy term employing the CH fragment, the energy separation between the CH bonding and antibonding orbitals is needed. This is approximately estimated in the semi-empirical theory as $\varepsilon_{\alpha k}\simeq -10$ eV. As to the electron repulsion terms, the exchange integral, $(ik;ki)$ is negligibly small, and the direct term, $(ii;kk)$ may be a little smaller than the one-center coulomb repulsion integral multiplied by the unpaired electron density at the carbon atom, ρ_{Ci}: $(ii;kk)\simeq 10\rho_{Ci}$ eV. These energy parametrizations make $\delta\sum^{\text{hf}}$ given by (28) simple as

$$\delta\textstyle\sum^{\text{hf}} = (1-\rho_{Ci})^{-1} - 1 \tag{35}$$

We tabulate observations and theoretical results of a few species as explanational examples. In table we have given values of δp and $\delta\sum^{\text{hf}}$; for example in the case of anthracene radical, the negative value of δp is independent of sites, while values of $\delta\sum^{\text{hf}}$ which are positive rapidly decrease in order of α, β, and γ. The overall value at each site agrees qualitatively with observation. In other species, we can get the negative values at γ positions, which were never explained by the current theories.

Somebody will be suspicious of our theoretical result, claiming that parametrizations in the present treatment mask the reliability. However, we think that a theory would be successful, if it present any possibility to explain the observed values under reasonable (to some extent) assumptions.

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