

The Correct McLachlan Method in Free Radicals and Radical Anions

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A recent modification to the McLachlan method is corrected. This modification, when correctly applied to odd alternant hydrocarbons, reproduces McLachlan's results instead of improving their agreement with experiment. The modification is irrelevant and erroneous for radical anions.

Key words: McLachlan method – Free radicals – Radical anions

The purpose of this paper is the correction of a number of serious errors in a recent modification [1] to McLachlan's method [2] for the calculation of π -electron spin densities in planar free radicals and radical anions. These errors fall into the categories of (1) general theory of the McLachlan method (2) free radicals and (3) radical anions; this paper is therefore subdivided accordingly.

1. The McLachlan Method

McLachlan's principal assumption is that, in the first approximation the β -electrons in free radicals and radical ions are unperturbed by the odd α -electron. The second assumption is that the perturbation imposed on α -electrons is given by the matrix $\Delta H = F^\alpha(1) - F^\beta(1)$ where $F^\alpha(1)$ and $F^\beta(1)$ are the first estimates of the SCF π -electron Hartree-Fock matrices as defined by Pople and Brickstock [3]. The matrix elements of ΔH , for $p\pi$ -atomic orbitals μ, ν are given by $\Delta H_{\mu\mu} = -G_{\mu\mu}c_{n\mu}^2$ and $\Delta H_{\mu\nu} = -G_{\mu\nu}c_{n\mu}c_{n\nu}$ where the $c_{n\mu} \dots$ are the atomic orbital coefficients in the unperturbed molecular orbital, n , in which the odd α -electron is placed in the zeroth (or Hückel [4]) approximation. The matrix elements of G are the repulsion terms as given by, for example, Nishimoto and Forster [5]. The unperturbed molecular orbitals are usually obtained from the Hückel matrix, H .

McLachlan's third assumption involves the behaviour of the odd α -electron; the assumption originally made was that this electron is unperturbed in all radical ions and free radicals. Honeybourne has shown that, although this assumption is acceptable in radical anions, it is unacceptable in radical cations [6] and free radicals [7-9]. In radical cations, the electron-pair breaking of ionization perturbs the odd α -electron; if this electron is not treated as being perturbed, then the Coulson-Rushbrooke Pairing Theorem [10] is violated [6]. Bickerton and Moss have also discussed this point [11]. In free radicals it is impossible to select a given α -electron which shall be taken as unperturbed throughout the formation of the species from its constituent atoms [7]; if the species has been generated by homolytic bond fission, then the electron-pair breaking perturbation is present. Therefore,

Devolder's Eq. (1) [1] is incorrect for free radicals and radical cations and should read

$$\rho_{\mu} = (c'_{n\mu})^2 + \sum_{j=1}^{n-1} [(c'_{j\mu})^2 - (c_{j\mu})^2] \quad (1)$$

in which ρ_{μ} is the π -electron spin density in orbital μ and the $c'_{j\mu}$ are the coefficients of the appropriate perturbed molecular orbitals obtained by diagonalizing the perturbed matrix $H' = H + \Delta H$. This particular way of introducing the perturbations has been called the $\Delta\alpha$ version if the off diagonal $\Delta H_{\mu\nu}$ elements are set to zero or the $\Delta\beta$ version if the $\Delta H_{\mu\nu}$ are included¹ [6].

An alternative way of introducing the perturbations is through the atom-atom and atom-bond polarizability coefficients of Coulson and Longuet-Higgins [12]. It has been pointed out [12] that the published expressions for these coefficients are not applicable to free radicals; a detailed derivation of the required atom-atom and atom-bond polarizability coefficients is now available [7]. It is important to remember that the polarizability coefficients describe the perturbation of charge, not spin; their use implies the perturbation of *all* the electrons in the neutral ground state, which agrees with the modified third assumption, inherent in the McLachlan method, concerning the behaviour of the odd α -electron. When applying polarizability coefficients to spin distribution problems, a factor of 0.5 must be introduced if pair-occupied orbitals are involved in the related charge distribution case (see Ref. [13] for the detailed working for radical anions and radical cations). The same set of physical assumptions is used in both versions of the McLachlan method and it has been claimed previously that, in the radical ion case, the $\Delta\alpha$ method and the use of atom-atom polarizability coefficients are "entirely equivalent" [6]. Devolder [1] has misquoted this latter as "exactly equivalent", and criticized the claimed equivalence. It is emphasized that the two versions *are* physically equivalent in free radicals and radical ions; Honeybourne deliberately avoided the use of the adjective "exact", because exact numerical agreement is impossible due to the non-orthogonality of the unperturbed molecular orbitals with the perturbed molecular orbitals. Devolder's [1] Table 1 serves to emphasize the triviality of the consequences of the non-orthogonality in small alternant systems. For heteroatomic systems the consequences of the non-orthogonality are serious.

2. Free Radicals

The correct atom-atom polarizability coefficients for free radicals, are given by [1, 7]

$$\begin{aligned} \pi_{\mu\nu}^{(2)} &= \pi_{\mu\nu}^{(1)} + \pi_{\mu\nu}^* \\ \pi_{\mu\nu}^{(1)} &= 4 \sum_{r=1}^{n-1} \sum_{s=n}^{2n-1} \frac{c_{\mu r} c_{\nu s} c_{\nu r} c_{\mu s}}{\epsilon_r - \epsilon_s} \\ \pi_{\mu\nu}^* &= 2c_{n\mu} c_{n\nu} \sum_{j=1}^{2n-1} \frac{c_{j\mu} c_{j\nu}}{\epsilon_j - \epsilon_n} \end{aligned}$$

The $\pi_{\mu\nu}^{(1)}$ describe the charge perturbation of the electron *pairs*, and the $\pi_{\mu\nu}^*$ describe the charge perturbation experienced by the single electron in the neutral free radical. The

¹ Note that the inclusion of the $\Delta H_{\nu\sigma}$ leads to slight violation of the pairing theorem.

related atom-bond polarizability coefficients, $\pi_{\mu,\nu\sigma}^{(2)}$ are given by [7]

$$\begin{aligned}\pi_{\mu,\nu\sigma}^{(2)} &= \pi_{\mu,\nu\sigma}^{(1)} + \pi_{\mu,\nu\sigma}^* \\ \pi_{\mu,\nu\sigma}^{(1)} &= 4 \sum_{r=1}^{n-1} \sum_{s=1}^{2n-1} \frac{c_{\mu r} c_{\mu s} (c_{\nu r} c_{\sigma s} + c_{\sigma r} c_{\nu s})}{\epsilon_r - \epsilon_s} \\ \pi_{\mu,\nu\sigma}^* &= 2 \sum_{j=1}^{2n-1} \frac{c_{n\mu} c_{j\mu} (c_{n\nu} c_{j\sigma} + c_{j\nu} c_{n\sigma})}{\epsilon_n - \epsilon_j}\end{aligned}$$

The perturbed charge, q_μ , is given by

$$q_\mu = P_{\mu\mu}^0 + \sum_{\nu} \pi_{\mu\nu}^{(2)} \Delta H_{\nu\nu} + \sum_{\nu\sigma} \pi_{\mu,\nu\sigma}^{(2)} \Delta H_{\nu\sigma} + c_{n\mu}^2 \quad (2)$$

where $P_{\mu\mu}^0 = 2 \sum_{j=1}^{n-1} c_{j\mu}^2$. This may be subdivided into the α - and β -electron contributions, q_μ^α and q_μ^β , and the assumption that the β -electrons are unperturbed introduced. This gives

$$\begin{aligned}q_\mu^\alpha &= 0.5 \left\{ P_{\mu\mu}^0 + \sum_{\nu} \pi_{\mu\nu}^{(1)} \Delta H_{\nu\nu} + \sum_{\nu\sigma} \pi_{\mu,\nu\sigma}^{(1)} \Delta H_{\nu\sigma} \right\} + c_{n\mu}^2 + \sum_{\nu} \pi_{\mu\nu}^* \Delta H_{\nu\nu} + \sum_{\nu\sigma} \pi_{\mu,\nu\sigma}^* \Delta H_{\nu\sigma} \\ &\quad (v \neq \sigma) \\ q_\mu^\beta &= 0.5 P_{\mu\mu}^0 \quad (3)\end{aligned}$$

If the $\Delta H_{\nu\sigma}$ ($v \neq \sigma$) are set to zero, then the spin density becomes

$$\rho_\mu = c_{n\mu}^2 + \sum_{\nu} \Delta H_{\nu\nu} \{ \pi_{\mu\nu}^* + 0.5 \pi_{\mu\nu}^{(1)} \} \quad (4)$$

Devolder's Eqs. (3) and (4) for ρ_μ [1] are wrong because he neglected the difference between perturbations on spin pairs and perturbations on the single electron. Devolder has performed McLachlan calculations for the odd alternant hydrocarbon benzyl, obtaining results very different from those of McLachlan. These differences Devolder has attributed to the correction term involving $\pi_{\mu,\nu}^*$. However, it is easy to show that, as a consequence of the Coulson-Rushbrooke Pairing Theorem, *all* $\pi_{\mu,\nu}^*$ are *zero* for *all* odd alternant hydrocarbons [7]. If μ and ν are in different sets (i.e. starred and unstarred sites), or both in the unstarred set, then $c_{n\mu}$ and/or $c_{n\nu}$ are zero. If μ and ν are both in the starred set then, for a pair of molecular orbitals related by the pairing theorem, the sign of $\epsilon_n - \epsilon_{n\pm i}$ alters (the magnitude remains constant) whilst the value of $c_{n\pm i,\mu} c_{n\pm i,\nu}$ is conserved; the net contribution of any pair of starred sites is zero. If Eq. (4) is correctly applied, then McLachlan's free radical results may be exactly reproduced. In non-alternant and heteroatomic free radicals, the inclusion of $\pi_{\mu,\nu}^*$ and $\pi_{\mu,\nu\sigma}^*$ is important. Their zero effect in odd alternant hydrocarbons may be attributed to the effective self-consistent field in such molecules [12].

3. Radical Anions

If the $\pi_{\mu\nu}^{(2)}$ are used in radical anions, then corrections to the limits of the summations are required; viz.

$$(\text{Anion}) \pi_{\mu\nu}^{(2)} = 4 \sum_{r=1}^{n-1} \sum_{s=n}^{2n-2} \frac{c_{r\mu} c_{r\nu} c_{s\mu} c_{s\nu}}{\epsilon_r - \epsilon_s} + 2c_{n\mu} c_{n\nu} \sum_{s=1}^{2n-2} \frac{c_{s\mu} c_{s\nu}}{\epsilon_n - \epsilon_s} = \pi_{\mu\nu}^{(1)} + \pi_{\mu\nu}^*$$

However, this is not a true polarizability coefficient because $\pi_{\mu\nu}^*$ attempts to describe the perturbation of an electron that was not present in the ground state! Further, its use (1) implies that the odd α -electron is perturbed in the first approximation in radical anions (which is not the case), and (2) leads to violation of the pairing theorem. The correct expression for ρ_μ in radical anions is either Devolder's Eq. (1) [1] or the corrected version of his Eq. (3):

$$\rho_\mu = c_{n\mu}^2 + 0.5 \sum_\nu \pi_{\mu\nu}^{(1)} \Delta H_{\nu\nu} + 0.5 \sum_{\nu\sigma} \pi_{\mu,\nu\sigma}^{(1)} \Delta H_{\nu\sigma} \quad (5)$$

It is customary to neglect the $\Delta H_{\nu\sigma}$, and we have

$$\rho_\mu = c_{n\mu}^2 - 0.5 \sum_\nu \pi_{\mu\nu}^{(1)} G_{\nu\nu} c_{n\nu}^2 \quad (6)$$

where $G_{\nu\nu}$ and ϵ_j, ϵ_k are in, say, electron volts. It is usual (1) to set all $G_{\nu\nu}$ to a constant value, $\bar{\gamma}$ (2) to multiply the summation term by $|\beta|/|\beta|$ and (3) to define a parameter $\lambda = \bar{\gamma}/(2|\beta|)$. This gives [2]

$$\rho_\mu = c_{n\mu}^2 - \lambda \sum_\nu \pi_{\mu\nu}^{(1)'} c_{n\nu}^2 \quad (7)$$

where the $\pi_{\mu\nu}^{(1)'}$ are the dimensionless polarizabilities. If the denominators of the polarizability coefficients are in β -units (not $|\beta|$), then

$$\rho_\mu = c_{n\mu}^2 + \lambda \sum_\nu \pi_{\mu\nu}^{(1)} c_{n\nu}^2 \quad (8)$$

The effect of $\lambda \pi_{\mu\mu}^{(1)} c_{n\mu}^2$ is to make the spin density more positive than the Hückel "spin density", $c_{n\mu}^2$.

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