PI-ELECTRON SPIN DENSITY CALCULATION ON ALLYL RADICAL

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Abstract. An attempt is made to remedy the overcompensation of spin contamination, inherent in Amos and Snyder method of unrestricted Hartree-Fock LCAO MO SCF. This may be done by using the charge and bond order matrices (J and K) obtained after annihilation, in the unrestricted molecular orbital equations, and calculating spin densities from P and Q matrices obtained from these eigenvalue equations. A calculation on allyl radical showed that the first iteration before annihilation gives almost exactly the same result as obtained by Sando and Harriman by their optimization method.

Unrestricted Hartree–Fock SCF LCAO MO, in its various forms,[1-13] have been used in the calculation of spin densities in neutral free radical as well as in free radical ions.[4-8,12,13] The single determinant wave-function of the unrestricted Hartree–Fock[1,2] suffers from defect that the wave-function is not eigen-function of S^2, the square of the spin angular momentum operator.[5] This wave-function gives negative spin densities of too large a magnitude.[12] When the wave-function is subjected to projection or annihilation, to remove spin containination, the process overcompensates (the spin containination). Harriman and Sando[12] optimized the wave-function after projection and the spin densities they calculated from their method for allyl and pentadienyl radicals were in excellent agreement with the experimental result.

An attempt to solve the problem of removing overcompensation may be made by developing a process by which some character of P and Q matrices are reintroduced.

An attempt has been made to study such a process by alternately annihilating and solving secular equation. Since allyl radical is the simplest system, such a calculation is carried out on this radical.

Results and Discussion

P and Q matrices for allyl radical were calculated from the molecular orbitals (single determinant UHF). The J and K matrices were obtained from these P and Q matrices.[7] The spin densities obtained from these P and Q matrices, and J and K are already given in ref. 7 as ρ_{sd} and ρ_{aa} respectively and are included in the table here for comparison.

These J and K matrices obtained for allyl radical were fed in equation (2) and (3), in place of P and Q, to solve equation (1) (appendix 1). The coefficients thus obtained were used to obtain P and Q matrices and therefrom J and K matrices. Spin densities calculated from equation (5) (appendix) are included in the Table 1 as the result of first iteration. Few more iterations were carried out and results of these successive iteration are also included in the Table 1. In these calculations the integrals were same as used in ref. 7.

From the Table 1 it is quite clear that spin densities calculated from P and Q matrices in the first iteration is almost exactly the same as calculated by Sando and Harriman.[12] This shows that by reusing J and K matrices in the eigenvalue equation the overcompensation of spin contamination is remedied to the same degree as in the method of Sando and Harriman. Also the result agrees excellently with the experimental result.

The spin densities calculated from J and K matrices in the first iteration is even worse. This is understandable. In the zero iteration (Table 1) J and K matrices were obtained from P and Q matrices of

TABLE 1. SPIN DENSITIES FOR ALLYL RADICAL.

Iterations	Atom (1)	Atom (2)
0[c]	+0.651	—0.302[a]
	+0.547	—0.093[b]
1[d]	+0.584	—0.168
	+0.527	—0.054
2	+0.575	—0.151
	+0.524	—0.048
3	+0.564	—0.128
	+0.520	—0.041
4	+0.562	—0.123
	+0.520	—0.039
5	+0.561	—0.122
	+0.520	—0.039
—	+0.583	—0.165[e]
—	+0.604	—0.208[f]
—	+0.589	—0.150[g]

[a] P–Q, [b] J—K and from ref. 7; [d] iterations as described in the text. Spin densities are rounded off on third decimal place to compare them with those cited in ref. 7; [e] ref. 12; [f] as a of ref. 7; [g] from experimental proton hyperfine splitting constant and using Mc-Connell equation with $Q_{CH}^H = 27\cdot0$ gauss, ref. 7.

single determinant (which was fully spin contaminated). In the first iteration, in P and Q some decontamination of spin has already taken place, further subjection to annihilation can only make situation worse.

The spin densities calculated from P and Q matrices in the second iteration also gives good agreement with the experimental values. The subsequent iterations, however, gives results neither in agreement with the values calculated by Sando and Harriman[12] nor with the experimental values.

There is, however, a convergence in the process (iterations 4 and 5) which gives the idea of the magnitude of overcompensation of negative spin densities.

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Appendix

In the unrestricted Hartree-Fock LCAO MO SCF, the coupled secular equations to be diagnolised are

$$F^{A \to A} C_i = C_i^{\to A} E_i \tag{1}$$

Where A=alpha, beta for two spins, C_i^A are the LCAO MO coefficients, F^A, in the Pariser–Parr–Pople formalism is given as

$$F_{\mu\mu}^A = U_{\mu\mu} + Q_{\mu\mu} \gamma_{\mu\mu} + \sum_{\rho \neq \mu} (P_{\rho\rho} + Q_{\rho\rho} - Z_\rho) \gamma_{\mu\rho} \tag{2}$$

$$F_{\mu\lambda}^A = \beta - P_{\mu\lambda} \gamma_{\mu\lambda} \tag{3}$$

$$P_{\mu\lambda} = \sum_i^P C_{\mu i}^A C_{\lambda i}^A \tag{4}$$

A is for electrons with alpha spin.

Similarly $Q_{\mu\lambda}$ is defined for beta spin electrons. P and Q are charge and bond order matrices for electrons spin alpha and beta respectively. While the sum of P and Q matrices give the charge density function, the difference gives spin density function (before annihilation). Spin densities, thus calculated, are not pure but contaminated with higher spin multiplates. Snyder and Amos[7] derived expression(s) for spin density and charge density function which are contamination free. These spin densities are obtained from the difference of J and K matrices. These J and K matrices obtained after annihilation play the same role to the annihilated wave-function that P and Q do for unannihilated one. Thus the spin density is given by expression.

$$\rho = R-S; R = P, S = Q; \text{ if } R = J \text{ then } S = K \tag{5}$$

J and K matrices can easily be obtained from P and Q. Formulae are given by Amos and Snyder[7] (equation (37), ref. 7). These J and K matrices if used in equation (2) and (3) in place of P and Q matrices, to solve (1) will generate new C_i^A, which can be used to evaluate new P and Q matrices from which new J and K can be obtained again. The whole cycle can be repeated and spin densities can be calculated from equation (5) above.