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CI Calculation of Spin Densities in π-Radicals and Ions using Hückel Orbitals as a Basis

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Spin Densities have been calculated for a series of Conjugated Organic Radicals and Radical Ions using Hückel one-electron basis orbitals to generate all those singly excited configurations which interact with the ground state to produce first order changes in Spin Densities. The effect of variations of the different integral values is discussed, and the results compare well with both experiment and more elegant SCF calculations.

Les densités de spin ont été calculées pour une série de radicaux organiques et d'ions radicaux conjugués en utilisant une base d'orbitales de Hückel pour engendrer toutes les configurations monoexcitées qui interagissent avec l'état fondamental en produisant des variations du premier ordre des densités de spin. L'effet des variations des différentes valeurs d'intégrales est discuté; les résultats sont bien comparables tant aux données expérimentales qu'aux calculs SCF plus élégants.

Für eine Reihe von konjugierten organischen Radikalen und ionischen Radikalen werden Spindichten berechnet. Aus einer Basis von Hückel'schen Einelektronenorbitalen werden alle die einfach angeregten Konfigurationen berechnet, die durch Wechselwirkung mit dem Grundzustand die Spindichte in 1. Näherung ändern. Der Einfluß der Variation verschiedener Integralwerte wird diskutiert. Die Ergebnisse zeigen gute Übereinstimmung sowohl mit dem Experiment wie mit ausführlicheren SCF-Rechnungen.

Introduction

The advantages of a RHF (Restricted Hartree Fock) calculation of spin densities are that the wavefunction is an exact eigenfunction of both S_z and S^2, only one kind of singly excited states $[\Psi'(a,x)]$ interact with the ground state function Ψ_0, and the calculation is self consistent with respect to the values of the integrals used, i.e. is not dependent upon the "trial" orbitals used as a first guess in the cyclic minimisation procedure. The UHF (Unrestricted Hartree Fock) method suffers from the disadvantages that the wavefunction is not usually an accurate eigenfunction of S^2, although annihilation of the spin state of next highest multiplicity is a very acceptable approximate method of bypassing this difficulty [4], and that two coupled minimisations generally have to be performed.

The Hückel method for neutral, closed shell alternant hydrocarbons is valid for ground state properties because of the association

$$\alpha_r^h = W_r + \tfrac{1}{2} P_r \gamma_{rr} + \sum_{t \neq r} (P_{tt} - z_t)\, \gamma_{rt} \qquad (1)$$

$$\beta_{rt}^h = \beta_{rt} - \tfrac{1}{2} P_{rt}\, \gamma_{rt}$$

between the Hückel parameters and the P-method parameters. The notation is that of McWEENY and PEACOCK (see e.g. [*3*]). Since $P_r = \mathrm{I}$ (all r) α_r^h is constant and the use of equal α's is roughly self consistent for calculations of this kind. Differences are brought in by different off diagonal elements (β_{rt}) but the variations are probably not very great.

For open shell systems, equations (1) correspond roughly to the RHF SCF equations, and do so exactly if the molecular integrals $[am \mid mm]$ and $[a_p m \mid mm]$ vanish, where "a" is a fully occupied orbital, and "a_p" its "paired" virtual orbital. This is the equivalent to saying that the singly excited states $\Psi(a,m)$ and $\Psi(m,a_p)$ do not mix in with the ground state. For symmetry reasons, this situation occurs in the allyl radical.

Thus, for an odd alternant radical such as allyl, it is justified to the same degree of approximation as above, to write equal α_r^h (all r). However, for other radicals, and radical ions, it is not so justified, and parameters should not be transferrable from position to position, and from molecule to molecule. Since the Hückel method is an independent electron model, no effects depending directly upon electron repulsions, (e.g. negative spin densities) will ever be predicted.

It would, however, be extremely convenient if the cyclic minimisation part of the RHF SCF calculations could be missed out completely, and Hückel orbitals, which are easy to obtain, used in a CI calculation. Many authors have used this approach, but no-one has questioned whether, and to what extent, do the final spin densities, depend on the Hückel parameters (e.g. [*13*]).

Methods

To first order, only singly excited states of the types $\Psi(m,x)$ $\Psi(a,m)$, $\Psi'(a,x)$ give changes in spin density*. The relevant formulae are given as an Appendix. In this paper, we present calculations of spin densities of a number of Conjugated Organic radicals and Radical Ions, calculated using Hückel MOs as basis orbitals, and perturbing the ground state function by allowing it to interact with all singly excited states, as above.

In order to compare our results both with more elegant SCF methods and, more important, with experiment, the spin densities were converted to coupling constants using the simple relation $a = Q\varrho$, where the Q values have been given previously by the present author [*1*, *2*]. Finer details of the coupling constants could be obtained by using one of the more elaborate relationships which are available, but the above treatment should give the gross features correctly.

Parameters

For the aza aromatics, the values

$$\alpha_{\mathrm{N}}^h = \alpha_{\mathrm{C}}^h + 0.5\,\beta_{\mathrm{CC}}^h \quad \text{and} \quad \beta_{\mathrm{CN}}^h = 0.8\,\beta_{\mathrm{CC}}^h$$

as given by STREITWIESER [*7*] were used. This set differs from that given by CARRINGTON [*8*] but in a later section many different parameter sets will be used. For the nitrile Radical Ions, the set

$$\alpha_{\mathrm{N}}^h = \alpha_{\mathrm{C}}^h + 1.0\,\beta_{\mathrm{CC}}^h \quad \text{and} \quad \beta_{\mathrm{CN}}^h = 2.0\,\beta_{\mathrm{CC}}^h$$

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* $\Psi(a,x)$ gives only a first order change in charge density.

as given by RIEGER and FRAENKEL [*9*] was used. The parameters needed in the CI calculation have been discussed previously [*1*, *2*] and are well established.

Results and Discussion

a) Odd alternant radicals. Singly excited states of the types $\Psi(a,m)$, $\Psi(m,x)$ must be included but it is easily shown as a consequence of the pairing theorem that the configurations $\Psi(a,m)$ and $\Psi(m,a_p)$ make equal contributions to the spin density distribution and so, it is sufficient to take only one of the pair, and double the contribution. For allyl, the Hückel orbitals are exactly equal to the SCF (RHF) ones, and so the spin densities are equal to the RHF values. The other two results are sufficiently close to the experimental, and the RHF values, to justify the method.

Table 1. *Spin densities and coupling constants in some odd alternant hydrocarbon radicals. For the numbering see Ref.* [*1*] *and* [*2*]. *The "simplified P-method" results are given in brackets. Coupling constants are in* gauss*

Molecule	Position	$\varrho(i)$	$a(i)_{\mathrm{calc}}$	$a(i)_{\mathrm{exp}}$
allyl	1	0.5963	−15.37	−14.38
		(0.5738)	−15.49	
	2	−0.1386	+ 3.74	+ 4.06
		(−0.1476)	+ 3.99	
pentadienyl	1	0.3795	−10.25	− 8.99
		(0.3681)	− 9.94	
	2	−0.1047	+ 2.83	+ 2.65
		(−0.1085)	+ 2.93	
	3	0.4504	−12.16	−13.40
		(0.4809)	−12.98	
perinaphthenyl	1	0.2186	− 5.90	− 7.30
	2	−0.0488	+ 1.32	+ 2.20
benzyl	2	0.1760	− 4.75	− 5.10
	3	−0.0599	+ 1.62	+ 1.60
	4	0.1488	− 4.02	− 6.30
	7	0.7091	−19.15	−16.40

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* There was an error in the calculated spin density in allyl reported previously [*1*]. The present values are correct.

b) Even alternant ions. HOIJTINK [*10*] first showed that the spin densities in pyrene mononegative ion could be understood using this method. He used a limited singly excited state treatment, using a few states of the type $\Psi'(a,x)$ only. Again, for a more rigorous calculation, and since configurations $\Psi(a,m)$ and $\Psi(m,a_p)$ clearly interact with the ground state, they should be included in the calculation. Our results in Tab. 2 show that it is quite adequate to use Hückel orbitals in this way, in place of the RHF orbitals. A "simplified" *P*-method, based on the fact that only differences between successive atomic two electron Coulomb integrals are really necessary in the calculation of molecular two electron integrals

Table 2. *Even alternant anions. "Simplified P-method" results given in brackets*

Molecule	Position	$\varrho(i)$	$a(i)_{calc}$	$a(i)_{obs}$
trans butadiene	1	0.3923	-10.59	-7.62
		(0.4239)	-11.45	
	2	0.1077	-2.91	-2.79
		(0.0761)	-2.05	
naphthalene	1	0.2227	-6.01	-4.90
	2	0.0476	-1.29	-1.83
anthracene	1	0.1189	-3.21	-2.74
	2	0.0324	-0.87	-1.57
	9	0.2475	-6.68	-5.56
phenanthrene	1	0.1452	-3.93	-3.60
		(0.1469)	-3.97	
	2	-0.0330	+0.89	+0.72
		(-0.0416)	+1.12	
	3	0.1198	-3.23	-2.88
		(0.1345)	-3.63	
	4	0.0453	-1.22	-0.32
		(0.0319)	-0.86	
	9	0.1865	-5.04	-4.32
		(0.1827)	-4.93	
pyrene	1	0.1699	-4.59	-4.75
	2	-0.0425	+1.15	+1.09
	4	0.0932	-2.52	-2.06
biphenyl	2	0.1967	-2.57	-2.75
	3	-0.0106	+0.29	+0.45
	4	0.1967	-5.31	-5.50

Table 3. *Aza substituted hydrocarbon radicals and ions*

Molecule	Position	$\varrho(i)$	$a(i)_{calc}$	$a(i)_{obs}$
anilino	2	0.1484	-4.01	-3.54
	3	-0.0460	+1.24	+0.86
	4	0.1260	-3.40	-2.36
	7	0.7627	-16.02	
pyridazine	1	0.1941	-4.08	-5.90
	2	-0.0885	+2.30	+0.16
	3	0.3944	-10.25	-6.47
pyrazine	1	0.3790	-7.96	-7.21
	2	0.0605	-1.57	-2.64
phenazine	1	0.0433	-2.88	-1.93
	2	0.1108	-1.13	-1.61
	9	0.2344	-4.92	-5.14
4,4′ bipyridyl	2	0.0913	-2.37	-2.35
	3	-0.0050	+0.13	+0.43
	4	0.1852	-3.89	-3.64

(II) has been given by HEILBRONNER [12], who calculated the π-electronic spectra of a number of hydrocarbons this way. To see whether this method will give comparable spin densities, we have used the method for a few alternant Ions and Radical Ions. The results, given in parentheses in Tab. 1 and 2, differ from the Hückel values, as expected, but are still quite acceptable. In fact, there is much to be said for this method for hydrocarbons, as no information other than the Hückel Hamiltonian matrix is required in the calculation.

c) Aza hydrocarbon anion radicals. Any two of the more sophisticated methods above of calculating spin densities in hydrocarbons appear to give very similar results; this may mean that the Hückel parameters are slowly varying from molecule to molecule, or it may be that the calculation is relatively insensitive to them, the dominating factors being the SCF parameters. The aza hydrocarbons should give a good test as to which is more important. The results for a variety of radical ions are presented in Tab. 3, and are in good agreement with experiment, and compare favourably with the SCF results [1].

Table 4. *Effect of varying h and k for pyrazine mononegative ion*

		Hückel		Hückel + CI	
h	k	ϱ(N)	ϱ(C)	ϱ(N)	ϱ(C)
−0.5	0.8	0.3627	0.0687	0.3864	0.0568
0.5	0.8	0.3112	0.0944	0.3790	0.0605
0.75	0.8	0.2813	0.1093	0.3760	0.0620
1.0	0.8	0.2500	0.1250	0.3754	0.0623
0.5	0.4	0.3511	0.0745	0.3746	0.0627
0.5	1.0	0.2935	0.1032	0.3788	0.0606
0.5	1.5	0.0000	0.2500	−0.0635	0.2817

We have also calculated the spin densities in pyrazine mono negative ion using values of the Hückel parameters as follows:

1. $h = 0, 0.5, 0.75, 1.0 \qquad k = 0.8$
2. $k = 0.4, 0.8, 1.0, 1.5 \qquad h = 0.5$

i.e. we have varied the integrals α_{N}^{h} and β_{CN}^{h} over a wide range. The results are presented in Tab. 4, from where it may be seen that, provided that the odd electron occupies an orbital having the correct nodal behaviour, the results are almost independent of the choice of the Hückel parameters h and k, to a very good approximation. In the case $h = 0.5$, $k = 1.5$ the odd electron occupies an orbital having a node through the nitrogens and so, the calculation predicts a small negative density on the nitrogen. This demonstrates the dangers of a calculation of this kind.

d) Nitrile mono negative Radical Ions. Spin densities calculated for a number of nitrile ions are presented in Tab. 5. As before, the values compare well both with experiment and the RHF calculations [2]. The spin densities in cyanobenzene were found to be almost independent of the values of the Hückel parameters used, provided the symmetry properties of the odd electron MO were correct.

Table 5. *The Nitrile anions studied*

Molecule	Position	$\varrho(i)$	$a(i)_{\text{calc}}$	$a(i)_{\text{exp}}$
cyano-benzene	2	0.1077	−2.70	−3.63
	3	0.0046	−0.12	+0.30
	4	0.3129	−7.82	−8.42
	8 (N)	0.1489	−2.75	−2.15
1,2 dicyano-benzene	3	−0.0424	+1.06	+0.42
	4	0.1675	−4.21	−4.13
	8 (N)	0.1102	−2.04	−1.75
1,3 dicyano-benzene	2	−0.0543	+1.36	−1.44
	4	0.2985	−7.50	−8.29
	5	−0.0598	+1.50	+0.08
	8 (N)	0.0815	−1.51	−1.02
1,4 dicyano-benzene	2	0.0529	−1.33	−1.59
	8 (N)	0.1122	−2.07	−1.80
4,4′ dicyano-biphenyl	2	0.0692	−1.74	−1.81
	3	0.0114	−0.29	−0.29
	14 (N)	0.0614	−1.13	−1.05
4, cyano-pyridine	2	0.0908	−2.30	−2.62
	3	−0.0119	+0.30	−1.40
	4 (N)	0.3447	−6.37	−5.63
	8 (N)	0.1457	−2.69	−2.33
tetracyano-ethylene (TCNE)	3	0.1077	−1.99	−1.57
tetracyano-benzene (TCNB)	3	−0.0529	+1.33	+1.11
	7	0.0729	−1.35	−1.15

Where (N) labels the nitrogen coupling.

Conclusions

The results indicate that the calculations are almost insensitive to the values of the Hückel parameters, so long as the orbital occupied by the odd electron has the correct nodal properties. The methods used are good short cuts to fully self consistent calculations, however, in some cases, the singly excited states interact so strongly with the ground state that first order perturbation theory is hardly adequate; in extreme cases, the calculation becomes *ill conditioned* in that a small change in one of the Hückel parameters produces a fairly large change in the calculated spin densities. This is the case for the Pyrimidine anion. Again, the vast saving in computing time, generally a factor of around 5 with the I.C.T. "Mercury" is sufficient justification for the methods described, as compared to more elaborate SCF methods.

Appendix

a) The determinantal functions used may be taken from Ref. [*1*] and [*2*].

b) The matrix elements needed to evaluate the perturbation coefficients have been given by POPLE [*5*].

c) If the perturbed wavefunction is not renormalised, the spin density at position i, ϱ_i, correct to first order is:

$$\varrho_i = m_i^2 + \frac{4}{\sqrt{6}} \sum_{a,x} \lambda(a,x)\, a_i x_i - 2 \sum_a \mu(a)\, m_i a_i + 2 \sum_x \xi(x)\, x_i m_i$$

where $\lambda(a,x)$; $\mu(a)$ and $\xi(x)$ are the relevant perturbation parameters.

If the wavefunction is renormalised, second order terms have to be included.

m_i is the i^{th} coefficient of MO "m".

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