McLachlan Spin Density Calculations

Spin Density (ρ) at atom μ

$$\rho_\mu = c_{0\,\mu}^2 - \lambda \sum_\nu \pi_{\mu\nu} c_\nu^2$$

Mutual atom-atom polarizability, $\pi_{\mu\nu}$

$$\pi_{\mu\nu} = -4\beta \sum_A \sum_B \frac{c_{A\mu} c_{A\nu} c_{B\mu} c_{B\nu}}{\left| E_B - E_A \right|}$$

A = Occupied orbitals
B = Unoccupied orbitals
μ and ν are atoms
E = Wavefunction energy

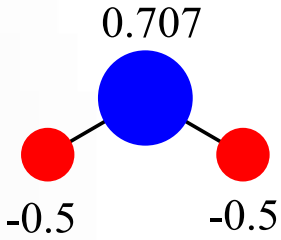
Summation does not include SOMO because effects cancel

McLachlan, A. D. *Mol. Phys.* 3.3 (1959): 233-52

McLachlan Spin Density Calculation : Allyl Radical

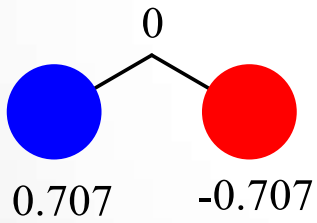
$$\pi_{\mu\nu} = -4\beta \sum_{A} \sum_{B} \frac{C_{A\mu} C_{A\nu} C_{B\mu} C_{B\nu}}{\left| E_B - E_A \right|}$$

ψ_3



E = α + 1.414β

ψ_2

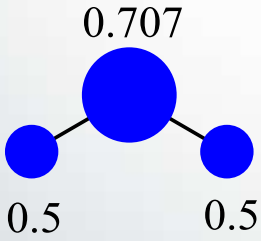


E = 0

$$\pi_{\mu\nu} = \pi_{\nu\mu}$$

π_{11} ; π_{12} ; π_{13} ; π_{22} ; π_{23} ; π_{33}

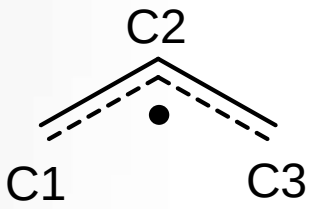
ψ_1

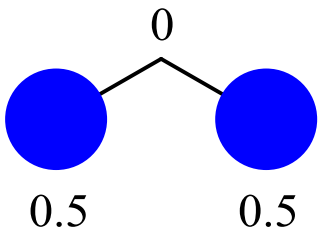


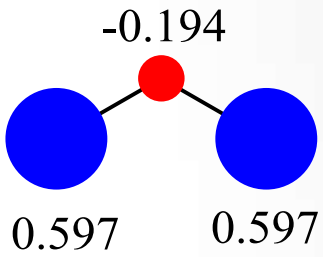
E = α - 1.414β

McLachlan, A. D. *Mol. Phys.* 3.3 (1959): 233-52

McLachlan Spin Density Calculation : Allyl Radical







$$\rho_\mu = c_{0\,\mu}^2 - \lambda \sum_\nu \pi_{\mu\nu} c_\nu^2$$

Hückel Spin Density

McLachlan Spin Density

	C1 atom1	C2 atom2	C3 atom3	energy	electrons	
phi3	-0.5	0.707	-0.5	-1.414	0	LUMO
phi2	0.707	0	-0.707	0	1	SOMO
phi1	0.5	0.707	0.5	1.414	2	HOMO

p11	-0.088
p12	0.177
p13	-0.088
p22	-0.353
p23	0.177

p21

p31

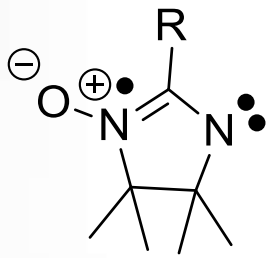
p32

SOMO Spin Density lambda = 1.1

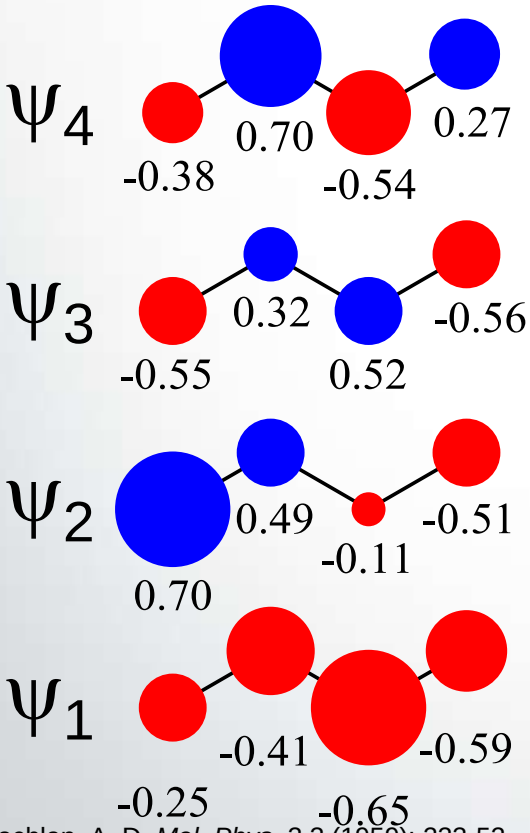
rho1	0.597
rho2	-0.194
rho3	0.597
sum	1.000

McLachlan, A. D. *Mol. Phys.* 3.3 (1959): 233-52

McLachlan Spin Density Calculation : Imino-nitroxide



$$\pi_{\mu\nu} = -4\beta \sum_A \sum_B \frac{C_{A\mu} C_{A\nu} C_{B\mu} C_{B\nu}}{|E_B - E_A|}$$



π_{11} ; π_{12} ; π_{13} ; π_{14}; π_{22} ; π_{23} ; π_{24} ; π_{33} π_{34} ; π_{44}

$\psi_1 \rightarrow \psi_4$

$\psi_2 \rightarrow \psi_4$

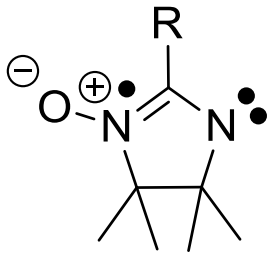
McLachlan, A. D. *Mol. Phys.* 3.3 (1959): 233-52

McLachlan Spin Density Calculation : Imino-nitroxide

	N	C	N	O			
	atom1	atom2	atom3	atom4	energy	electrons	
phi4	-0.38	0.7	-0.54	0.27	-1.355	0	LUMO
phi3	-0.55	0.32	0.52	-0.56	0.088	1	SOMO
phi2	0.7	0.49	-0.11	-0.51	1.223	2	HOMO
phi1	-0.25	-0.41	-0.65	-0.59	2.21	2	HOMO-1

p11	-0.090
p12	0.172
p13	-0.013
p14	-0.040
p22	-0.275
p23	0.081
p24	0.022
p33	-0.144
p34	0.075
p44	-0.058

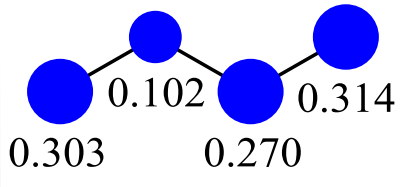
p21
p31
p41
p32
p42
p43

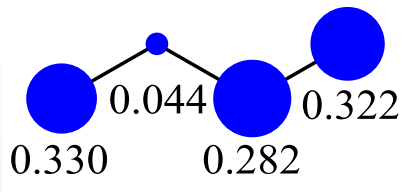


SOMO Spin Density	
rho1	0.330
rho2	0.044
rho3	0.282
rho4	0.322
sum	0.979

lambda = 1.1

$$\rho_\mu = c_{0\,\mu}^2 - \lambda \sum_\nu \pi_{\mu\nu} c_\nu^2$$



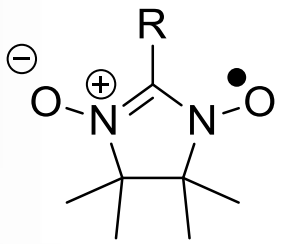


Hückel Spin Density

McLachlan Spin Density

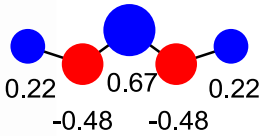
McLachlan, A. D. *Mol. Phys.* 3.3 (1959): 233-52

McLachlan Spin Density Calculation : Nitronyl-nitroxide

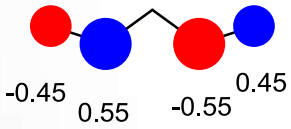


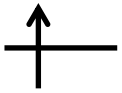
$$\pi_{\mu\nu} = -4\beta \sum_{A} \sum_{B} \frac{C_{A\mu} C_{A\nu} C_{B\mu} C_{B\nu}}{\left| E_B - E_A \right|}$$

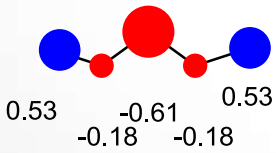
π_{11} ; π_{12} ; π_{13} ; π_{14} ; π_{15} ;
π_{22} ; π_{23} ; π_{24} ; π_{25} ; π_{33} ;
π_{34} ; π_{35} ; π_{44} ; π_{45} ; π_{55}

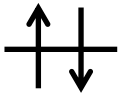
ψ_5 

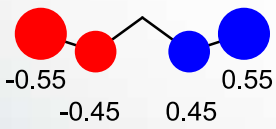
 E = α + 1.455β

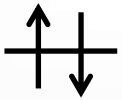
ψ_4 

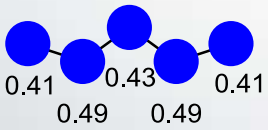
 E = α + 0.423β

ψ_3 

 E = α - 0.592β

ψ_2 

 E = α - 1.903β

ψ_1 

 E = α - 2.344β

$\psi_1 \rightarrow \psi_5$

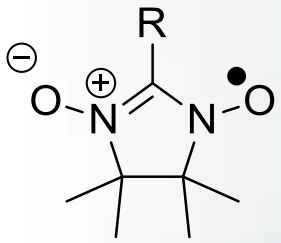
$\psi_2 \rightarrow \psi_5$

$\psi_3 \rightarrow \psi_5$

McLachlan, A. D. *Mol. Phys.* 3.3 (1959): 233-52

McLachlan Spin Density Calculation : Nitronyl-nitroxide

	O	N	C	N	O			
	atom1	atom2	atom3	atom4	atom5	energy	electrons	
phi5	0.22	-0.48	0.67	-0.48	0.22	-1.455	0	LUMO
phi4	-0.45	0.55	0	-0.55	0.45	-0.423	1	SOMO
phi3	0.53	-0.18	-0.61	-0.18	0.53	0.592	2	HOMO
phi2	-0.55	-0.45	0	0.45	0.55	1.903	2	HOMO-1
phi1	0.41	0.49	0.43	0.49	0.41	2.344	2	HOMO-2

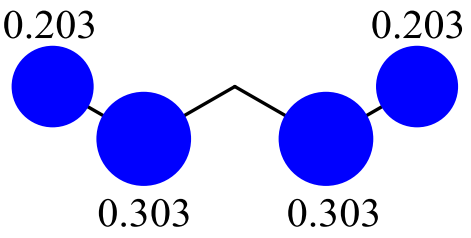


p11	-0.053		
p12	0.034	p21	
p13	0.066	p31	
p14	-0.028	p41	
p15	-0.018	p51	
p22	-0.128		
p23	0.140	p32	
p24	-0.017	p42	
p25	-0.028	p52	
p33	-0.414		
p34	0.140	p43	
p35	0.066	p53	
p44	-0.128		
p45	0.034	p54	
p55	-0.053		

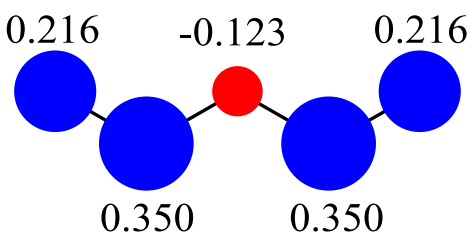
SOMO Spin Density	
rho1	0.216
rho2	0.350
rho3	-0.123
rho4	0.350
rho5	0.216
Sum	1.010

lambda = 1.1

$$\rho_\mu = c_{0\,\mu}^2 - \lambda \sum_\nu \pi_{\mu\nu} c_\nu^2$$

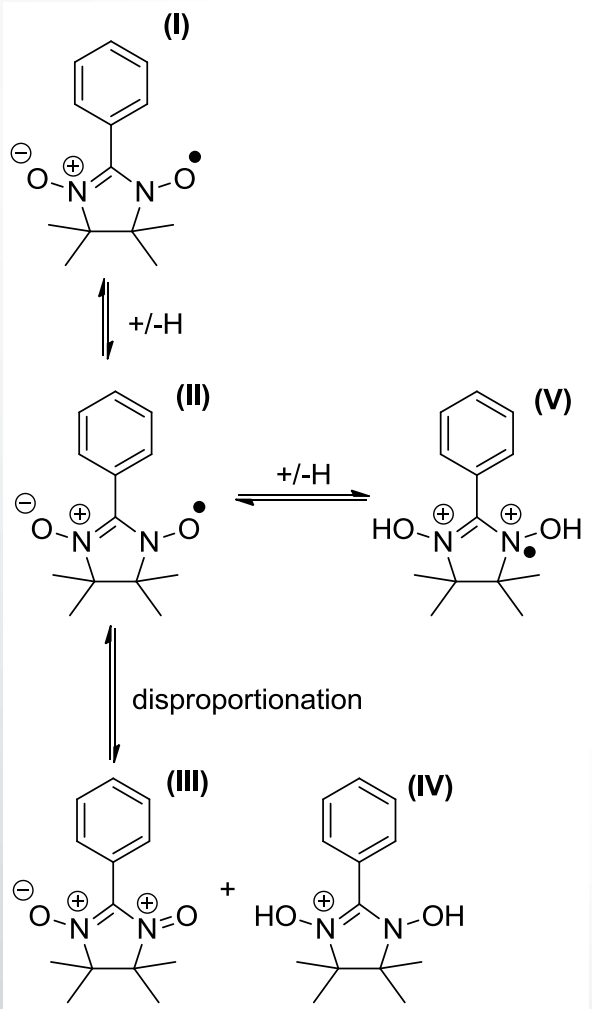


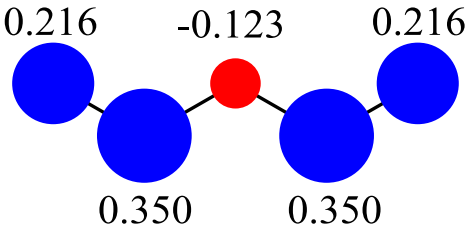
Hückel Spin Density



McLachlan Spin Density

Spin Density Calculations Compared - McLachlan vs. DFT



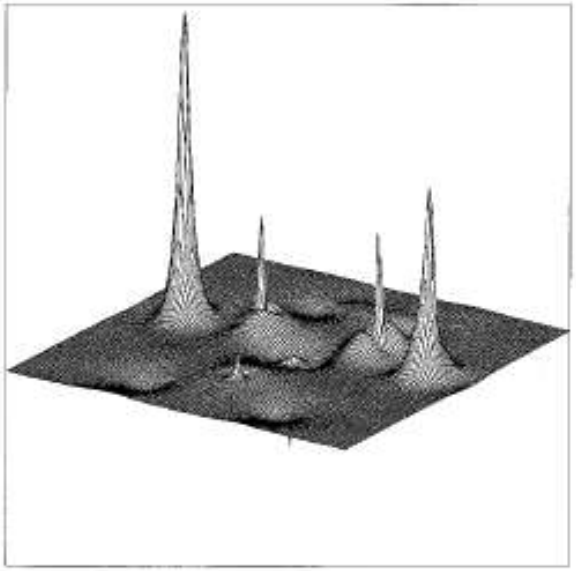


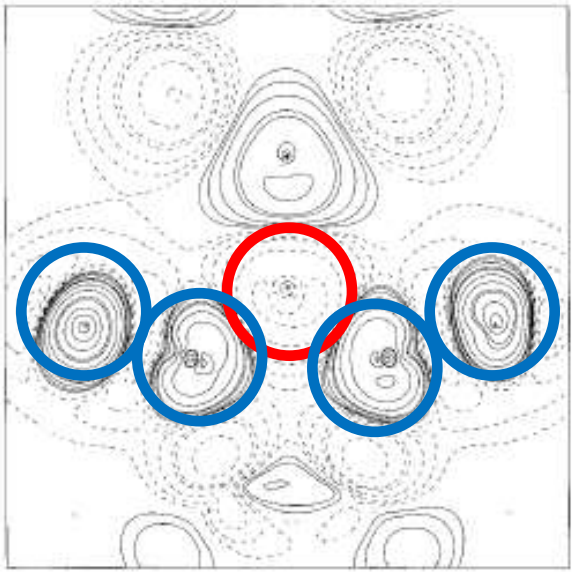
Spin Density of Nitronyl-nitroxide		
Atom	Ph-NN (I)	McLachlan
O	0.3201	0.216
N	0.2948	0.35
C	-0.2053	-0.123
N	0.2949	0.35
O	0.3200	0.216

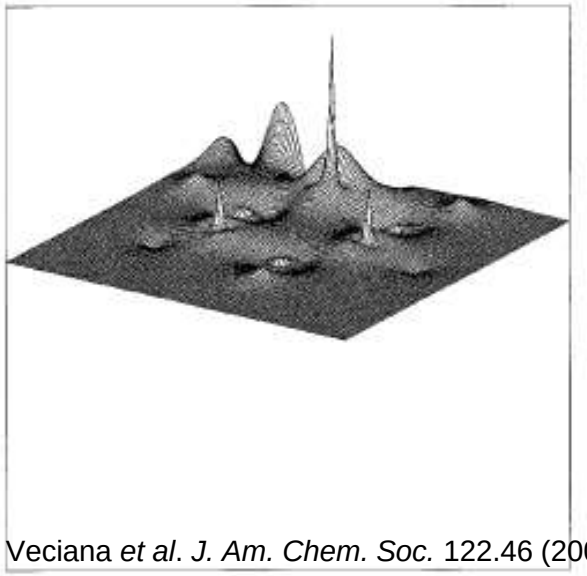
Mulliken spin densities calculated for Ph-NN (I) using the UB3LYP/TZVPP/COSMO method in methanol

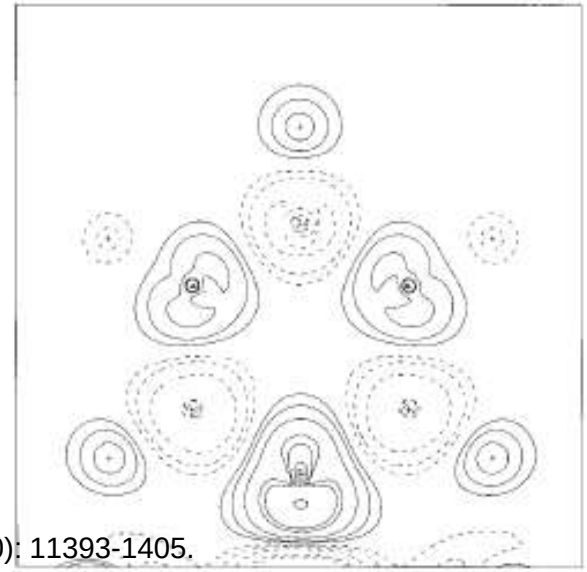
Eva Rentschler *et al*. *Phys. Chem. Chem. Phys.* 14 (2012): 1649-653.

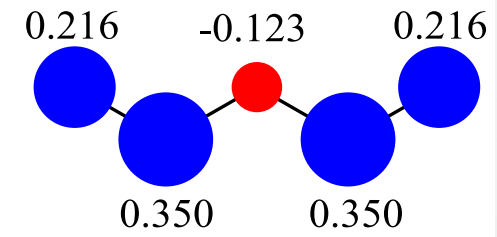
Spin Density Calculations Compared - McLachlan vs. DFT

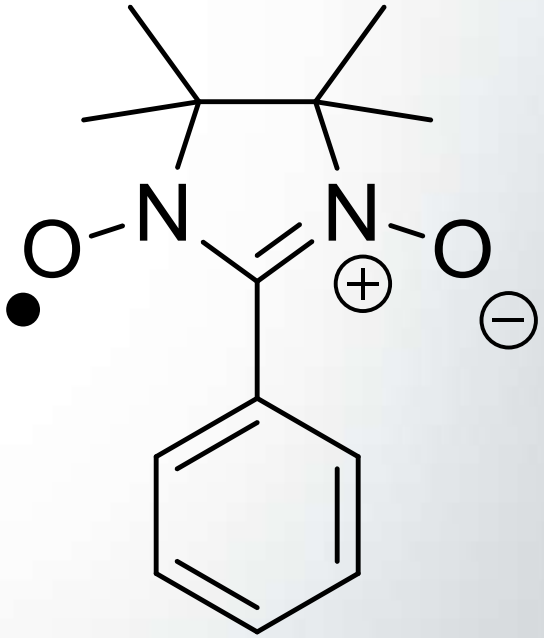












DFT
B3LYP/cc-pVDZ

Jaume Veciana *et al. J. Am. Chem. Soc.* 122.46 (2000): 11393-1405.