Computingspin-dependentproperties

Ifthe molecule underconsiderationisnotina spinsingletelectronic state**(s≠0),**itcarriesa net non-zero electronic spin angular momentum.If some of the nuclei **in the molecule** carries non zero nuclear spin, the electronic spin **can** couple **with the non-zero nuclear spin**. The energetic of this coupling depends on whether **electronic** spin, projected along the z-axis is aligned **with the** nuclear spin projected on the same axis or is in opposition. The difference in the energies corresponding to the two possibilities is probed in electron spin resonance spectroscopy. The measurement leads the extraction of isotopic hyperfine splitting or equivalently as hyperfine coupling constant (a_X) of the nucleus x. The theoretical calculation of a_x is fairly straight forward and leads to the expression.

$$a_X = \frac{4}{3}\pi < s_z >^{-1} g\beta g_x \beta_x \rho(x) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{(23.1)}$$

Where g ,β are the electronic ‘g’ factor and the Bohr magnetron respectively. g_X, β_X are the corresponding quantities for the nuclei designated as x.$<s_Z>$ is the average value of the z-component of the electronic spin angular momentum and ρ(x) is the Fermi contact integral. If the wavefunction Ψ is represented as a single Slater determinant, the ρ(x) can be written as,

$$\rho(x) = \sum_{\mu\nu} P_{\mu\nu}^{spin}\{\chi_\mu(r_x)\chi_\nu(r_x)\} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \mathbf{(23.2)}$$

In equation (2)$\{\chi_\mu(r_X)\chi_\nu(r_X)\}$ is theoverlap ofthebasisfunctions, $\chi_\mu$and $\chi_\nu$at thenucleus x. $P_{\mu\nu}^{spin}$ is theμνthelement ofthespin densitymatrixconstructed in theAO basis.

If the MOs carrying electrons of $+\frac{1}{2}$ spin (α-spin) and $-\frac{1}{2}$ spin (β-spin) are expressed separately as linear combination of the atomic orbital basis set we have,

$$(\phi_1^\alpha, \varphi_2^\alpha, \ldots\ldots\ldots\ldots \varphi_{N_\alpha}^\alpha) \equiv \phi(\alpha) = (\chi_1, \chi_2, \ldots\ldots\ldots\ldots\ldots\ldots \chi_N)C_\alpha \qquad (23.3)$$

$$(\phi_1^\beta, \varphi_2^\beta, \ldots\ldots\ldots\ldots \varphi_{N_\beta}^\beta) \equiv \phi(\beta) = (\chi_1, \chi_2, \ldots\ldots\ldots\ldots\ldots\ldots \chi_N)C_\beta \qquad (23.4)$$

Where C_α is the N×N$_\alpha$ dimensional co-efficient matrix of expansion co-efficient of the α-spin molecular orbitals, while C_β is N×N$_\beta$ dimensional co-efficient matrix of the β-spin molecular orbitals ($C_\alpha^\dagger S\, C_\alpha = 1$, $C_\beta^\dagger S\, C_\beta = 1$, S being the N×N overlap electrons in the AO basis given by,

$$P^\alpha = C_\alpha\, C_\alpha^\dagger \qquad (23.5)$$

$$P^{\beta}= C_{\beta}\, C_{\beta}^{\dagger} \quad (23.6)$$

The spin-density matrix $P^{spin}$is the difference between $P^{\alpha}$and P^{β}

$$P^{spin} = (P^{\alpha} - P^{\beta}) \quad (23.7)$$

If S=0, and each spatial orbital is occupied by two electrons of opposite spin, $P^{\alpha} = P^{\beta}$ and P^{spin}=0 leading to a_x= 0. If, $S \neq 0$ $(=\frac{1}{2}, \frac{3}{2}$, etc.), $P^{\alpha} \neq P^{\beta}$, $P^{spin} \neq 0$, $a_x \neq 0$.

IntherestrictedHartree-Fockdescriptionthespatialorbitalsusedtodescribeelectronsofαand β-spinareidentical.So,thecontributiontoP^{spin}comesonly fromtheorbitalsoccupiedsingly.It maysohappenthatthesingly occupiedMOhasanodalplanepassingthroughtheatom‘x’.In thatcasethea$_x$ value wouldbepredictedtothezerointheRHFdescription.Thiswouldbe wrongasapartfromthedelocalizationcontribution,spindensity isalsocreated byspin-polarization which is not accounted forin RHFtheories.

TheUHF methodassignsdifferentspatialorbitalstoαandβ-spinelectrons.HenceP^{spin}naturally containscontributionfromspinpolarizationaswellasdelocalizationeffects.The probleminUHF isthatΨ_{UHF}isnotaneigenfunctionof the S^2operator sothatthe doubletwill havecontaminationsfromspin quartetand stateswith stillhigher spin multiplicities. (Tripletwill have contaminations from quintet,etc.)

Onemustthereforeprojectouthigherspincomponentsandtheprojected UHF spin density matrix should beusedinthecomputationofP^{spin}. Projection after variational optimizationis usuallydone, though it is bettertoperform it beforeoptimization.

Note:

1. TheexpressionfortheFermicontactintegralshowsthat $P_{\mu\nu}^{spin}$ ismultipliedwiththe overlapofthebasisfunctionsχ_{μ}(x), andχ_2(x)atthenuclearpositionx.Themaximum amplitudeofthebasisfunctionatnuclearposition(x)comesfromthe s-typeatomic orbitalsinthebasis.Unfortunatelythecoreorbitalsarenotusuallyendowedwiththe samedegreeofflexibility asthevalenceorbitalsinthebasisandthiscouldaffectthe computed couplingconstant (a_x).

2. ThenuclearcuspbehaviorisbetterrepresentedwhenSlatertypeofatomicorbitalsareused. TheGTOsarerelativelyunsatisfactoryin this respect.

3. The derivation of equation (1) follows easily from the application of Hellmann-Feynmann theorem (HFT) to the molecular electronic Hamiltonian containing an addiction perturbation arising from the interaction between the electronic spin and nuclear spin magnetic moments.

4. At the post Hartree Fock level, both MP2 and DFT calculation are recommended for the calculation of a_X values.