Spin Coupling Effects in Excited States

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The Spin Coupling concepts offer tools (e.g. the Valence Bond and its modern CASVB versions in quantum computation or the phenomenological Heisenberg Hamiltonian, routinely employed in magnetochemistry) and explanatory clues to the problems from a large area of theoretical and applied chemistry. Heuristically, the chemical bond itself is a matter of effective spin coupling. Special varieties of chemical bonding, like the resonance and aromaticity also naturally belong to the Spin Coupling paradigm. Phenomena of direct interest for the material science (localization vs. delocalization bistabilities, conducting polymers, organic magnets) are also properly addressable in terms of VB-like phenomenology and as subject of theoretical investigation are, in fact, much akin to the academic topics like aromaticity vs. antiraomaticity, being driven by general spin coupling effects.

We selected as case study the bonding in the electronic excited states of the C_nH_n series of conjugated cyclic polyenes and the related polyhedrane valence isomers of the C_nH_n (n=4,8,6) hydrocarbons. The antiaromatic molecules with 4k electron count are turning aromatic-like in the triplet excited states, by reaching a set of 4(k-1)+2 electrons in doubly occupied π orbitals, aside to the triplet electron pair. The DFT optimized geometries show regular planar polygons with D_{4h} and D_{8h} symmetry for the n=4,8 members. For polyhedranes, the excitation is in principle related with possibilities of disconnecting a C-C bond, but the nature of the excited state geometry distortion is dictated by the symmetry factors of the frontier orbitals. Thus, the triplet state optimized starting from tetrahedrane is a regular square-planar, the same as starting from the rectangular cyclo-butadiene. The triplet state of the cubane is an elongated square prism, while hexa-prismane ends in a nonplanar Dewar-like skeleton.

**Table 1.** TD-DFT excited states of cyclobutadiene

	Triplet E_T(eV)		Singlet E_S(eV)		ΔE_{ST} (eV)
B_{3g}	1	0.544	1	2.620	2.077
B_{2u}	2	4.107	8	6.249	2.142
B_{3u}	3	4.849	3	5.039	0.190
B_{2g}	4	4.915	2	4.950	0.035
B_{3u}	5	4.995	5	5.503	0.508
A_u	6	5.219	4	5.269	0.050
B_{1g}	7	5.777	6	5.864	0.087
B_{1u}	8	5.990	7	6.092	0.102
B_{2g}	9	6.169	9	6.380	0.212
B_{2u}	10	6.243	12	7.228	0.985
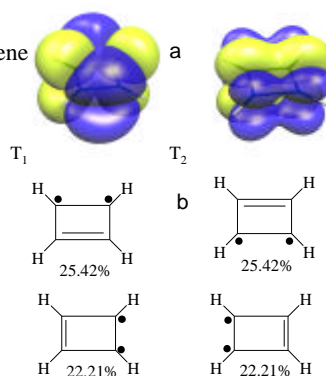
Fig 1. C_4H_4: a) TD-DFT density flow of first two triplets; b) NRT weights of the first triplet (excited state aromaticity)

The Spin Coupling and aromatic resonance are properly described in the CASSCF and related frames. For the sake of methodological purposes we aimed to check the applicability of DFT and TD-DFT in this topic. In principle, there are limitations, if consider the single determinant nature of DFT, and single-excitation definition of the TD-DFT excited states. However, for processes

accompanied by a density flow, like the redistribution of the bonding densities, charge transfer excitations in chromophores, the TD-DFT is appropriate. Moreover, the TD-DFT transitions can be completely characterized with the help of difference density map (excited vs. groundstate). For cyclobutadiene (see Fig.1) the first excitations (singlet and triplet) look like a π density flow from

C=C bonds toward the former C-C of the rectangular C_4H_4 frame. The Natural Resonance Theory (NRT [1]) offers an analysis of excited state resonance structures, the triplet state aromaticity consisting in the manifestation of almost equal weights of the four components from in Fig.1b. The aromatic benzene turns antiaromatic in excited state, showing tendencies of D_{2h} distortion in the geometry and spin distribution (see Fig.2).
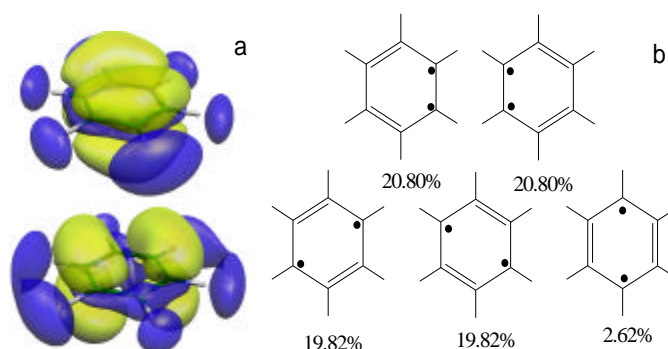
Fig 2. C_6H_6: a) TD-DFT density flow in triplet states; b) Corresponding NRT weights

A problem of different nature, treated also in terms of TD-DFT is the modeling of charge transfer induced spin transition in Prussian-Blue type Fe-Co systems,[2] considered here in the minimal molecular unit $[(LiNC)_5Fe-CN-Co(NCLi)_5]^{4+}$ (the Li atoms were added as charge surrogate for neighbor lattice). The closed shell nature of the low spin state (LS), with d^6 configurations on Fe and Co makes appropriate the TD-DFT study of singlet and triplet states.
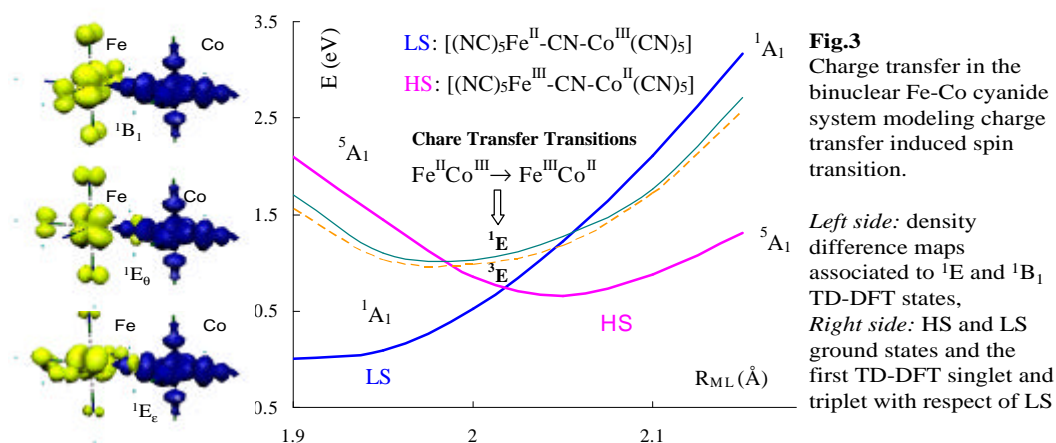
Fig.3
Charge transfer in the binuclear Fe-Co cyanide system modeling charge transfer induced spin transition.

Left side: density difference maps associated to ^1E and $^1B_1$ TD-DFT states,
Right side: HS and LS ground states and the first TD-DFT singlet and triplet with respect of LS

The switch of the system between LS ($^1A_1$) and HS ($^5A_1$) states is spin forbidden. The interaction of S=0 and S=2 ground states via spin coupling in excited state (singlet and triplet of charge transfer excitation in $Fe^{II}Co^{III}$ with the corresponding states resulted by exchange coupling in $Fe^{III}Co^{II}$) points a new perspective on the intimate mechanism of the spin transition. The density difference map confirms the charge transfer nature of the first excitations. The light color shows density depletion and dark color density accumulation areas. The first excited states correspond to a Fe to Co electron jump.

[1] Glendening ED, Weinhold F, *J. Comput. Chem.* 1998, **19**, 593.

[2] N. Shimamoto, Shin-ichi Ohkoshi, O. Sato and K. Hashimoto, *Inorg. Chem.* 2002, **41**, 678-684.