In search of organic compounds presenting a double exchange phenomenon

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Introduction

"... we (can) visualize the electron transfer of an electron from one Na⁺ ion (Sodium Chloride) to the adjacent Na⁺ ion as the transfer of an electron from the left Na atom to the central Cl⁻ ion simultaneously with the transfer of an electron from the central Cl⁻ ion to the right Na⁺ ion. Such a transfer we shall call a double exchange"

- Clarence Melvin Zener(1951)

► The Aim of this work is to design a consistent series of organic molecules which may present a double exchange(DE) mechanism and study their low energy spectra.

Extraction of Phenomenological Model Hamiltonian

- ➤ On the right one can see a schematic of the systems studied. The bold lines represent the Tri Methyle Methane (TMM) subunits which have a maximum spin(**S**) of one, i.e. di-radical like. The systems studied consist of two TMM's bridged by organic subunits of varying lengths and shapes.
- ▶ DFT calculations on prospective series of DE molecules
- ▶ Geometry optimization for each system was carried for the following states with the 6-311G**/B3LYP protocol:
 - $M_s = 0$ and $M_s = 1$ for the neutral system.
 - $M_s = \frac{1}{2}$ and $M_s = \frac{3}{2}$ for the cationic system.
- DFT wavefunctions are not eigen-solutions of the Spin density operator (\hat{S}^2) . One must therefore work with the magnetic quantum number M_s .
- \triangleright Broken Symmetry(BS) calculations have been carried out to obtain the energies of the seven ($E_1 E_7$) configurations for each system at appropriate geometries and symmetry.
- Extraction of DE parameters and recalculation of the low energy spectrum
- ▶ The various parameters(six in number) listed in the adjacent figure can be computed using the seven determinants and their energies.
- ▶ The DE parameters are used to construct the model space consisting of the correct Doublet and Quartet states. Thus, the low energy spectrum is obtained and presented in the graph on the right.
- \triangleright Finally, a simplified phenomenological Hamiltonian is extracted, this gives the us \mathbf{K}_{DE} and \mathbf{J} values. These values can be used to model bigger systems made of similar subunits.

Results and Discussion

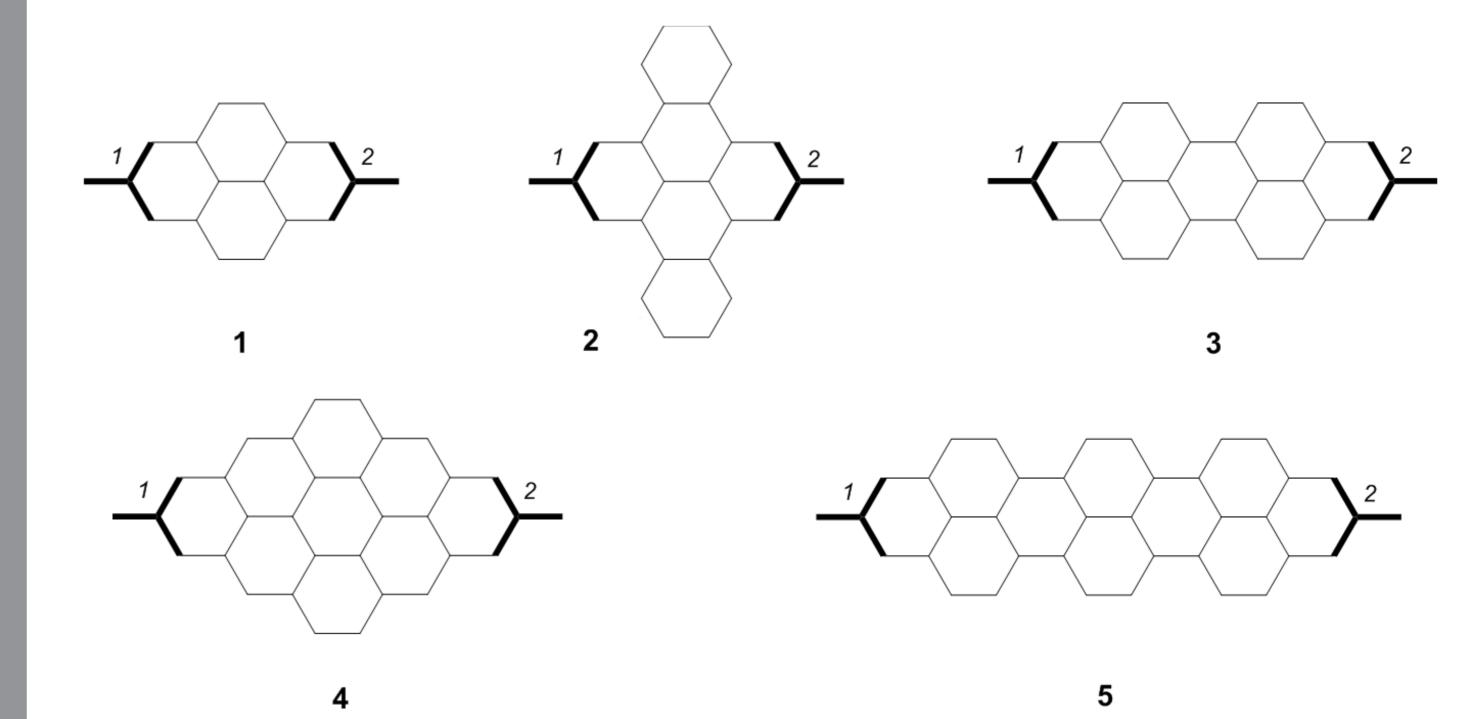
- ► The spin density values for the various electronic states(neutral/cationic) given in the table gives important information on the extent of their open shell character. It shows that the TMM units, which have a triplet state ground state in isolation, are not in their S=1 state.
- ➤ One can see that the DE mechanism is influenced by the geometry of the bridging subunits, namely their length (number of benzene units) and their width. This dependence can be simply explained by the following two points:
 - ▶ The large gap between the HOMO and LUMO orbitals of the bridging units.
 - ▶ Small coefficients on the atoms to which the magnetic TMM units are connected.
- ► In accordance with the second factor, longer bridges lead to more open shell character. On the other hand, the relation between the HOMO-LUMO gap and the geometry of the bridge subunits is not evident.
- ▶ The hopping integral \mathbf{t}_2 (i.e. family 2) is related to the length of the bridge whereas \mathbf{t}_1 also depends on the geometry of the bridging units.

Conclusions

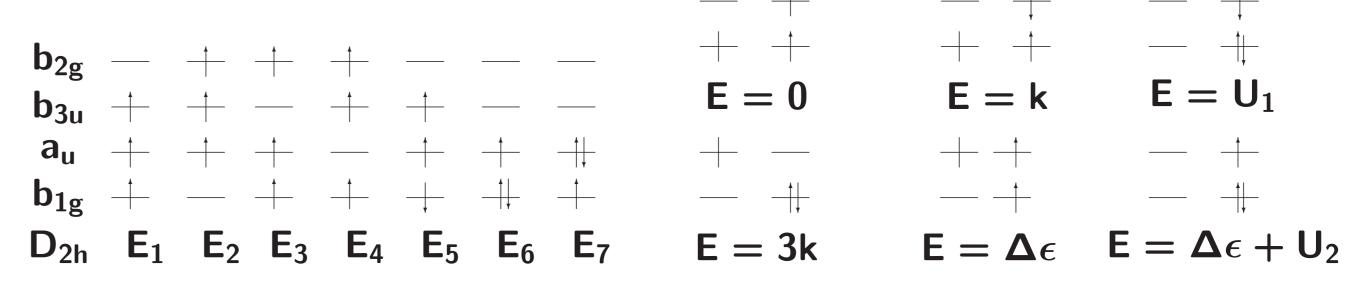
- ► Magnetic orbitals in the organic molecules being delocalised makes their low energy spectrum sensitive to several factors such as geometry of bridge and strength of their covalent interactions. As a result their low energy spectrum may not be well reproduced by simple models.
- ► The TMM units cannot be considered as S=1 units because of the influence of the bridging subunits.
- ► The lowest local excited state of the TMM being a Non Hund state, participates strongly in the physics of the low energy spectrum.

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Figures



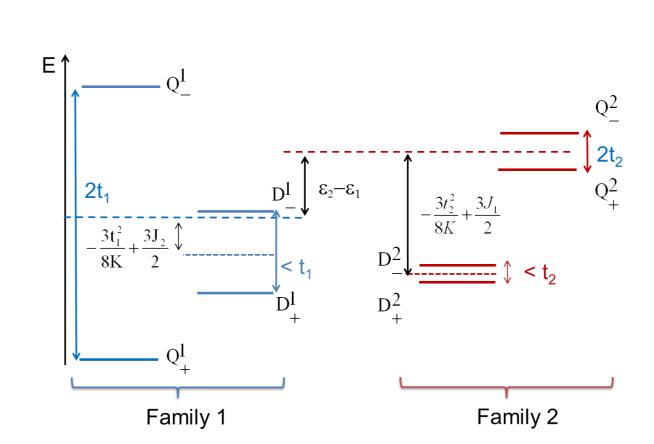
Schematic of various systems studied (all molecules have D_{2h} symmetry)



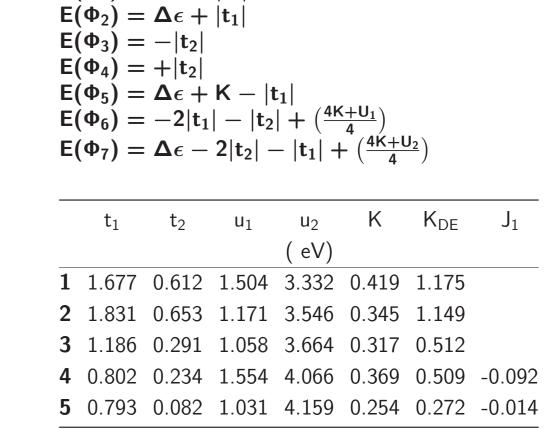
MO configurations used for UDFT calculations

Energy of determinants with the Hubbardization parameters

 $\mathsf{E}(\mathsf{\Phi}_1) = \mathsf{\Delta}\epsilon - |\mathsf{t}_1|$



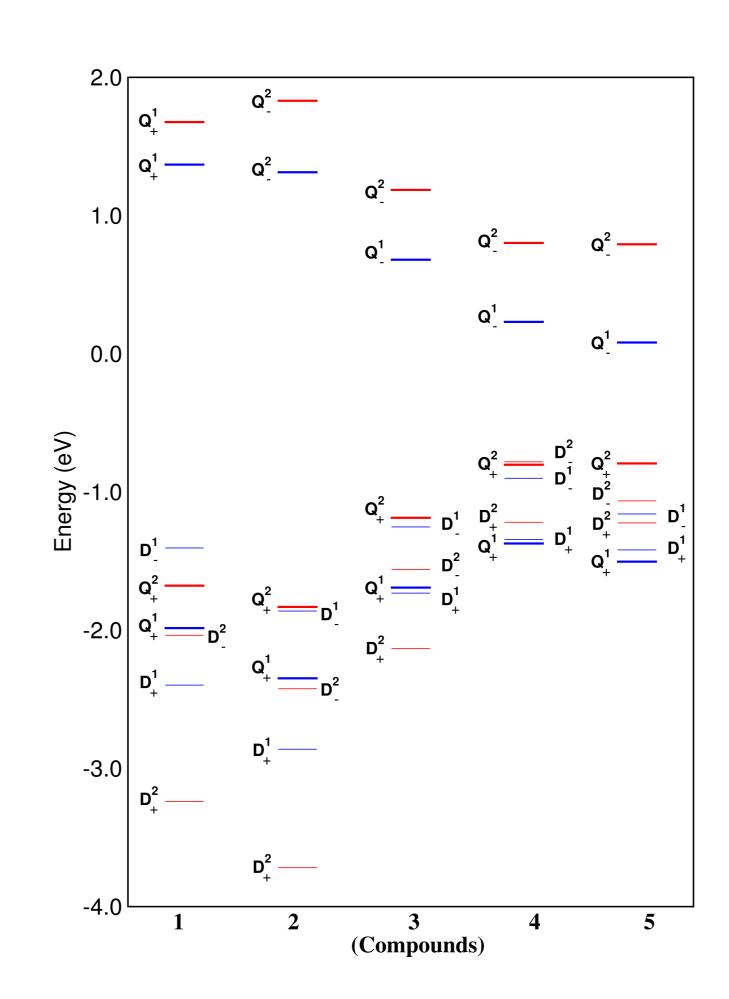
Schematic representation of DE spectrum



Parameters extracted from UDFT calculations

Results

- ▶ The plot below shows the reconstructed low energy specta of the cationic compounds $\mathbf{1}-\mathbf{5}$, followed by the energies tables. The bold lines show quartet states and the thin lines show doublet states.
- ➤ The colors represent the two families, blue represents the electron/hole in the interior TMM orbitals(family 1) and red for the electron/hole in the exterior TMM orbitals(family 2.) at the edges,



				(a.u.)	
	triplet (vert.)	2.03	-69	3.253712	
	triplet	2.03	-69	3.256048	
	BS Ms=0 ("vert.")	0.92	-69	3.265296	
1	BS Ms=0	0.8	-69	-693.266979	
	ΔE_{ST} (vertical)		0.616		
	ΔE_{ST} (adiab.)		0.532		
	triplet (vert.)	2.07	-14	-1460.451337	
	triplet	2.07	-14	60.451356	
5	BS Ms=0 ("vert.")	1.13	-14	-1460.449958	
	BS Ms=0	1.14	-14	-1460.452359	
	ΔE_{ST} (vertical)		0.062		
	ΔE_{ST} (adiab.)		0.061		
_				Г	
		<	$\langle S^2 \rangle$	Energy	
_				(a.u.)	
	quartet (vert.)		3.81	0.044	
1			2.01		
	quartet		3.81	0.034	
	BS Ms=1/2 ("vert	")	0.82	0.034 0.010	
		")			
	BS Ms=1/2 ("vert BS Ms=1/2 BS Ms=1/2 ("vert	")	0.82	0.010	
	BS Ms= $1/2$ ("vert BS Ms= $1/2$ BS Ms= $1/2$ ("vert 3 open-shells (ϕ_5	:.") ;)	0.82 0.81 1.78	0.010 0.000 0.009	
5	BS Ms= $1/2$ ("vert BS Ms= $1/2$ BS Ms= $1/2$ ("vert 3 open-shells (ϕ_5 BS Ms= $1/2$ ("vert	:.") ;)	0.82 0.81	0.010 0.000	

Cationic molecules

References and Further Information

- ► Boilleau Corentin, Suaud Nicolas, Bastardis Roland; *et al.* Theor. Chem. Acc. 126, 231 (2010)
- Pierre Labèguerie, Boilleau Corentin, Bastardis Roland; *et al.* J. Chem. Phys. 129, 154110 (2008)
- Anderson P.W., Hasegawa H, Phys. Rev. 100, 675 (1955)
- ► Grisch, M. J. *et al.* Gaussian 03, revision B.05; Gaussian, Inc.: Wallingford, CT, 2004. The geometry optimizations are carried on up to the energy gradients of 10⁻⁴ to 10⁻⁶ according to the cases.

3.87 0.000