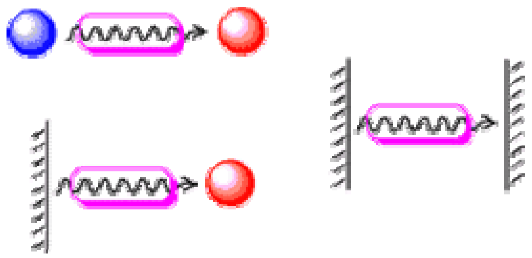
Long range Intramolecular communication (Electrons, spins and energy)

How different parts of a molecule or nanometer-sized object feel each other....



Most experiments studied in our group and involving quantum exchange use one of the three following topologies : (i) redox site - bridge - redox site ; (ii) microelectrode - bridge - redox site ; (iii) nanoelectrode - bridge - nanoelectrode, and they involve electron motions. An ubiquitous process is then the so-called "tunnel effect" : since the energy of the electrons is lower on the outer parts (redox site or electrodes) than in the inner part, they should not be able to travel across the system according to our conventional classical view. The tunnel effect is a fundamentally quantum effect in which particles with unsufficient energy behave as if they cold bore a tunnel under the high energy obstacle.

The "redox site - bridge - redox site" topology is realized in the so-called mixed-valence complexes, in which two metal atoms in different oxidation states are linked by a bridging ligand. Note that mixed-valence effect occurs also when the redox sites are organic parts rather than metal atoms : in both systems, *electron transfer* can occur. It can be studied over large distances (up to 20 Angstroms), with a particular interest on the rate of decay of the electronic interaction with distance. In addition, the insertion of an active part on the electron transfer path allows the demonstration of intervalence molecular switching .

A process related to electron transfer is exchange interaction : if the two terminal sites are in the same oxidation state, but bear magnetic moments, then a magnetic coupling can occur. The magnetic moments can indeed be

Also, through a collaboration with colleagues from Morocco (T. Ben Hadda, M. Daoudi...), we investigate the potentialities of new ligands of the "tripod" type .

In the "microelectrode - bridge - redox site" topology , one can study electron transfer by electrochemical methods (impedance spectroscopy). Preliminary results show that the electron transfer rate is very large for conjugated spacers, and could certainly be studied for very long distances (more than 40 Angstroms).

The "nanoelectrode - bridge - nanoelectrode" topology is the most closely related to the concept of Hybrid Molecular Electronics. There is an *electron transport* from one electrode to parallel (ferromagnetic coupling) or antiparallel (antiferromagnetic coupling). The theory of magnetic coupling shows analogies with the theory of electron transfer.

The above studies have been the opportunity to develop original chemistries. Thus we have succeeded in functionalizing the phenylpyridine ligand of the [Ru(bpy)(pp)]+ complex, and had access to a variety of binuclear complexes with cyclometallated end groups and various bridging parts.

the other through the organic molecule thanks to the tunnel effect, and one can measure a current. The major questions are: is it possible to build efficient molecules with a minimum rate of decay of the current with distance ? when does the quantum-to-classical transition (decoherence) occurs ?

Detailed pages corresponding to this topic :

Long Distance Intervalence Electron Transfer
Intervalence Molecular Switching
Long Distance Magnetic Coupling

Tunnel Transport