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Electron excitation and transfer in photoelectrochemical solar cells

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In connection with a project aimed at developing industrial production schemes for photoelectrochemical (PEC) solar cells [1], I am trying to improve the understanding of the basic processes involved, by studying the transfer of electrons following absorption in the sensitiser dye, from the central to the peripheral parts of the sensitiser molecule, further on to the surface of the semiconductor electrode, from where it works its way into the regular periodic lattice structure. The electrolyte is believed to contribute to shaping the potential in which the transfer process takes place, both in a bulk way (modelled by treating the electrolyte as a continuous and homogeneous dielectric substance) and through individual ions present in the electrolyte, notably near the semiconductor surface. The electrolyte also mediates the redox process by which the electron transferred to the semiconductor is replaced in the sensitiser dye. This is a slow process likely to limit the overall rate of current formation.

The first step in the quantum mechanical description of the electron transfer is to calculate the excitation of the sensitiser dye caused by the absorption of light. Only this step will be described in the present communication. The example used is an organic coumarin derivative recently synthesised [2]. It has the best absorption properties of any organic sensitiser studied, but falls short of the highest efficiency ruthenium complex dye in use with PEC cells [3].

Figure 1 shows the results of a time-dependent Hartree-Fock calculation of the lower states of the coumarin-derivative [4]. The molecular structure used in the pilot calculation is a basic structure geometrically optimised. However, a Berny optimisation subsequently performed showed modest change in the molecular structure [4]. The Figure shows the difference between the electron densities in the first excited and the ground states. For comparison, the HOMO, LUMO and 2nd lowest excited state molecular orbitals are shown in the right-hand side of the Figure. The orbital gap is a little above 6 eV, while the lowest TDHF excited state is at 1.8 eV, indicating a strongly correlated structure. The Figure shows that the electron density is thinned in the central part of the molecule under excitation, and is regained at the peripheral part, notably around the oxygen atoms of the "arm" added to coumarin-343. This makes the excited electron very easy to transfer to the semiconductor surface. The next excited state is as high as 3.5 eV.

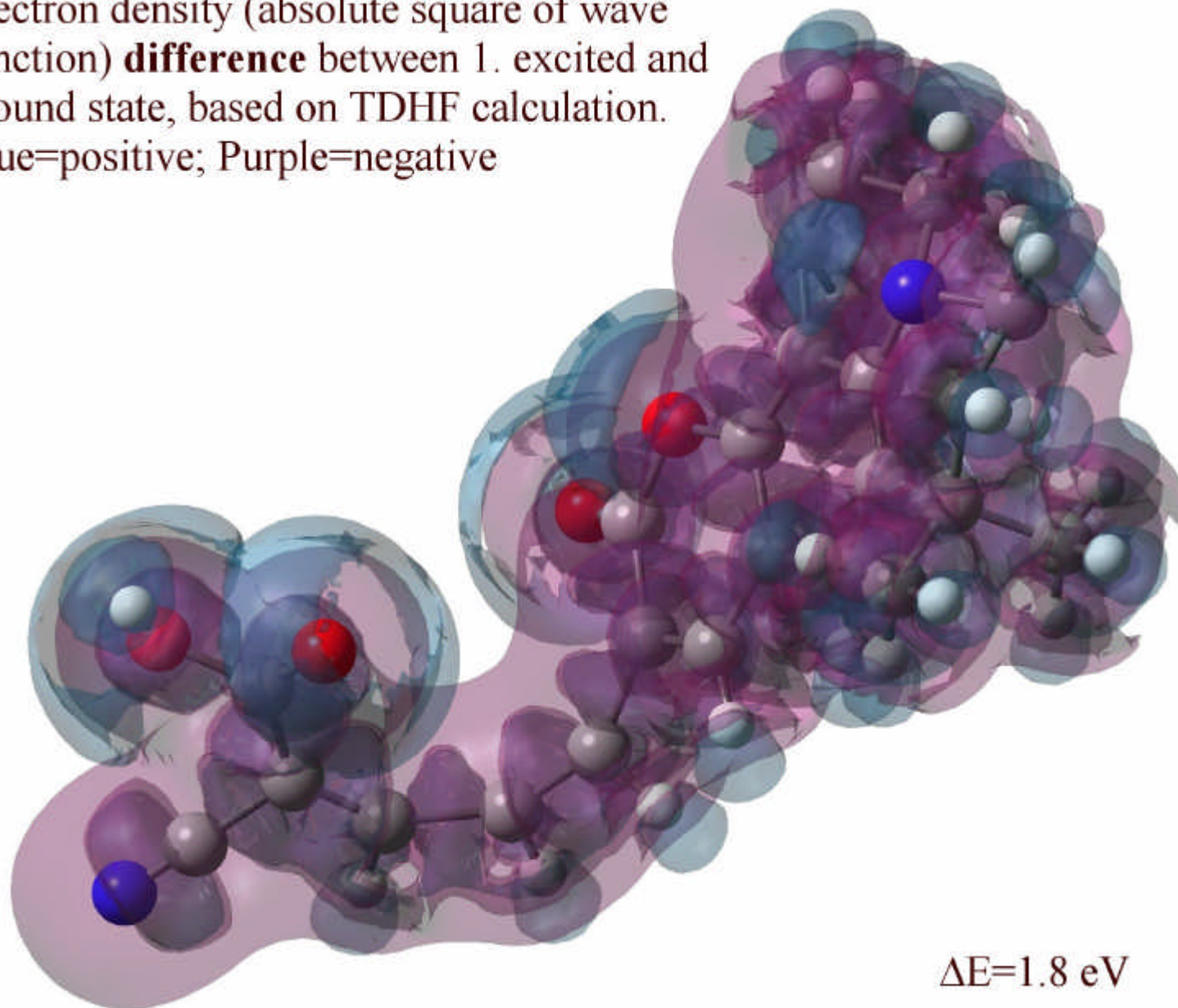
[1] B. Sørensen et al., Production oriented development of photoelectrochemical solar cells, contribution to this conference (2001).

[2] K. Hara et al., A coumarin-derivative dye sensitized nanocrystalline TiO₂ solar cell having a high solar-energy conversion efficiency up to 5.6%. *Chem. Comm.* 569-570, 2001.

[3] S. Zakeeruddin et al., *Inorg. Chemistry*, 36, 5937-5946 (1997).

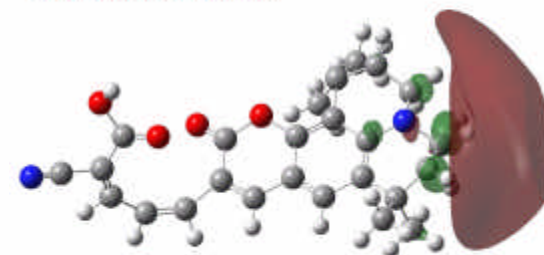
[4] M. Frisch et al., Gaussian-98 vA.9 software, Gaussian Inc. Pittsburgh 2000.

coumarin343-derivative (basic structure used)
 Electron density (absolute square of wave function) **difference** between 1. excited and ground state, based on TDHF calculation.
 Blue=positive; Purple=negative

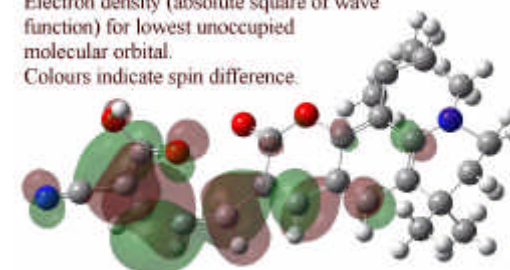


$$\Delta E = 1.8 \text{ eV}$$

coumarin343-derivative (basic structure used)
 Electron density (absolute square of wave function) for second lowest unoccupied molecular orbital.
 Colours indicate spin difference.



coumarin343-derivative (basic structure used)
 Electron density (absolute square of wave function) for lowest unoccupied molecular orbital.
 Colours indicate spin difference.



coumarin343-derivative (basic structure used)
 Electron density (absolute square of wave function) for highest occupied molecular orbital.
 Colours indicate spin difference.

