THE V STATE OF ETHYLENE: VALENCE BOND THEORY TAKES UP THE CHALLENGE

The computation of the excitation from the ground state into the first singlet $\pi\pi^*$ state of ethylene - or the N→V transition as it is known - has been a challenge for decades.[1-4] Conventional molecular-orbital (MO) theories tend to overshoot the transition energy by far too much. A CASSCF (complete active space self-consistent field) computation in a 2-electrons/2-orbitals space with a modest basis set as the 6-31G*, for instance, predicts this transition to be 2.5 eV larger than the experimental value, 7.88 eV.

Far from being a simple curiosity restricted to ethylene, the difficulty for describing this type of state is overspread everywhere in organic photochemistry. The prediction of the Soret band in porphyrin, for example, will suffer from the same deficiencies, for the same reasons.

Two main factors contribute to the problem:

- Lack of proper electron dynamic correlation: usually, dynamic correlation is computed after the CASSCF step via perturbative or configuration interaction (CI) methods. In the case of the N→V transition, the convergence is anomalously slow.

Some hardcore calculations have employed 80 million configurations in the CI expansion to obtain acceptable energies.[2]

- Basis set effects: due to the ionic character of the V state, diffuse functions are essential to describe the molecular orbitals. However, the inclusion of diffuse functions also induces an artificial mixing of the V state with Rydberg states, which brings the the excitation energy closer to the experimental value by wrong reasons.

For decades, theoreticians have investigated the V state of ethylene with the most diverse methods. In 2009, Angeli showed that the dynamic response of the σ framework to the fluctuation of the π electrons is of central importance.[3] It explains the reason underlying the poor convergence of the CI methods: in conventional methods, dynamic correlation is computed with a pre-optimized set of MOs, which does not include such σ-π dynamic mixing.

In this highlighted paper,[4] Wu and co-workers systematically investigate the N→V transition using valence-bond (VB) methods. Two properties are taken into account, the transition energy and the spatial extension of the V state.With a clever sequence of calculations using different methods and levels, they showed the impact of several different factors to the predictions of the V state.

Most impressive, they also showed that a compact set of only 5 valence bond structures (Fig. 1) is already enough to obtain a quantitatively accurate description of the N→V transition, just 0.13 eV above the experimental value. To achieve that result, however, each VB structure must have its own set of orbitals.

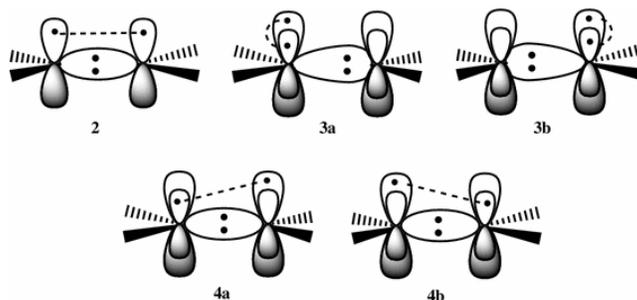Fig. 1 - Set of VB structures for the computation of the N and V states in the (2,2) space. Reproduced from Ref.1.