

π - π^* transition in the para-nitroaniline molecule

1/ Configuration Interaction calculation

Optimize the geometry of the para-nitroaniline molecule by performing a configuration interaction calculation at the PM6 level (CI/PM6) with an active space including the two frontier MOs (HOMO and LUMO). Set to 4 the number of final CI eigenstates to be calculated and printed (keyword CISTATE), and calculate the atomic Mulliken charges and dipole moments for all CI eigenstates by checking the option "charge and dipoles" in AGUI (keyword CIDIP). The keyword section of the data file should read as follows:

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AM1 C.I.=2 CIDIP CISTATE=4 SINGLET TRUSTE T=AUTO VECTORS
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Check in the output file:

- The symmetry (σ or π) of the frontier orbitals
- The HOMO-LUMO gap
- The dipole moment of the ground state
- The transition energy, wavelength, transition dipole and oscillator strength between the ground and first singlet excited state
- The CI expansion coefficients of the first excited state
- The dipole moment of the first excited state

2/ Description using a 2-state model

a/ Write down the ground and excited state wavefunctions ($|g\rangle$ and $|e\rangle$) of the para-nitroaniline molecule by using a 2-state model implying a neutral form $|N\rangle$ and a zwitterionic form $|Z\rangle$ as basis functions. These latter are orthonormal:

$$\langle N|Z\rangle = \delta_{NZ}$$

b/ Build the associated Hamiltonian matrix \mathbf{H} with elements:

$$\langle N|\hat{H}|Z\rangle = -\sqrt{2}t, \quad E_N = \langle N|\hat{H}|N\rangle = 0, \quad E_Z = \langle Z|\hat{H}|Z\rangle = 2\eta$$

c/ Diagonalize the \mathbf{H} matrix. Write the energies of the eigenstates and their expansion coefficients in the $\{N, Z\}$ basis as a function of t and η .

d/ Deduce the expression of the excitation energy ΔE_{ge} , as a function of the parameter ρ measuring the charge transfer between D and A in the ground state. Plot the evolution of ΔE_{ge} with respect to ρ (using $t=1.0$ eV), and comment.

e/ We consider the dipole moments associated to the $|N\rangle$ and $|Z\rangle$ forms:

$$\mu_N = \langle N|\hat{u}|N\rangle = 0$$

$$\mu_z = \langle Z | \hat{\mu} | Z \rangle = \mu_0$$

Write the expression of the transition dipole moment μ_{ge} along the C_2 -symmetry axis between the ground ($|g\rangle$) and excited state ($|e\rangle$) as a function of μ_0 and ρ . Plot the evolution of μ_{ge} with respect to ρ (using $\mu_0=1.0$ D), and comment.

f/ Owing to $f_{ge} \propto \Delta E_{ge} |\mu_{ge}|^2$ deduce the oscillator strength f_{ge} between $|g\rangle$ and $|e\rangle$. Plot the evolution of f_{ge} with respect to ρ (using $t=1.0$ eV and $\mu_0=1.0$ D), and comment.

3/ Extraction of the effective electronic parameters

By performing a mapping between the electronic eigenstates $|g\rangle$ and $|e\rangle$ obtained in 2/ and the CI eigenstates calculated in 1/, extract the effective electronic parameters t , η and μ_{ge} for the para-nitroaniline molecule.