Theoretical Photochemistry WiSe 2017/18 - Exercise 13

1. We return to the example of ammonia treated in Lecture 12, and construct a *symmetry-adapted basis* by applying projection operators to an arbitrary basis (here, the *s*-orbital basis $\{ s_N, s_A, s_B, s_C \}$).

- Use the projector of symmetry species $\Gamma^{(l)}$ (where l labels a given irrep),

$$\mathcal{P}^{(l)} s_n = \frac{d_l}{h} \sum_R \chi^{(l)}(R)^* \left(R\, s_n \right)$$

  to construct symmetry-adapted orbitals for all irreps.

- Verify whether the projected orbitals resulting from the above procedure are orthogonal to each other.

- Construct orthogonal combinations of orbitals. How do these compare with the symmetry-adapted combinations that were introduced previously in the lecture?

2. Consider the electronic transition between the $S_0(^1A_1)$ ground state and the $S_1(^1A_2)$ first excited state of formaldehyde.

- What is the point group of formaldehyde?

- Verify whether the electronic transition $S_1(^1A_2) \leftarrow S_0(^1A_1)$ is allowed. To this end, (i) infer from the character table according to which irreducible representation(s) Γ_μ the dipole operator transforms, (ii) check whether the direct product $A_2 \otimes \Gamma_\mu \otimes A_1$ contains the totally summetry (A_1) representation.

- The out-of-plane bending mode of formaldehyde transforms according to the irreducible representation B_1. Explain why displacements in this mode can turn an electronically forbidden transition into a *vibronically allowed* transition.

Here's an interesting article on the topic: Lin et al., *Phys. Chem. Chem. Phys.* **12**, 11432 (2010).