

# Electronic structure of proteins in the deep-UV

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Charge-transfer transitions in proteins play a key role in many biophysical processes, from the behaviour of redox proteins to photochemical reactions. We present ab initio calculations on a model dipeptide and more approximate calculations of the electronic excited states of proteins which, taken together, provide the most definitive assignment and characterisation of charge-transfer transitions in proteins to date [1]. We have calculated from first principles the electronic circular dichroism (CD) spectra of 75 proteins based on their structures. Compared to previous studies, we achieve more accurate calculated CD spectra between 170 and 190 nm, due mainly to the importance in  $\alpha$ -helices of a charge-transfer transition from the lone pair on one peptide group to the  $\pi^*$  orbital on the next peptide group.

[1] Oakley MT & Hirst JD (2006). *J. Am. Chem. Soc.*, **128**, 12414–12415.

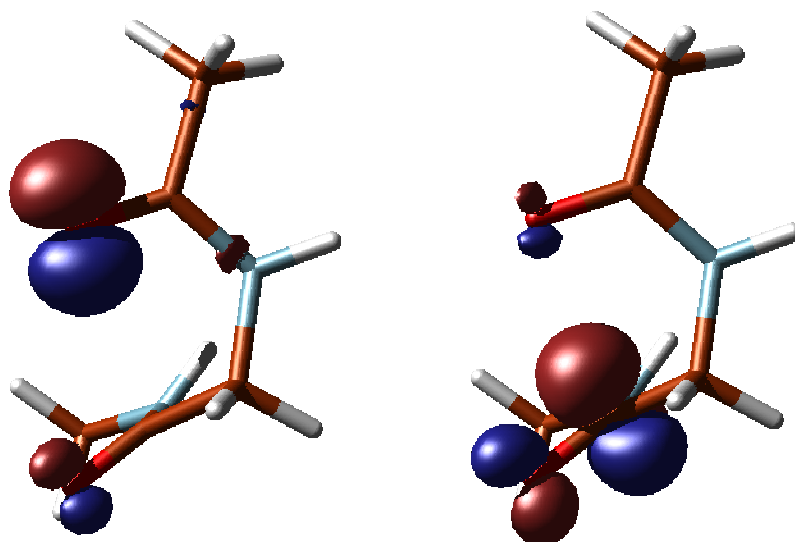


Figure 1. The  $n_1$  (left) and  $\pi^*_2$  (right) orbitals (from CASSCF calculations) involved in the charge-transfer transition responsible for the band at 175 nm in the deep-UV circular dichroism spectra of  $\alpha$ -helices.