

Supplement for

Towards molecular-level characterization of photo-induced decarboxylation of the green fluorescent protein: Accessibility of the charge-transfer states

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1. The details the QM/MM model

Numbering of the residues is consistent with the 1EMA structure. The QM part includes:

- a) the residues representing the chromophore (Ser65, Tyr66, Gly67);
- b) side chains of the residues Arg96, Ser205, Glu222;
- c) a water molecule connecting the chromophore with Ser205.

The MM part includes side chains of the residues from 11 to 64 and from 68 to 227.

2. The QM/MM optimized coordinates of the QM-subsystem in the ground state (S_0)

Table S1. Cartesian coordinates (Å) of the QM part

C	22.720	27.252	36.337
O	22.334	26.193	36.823
N	24.032	27.533	36.182
H	24.284	28.459	35.879
C	25.105	26.616	36.466
H	24.639	25.653	36.706
C	26.029	26.427	35.254
H	25.384	26.150	34.410
H	26.510	27.381	35.021
O	26.960	25.407	35.460
H	27.821	25.795	35.730
C	25.896	27.068	37.649
N	27.129	27.454	37.597
C	27.507	27.701	38.909
C	28.656	28.251	39.374
H	28.693	28.345	40.459
C	29.784	28.817	38.669
C	29.971	28.777	37.273
H	29.294	28.210	36.642
C	30.740	29.511	39.436
H	30.616	29.541	40.515
C	31.057	29.419	36.689
H	31.194	29.338	35.614
C	31.819	30.153	38.860
H	32.565	30.653	39.467
C	31.991	30.110	37.474
O	33.087	30.717	36.956
H	33.339	30.310	36.067
C	26.364	27.412	39.793
O	26.229	27.522	41.016
N	25.372	27.024	38.940
C	24.006	26.907	39.397
H	23.775	27.722	40.074
H	23.319	26.984	38.561
C	23.717	25.595	40.078
O	22.861	25.479	40.958
N	24.443	24.598	39.569
H	25.186	24.808	38.916
N	25.256	31.749	43.263
H	25.881	31.434	43.991
C	25.069	30.887	42.242
N	24.007	30.954	41.473
H	23.956	30.331	40.684
H	23.270	31.621	41.632
N	25.988	29.962	42.063
H	25.874	29.182	41.413
H	26.846	29.959	42.599
C	32.316	28.614	32.193
H	32.647	29.653	32.198
H	31.288	28.629	31.825
O	32.258	28.210	33.546
H	31.358	27.831	33.812
C	31.333	25.273	34.452
H	31.463	24.430	35.129
H	32.258	25.847	34.430

C	30.250	26.167	35.050
O	30.069	27.285	34.501
O	29.602	25.733	36.036
O	34.237	29.680	34.947
H	34.513	30.355	34.332
H	33.571	29.156	34.493

3. Additional data complementing Table 1 of the main text

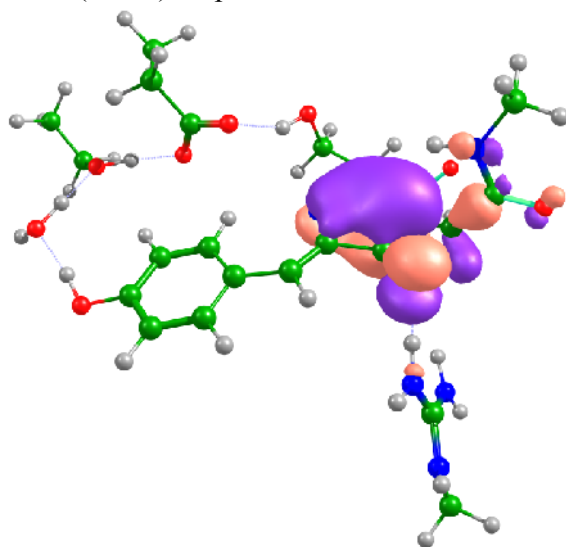
Table S2. S₀-S₁ excitation energy (eV)

Model system	Computational protocol	Excitation energy
Chro	sa(10)-CASSCF(12/11)/6-31G*	5.32
Chro + all effective fragments for the protein	sa(10)-CASSCF(12/11)/6-31G*	5.23
Model cluster shown in Fig.1	sa(10)-CASSCF(12/11)/6-31G*	4.37
Model cluster shown in Fig.1 + remaining effective fragments	sa(10)-CASSCF(12/11)/6-31G*	5.20
Model cluster shown in Fig.1	XMCQDPT2/sa(10)-CASSCF(12/11)/cc-pVDZ	3.18
Model cluster shown in Fig.1	XMCQDPT2/sa(4)-CASSCF(12/11)/cc-pVDZ	3.08
Model cluster shown in Fig.1+remaining effective fragments	sa(3)-CASSCF(12/11)/cc-pVDZ	4.62
Model cluster shown in Fig.1+remaining effective fragments	XMCQDPT2/sa(3)-CASSCF(12/11)/cc-pVDZ	3.40

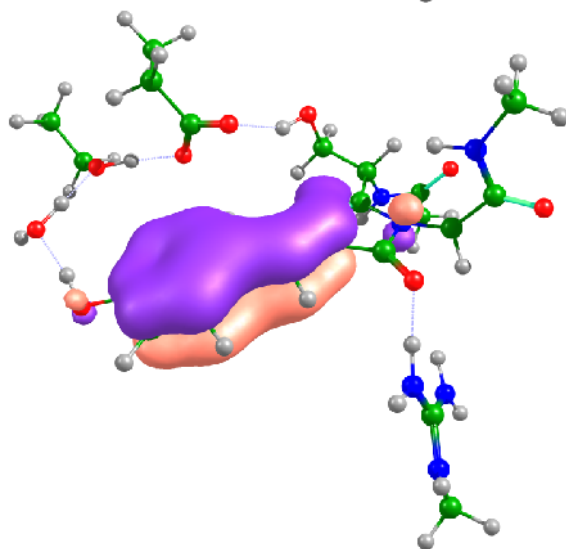
4. Active space orbitals from the CASSCF(12/11) and ORMAS calculations

sa(10)-CASSCF(12/11)/cc-pVDZ natural orbitals

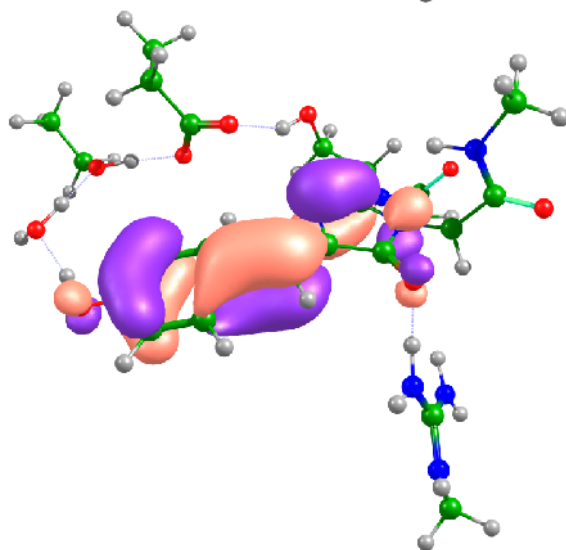
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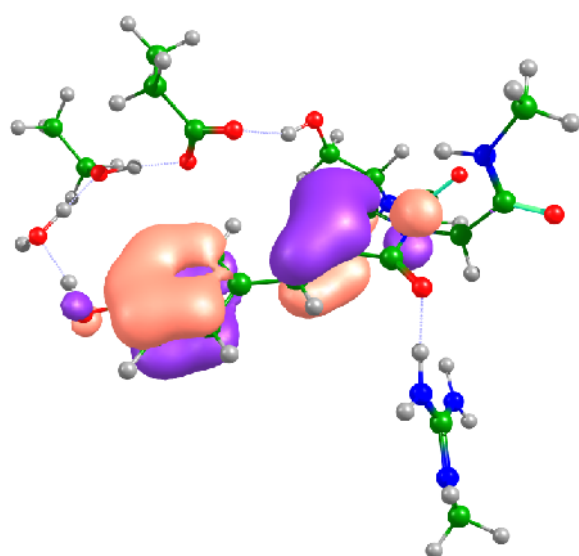
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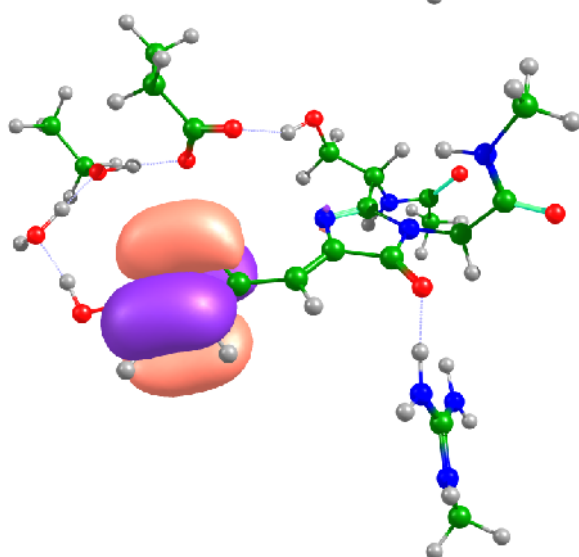
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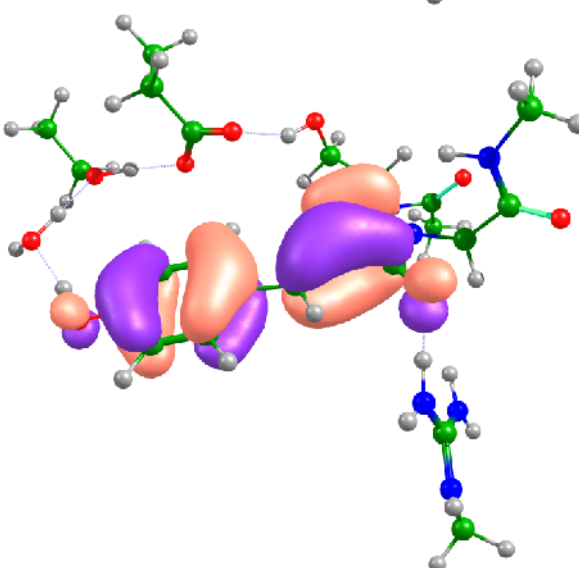
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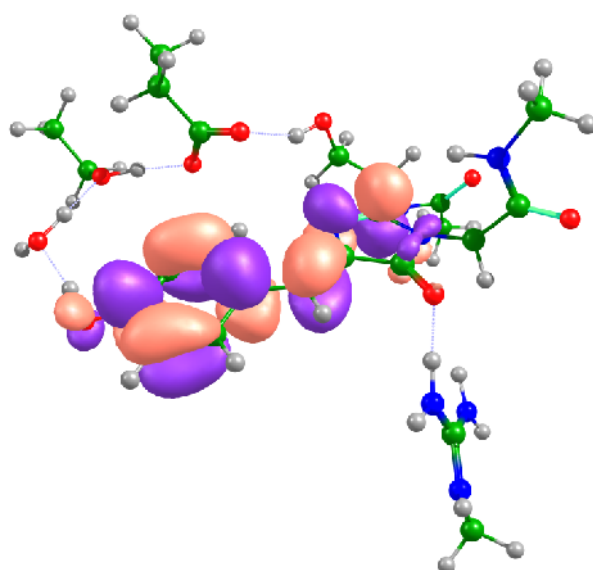
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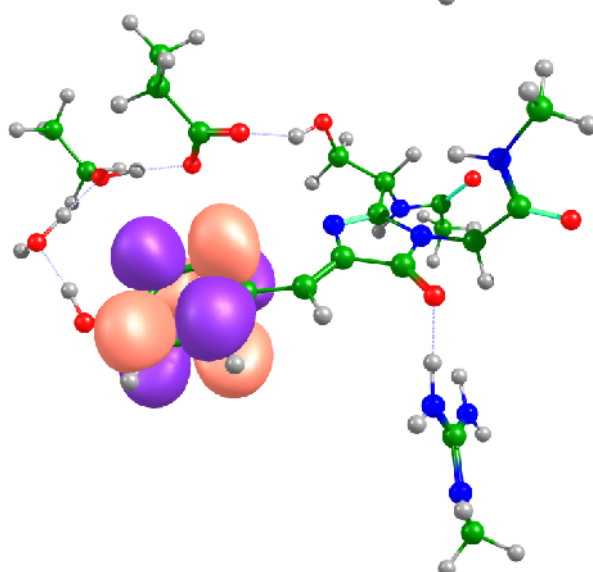
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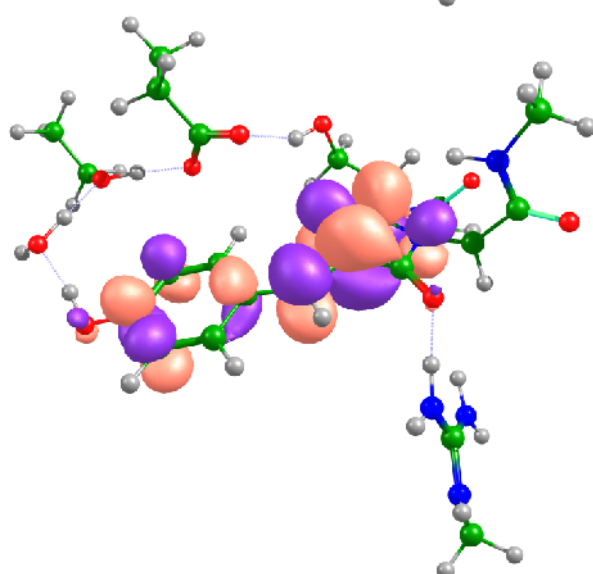
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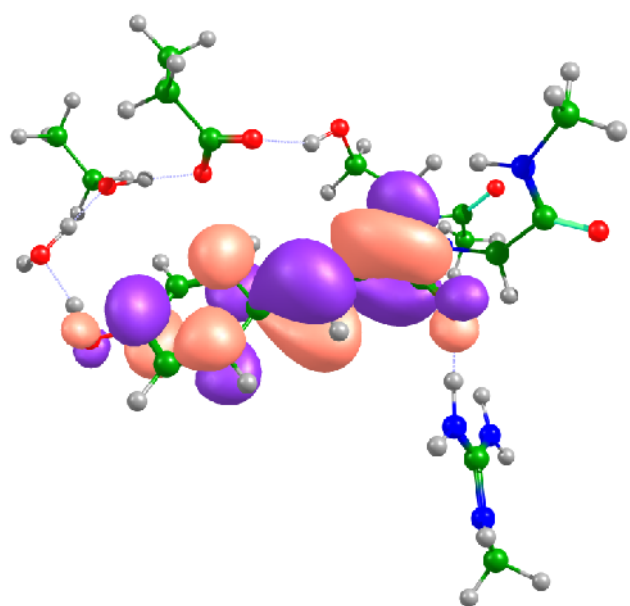
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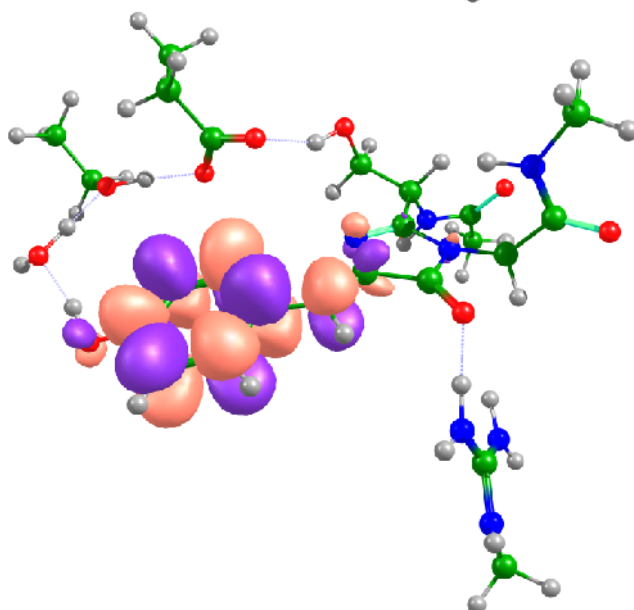
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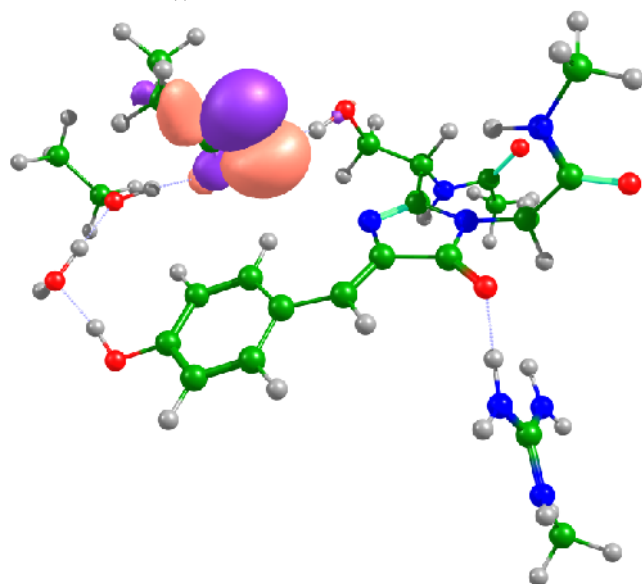
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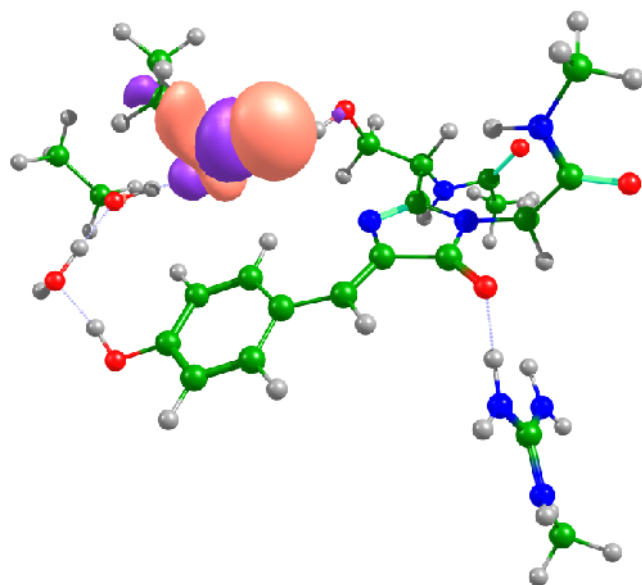
sa(5)-MCSCF/ORMAS/cc-pVDZ optimized orbitals

(i) Glu222 orbitals

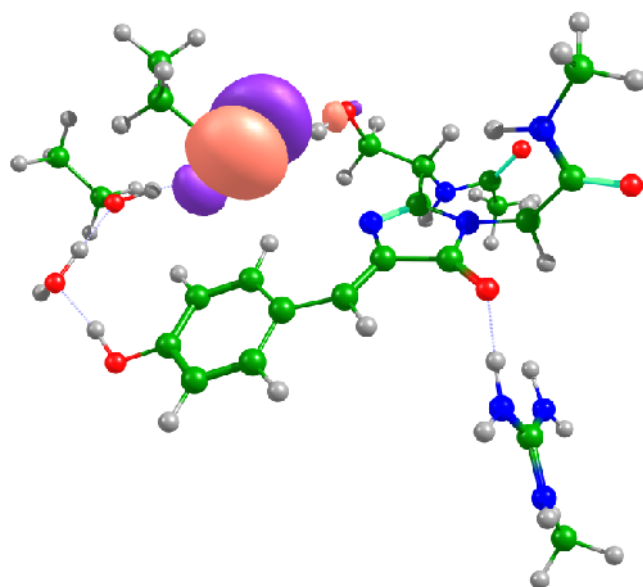
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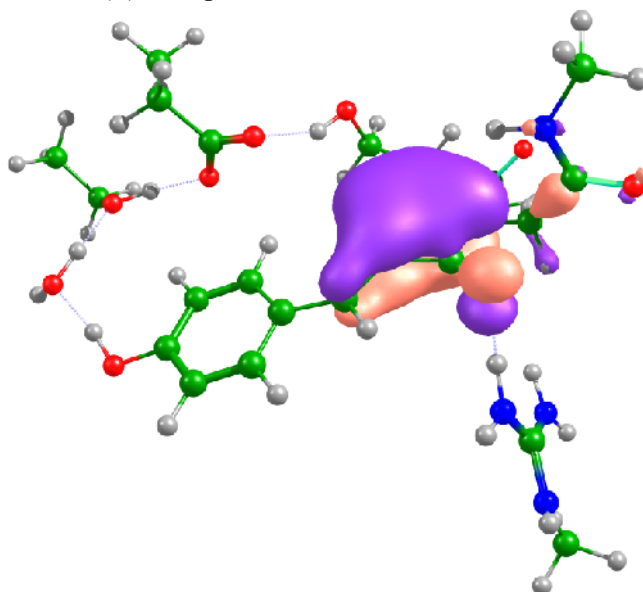


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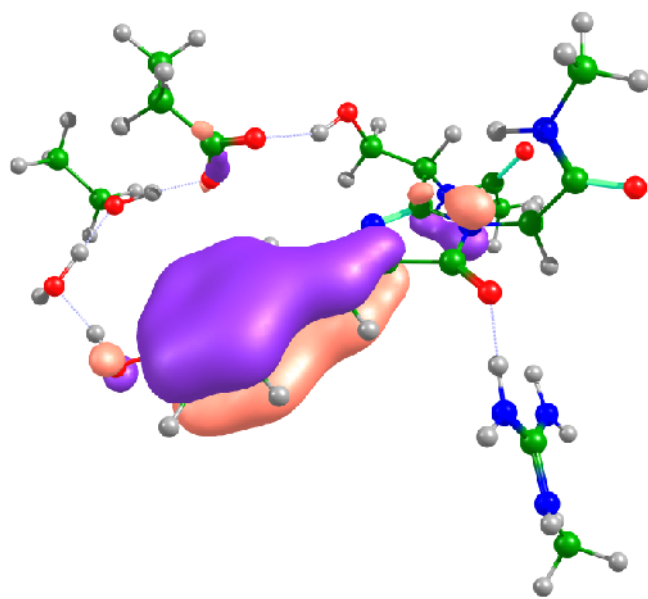


(ii) occupied Chro orbitals

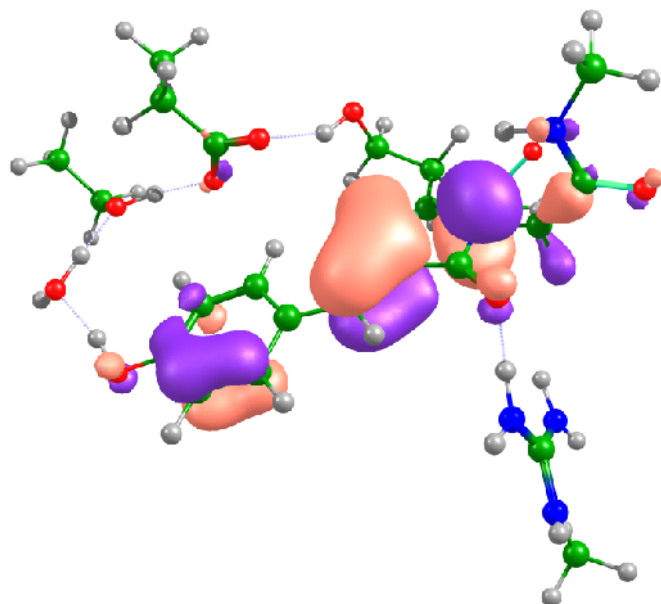
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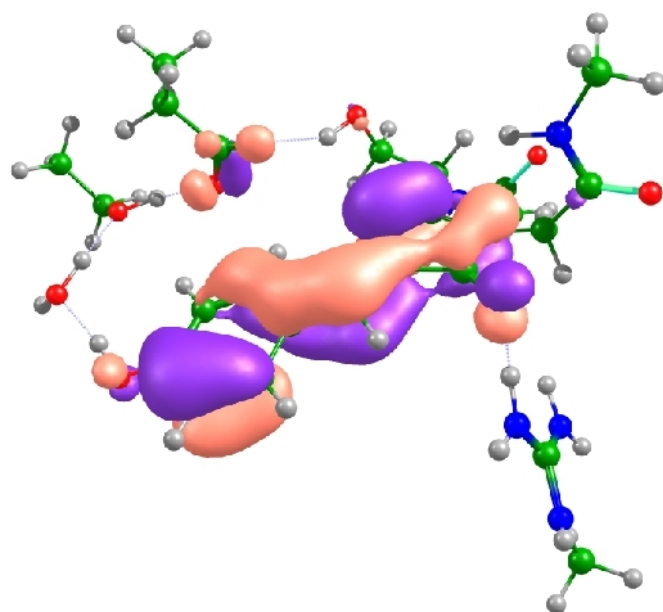
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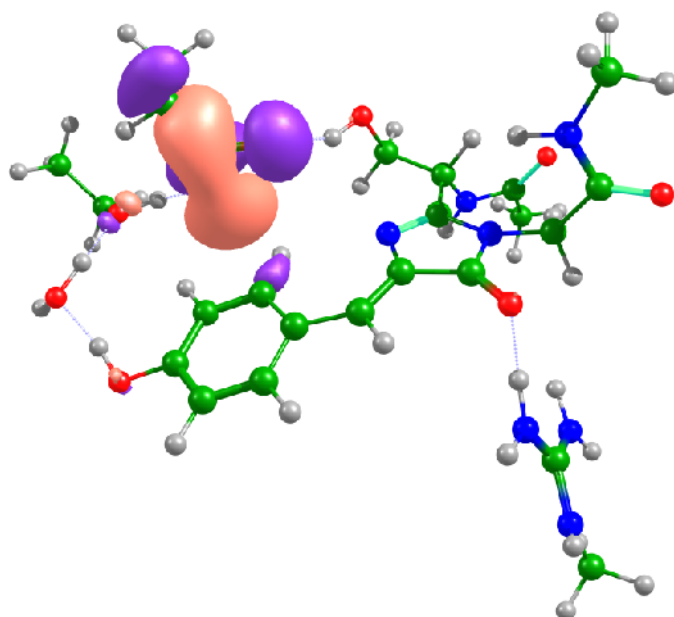
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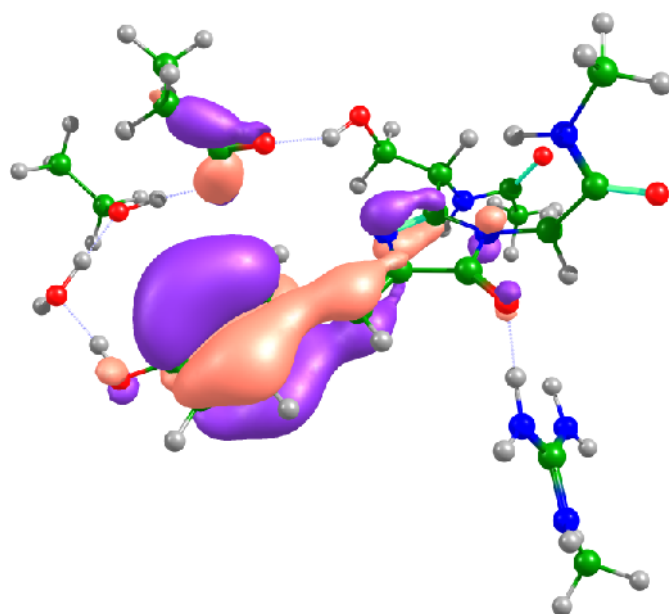
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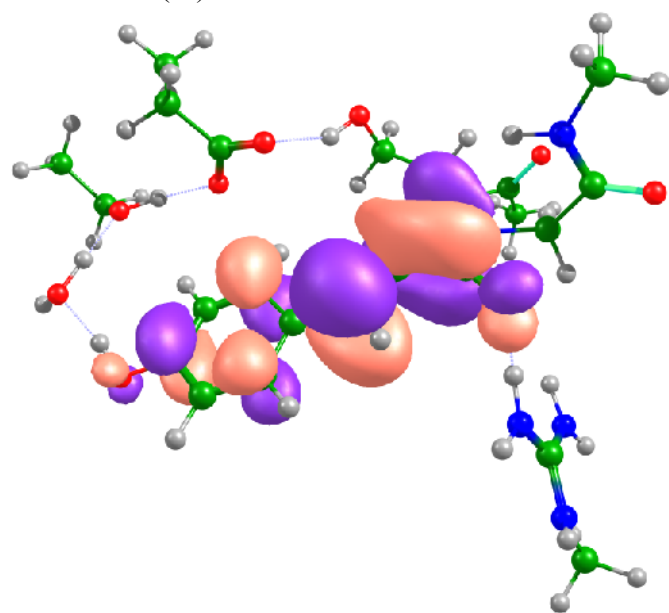


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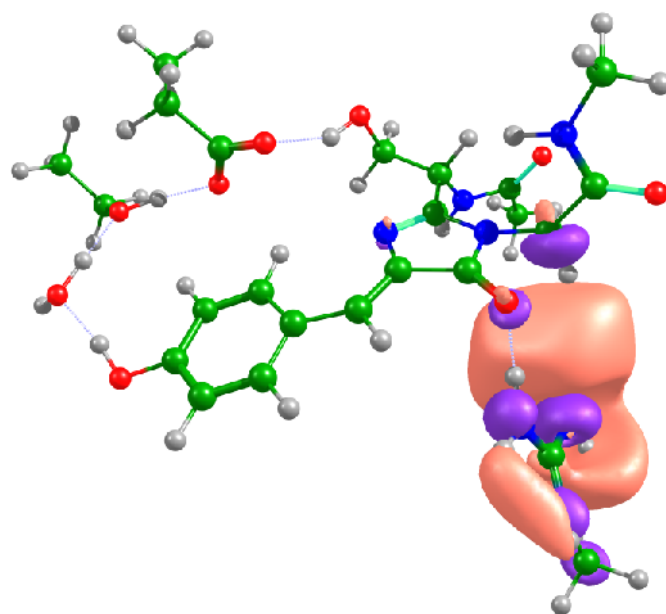


(iii) virtual orbitals

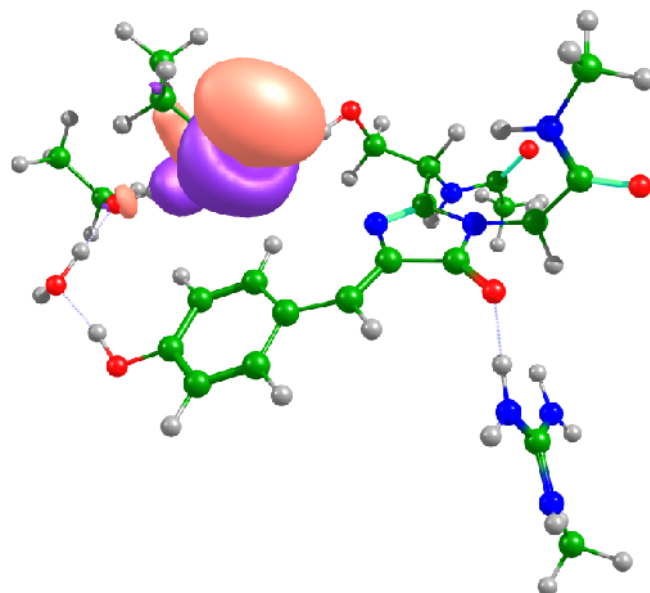
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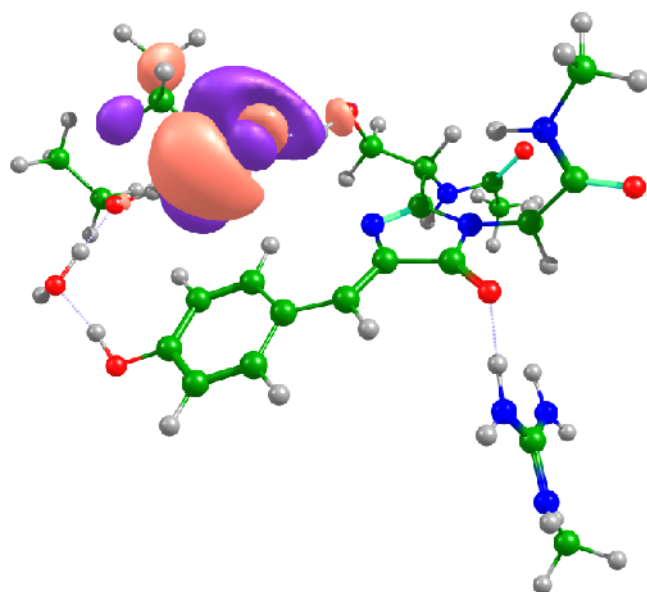
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