A Quantum-Mechanical investigation of Oxygen Vacancy and Copper Doping in the Orthorhombic $CaSnO_3$ Perovskite

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Animation of the vibrational modes of $CaSnO_3$ for the pristine and oxygen vacancy cases, as calculated at PBE level, can be found in the following links respectively:
`http://www.crystal.unito.it/vibs/CaSnO3/index.html?name=CaSnO3_Pristine_PBE.xyz`
`http://www.crystal.unito.it/vibs/CaSnO3/index.html?name=CaSnO3_Oxygen_Vacancy_PBE.xyz`

TABLE I: Bond lengths of oxygen atoms toward Sn in octahedral site and its defective counterpart (XX represent vacant atom), in both position O_{ap} and O_{eq} and calculation level (PBE and PBE0). The bond lengths are given in Å and the volume (D_{VOL}) is given in % tanking as reference the bulk volume.

Level	Position	Method	Config.	D_{VOL}	O_{ap}1/XX	O_{ap}2	O_{eq}1	O_{eq}2	O_{eq}3/XX	O_{eq}4
PBE	*Bulk*		closed-shell	ref	2.102	2.102	2.095	2.095	2.098	2.098
PBE0	*Bulk*		closed-shell	ref	2.070	2.070	2.066	2.066	2.069	2.069
PBE	O_{ap}	AR	closed-shell	-0.04	-	2.155	2.121	2.112	2.127	2.124
			singlet	-0.04	-	2.155	2.121	2.112	2.127	2.124
			triplet	0.35	-	2.079	2.123	2.126	2.134	2.133
		GH	closed-shell	-0.03	2.145	2.150	2.122	2.111	2.126	2.123
			singlet	-0.03	2.134	2.150	2.122	2.111	2.126	2.123
			triplet	0.36	2.029	2.076	2.122	2.125	2.132	2.131
	O_{eq}	AR	closed-shell	-0.02	2.129	2.128	2.122	2.130	-	2.168
			singlet	-0.02	2.129	2.128	2.122	2.130	-	2.168
			triplet	0.37	2.123	2.140	2.124	2.122	-	2.079
		GH	closed-shell	0.00	2.127	2.127	2.120	2.127	1.744	2.154
			singlet	0.00	2.128	2.127	2.121	2.128	1.898	2.155
			triplet	0.38	2.121	2.136	2.121	2.120	2.159	2.075
PBE0	O_{ap}	AR	closed-shell	-0.10	-	2.137	2.090	2.079	2.093	2.091
			singlet	-0.10	-	2.137	2.090	2.079	2.093	2.091
			triplet	0.28	-	2.053	2.102	2.111	2.121	2.112
		GH	closed-shell	-0.09	2.201	2.134	2.091	2.080	2.093	2.092
			singlet	-0.12	2.665	2.136	2.088	2.078	2.092	2.090
			triplet	0.28	2.181	2.050	2.102	2.111	2.119	2.111

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TABLE II: Atomic net charge (q) and spin density (μ) as calculated by both Mulliken (q_M and μ_M) and Hirshfeld-I (q_H and μ_H) of SnO_6 octahedral site and vacancy alike at PBE and PBE0 level. Two oxygen position (O_{ap} and O_{eq}) taking as reference the central Sn are displayed, with quantities given in |e|.

Level	Position	Method	Config.	q/μ	Sn	O_{ap}1/XX	O_{ap}2	O_{eq}1	O_{eq}2	O_{eq}3	O_{eq}4
	Bulk PBE			q_M	1.516	-1.010	-1.010	-1.014	-1.014	-1.014	-1.014
				q_H	2.258	-1.274	-1.274	-1.272	-1.272	-1.272	-1.272
			closed-shell	q_M	0.979	-	-1.015	-0.990	-1.002	-0.995	-0.995
				q_H	1.246	-	-1.173	-1.172	-1.177	-1.176	-1.168
			singlet	q_M	0.979	-	-1.015	-0.990	-1.002	-0.995	-0.995
				q_H	1.246	-	-1.173	-1.172	-1.177	-1.176	-1.168
			triplet	q_M	0.991	-	-1.006	-0.975	-0.989	-0.981	-0.979
		AR		q_H	1.350	-	-1.174	-1.183	-1.184	-1.183	-1.177
				μ_M	0.492	-	0.001	0.073	0.045	0.055	0.070
				μ_H	0.367	-	0.005	0.095	0.072	0.082	0.091
			closed-shell	q_M	1.055	0.174	-1.014	-1.001	-0.998	-0.990	-0.994
				q_H	1.220	0.000	-1.169	-1.166	-1.170	-1.168	-1.162
	O_{ap}		singlet	q_M	1.056	0.175	-1.014	-1.001	-0.998	-0.990	-0.995
				q_H	1.227	0.000	-1.170	-1.167	-1.171	-1.169	-1.163
			triplet	q_M	1.059	0.139	-1.002	-0.973	-0.992	-0.985	-0.977
		GH		q_H	1.327	0.000	-1.275	-1.177	-1.178	-1.273	-1.172
				μ_M	0.417	0.126	0.002	0.071	0.045	0.055	0.068
				μ_H	0.378	0.000	0.005	0.091	0.067	0.077	0.087
			closed-shell	q_M	0.987	-0.987	-0.993	-1.001	-0.991	-	-1.018
				q_H	1.250	-1.170	-1.174	-1.177	-1.168	-	-1.174
			singlet	q_M	0.987	-0.987	-0.993	-1.001	-0.991	-	-1.018
				q_H	1.250	-1.170	-1.174	-1.177	-1.168	-	-1.174
PBE			triplet	q_M	1.025	-0.970	-0.977	-0.985	-0.978	-	-1.010
		AR		q_H	1.413	-1.180	-1.186	-1.187	-1.181	-	-1.180
				μ_M	0.454	0.067	0.053	0.048	0.061	-	0.000
				μ_H	0.338	0.087	0.075	0.072	0.084	-	0.004
			closed-shell	q_M	1.093	-0.990	-0.992	-0.994	-0.996	0.176	-1.016
				q_H	1.242	-1.166	-1.170	-1.171	-1.163	0.000	-1.171
	O_{eq}		singlet	q_M	1.088	-0.990	-0.993	-0.995	-0.997	0.180	-1.017
				q_H	1.237	-1.166	-1.170	-1.171	-1.163	0.000	-1.170
			triplet	q_M	1.123	-0.975	-0.980	-0.983	-0.986	0.167	-1.008
		GH		q_H	1.400	-1.176	-1.181	-1.272	-1.176	0.000	-1.178
				μ_M	0.370	0.065	0.052	0.046	0.061	0.138	0.001
				μ_H	0.345	0.081	0.069	0.066	0.079	0.000	0.004
	Bulk PBE0			q_M	1.762	-1.115	-1.115	-1.115	-1.115	-1.115	-1.115
				q_H	2.409	-1.355	-1.355	-1.351	-1.351	-1.351	-1.351
			closed-shell	q_M	1.163	-	-1.120	-1.090	-1.103	-1.097	-1.097
				q_H	1.479	-	-1.276	-1.276	-1.277	-1.281	-1.273
			singlet	q_M	1.162	-	-1.120	-1.090	-1.104	-1.097	-1.097
				q_H	1.477	-	-1.276	-1.277	-1.283	-1.280	-1.273
			triplet	q_M	1.128	-	-1.112	-1.075	-1.092	-1.087	-1.082
		AR		q_H	1.489	-	-1.262	-1.285	-1.284	-1.284	-1.281
				μ_M	0.653	0.000	-0.001	0.077	0.043	0.054	0.073
				μ_H	0.482	-	0.001	0.110	0.077	0.087	0.103
PBE0			closed-shell	q_M	1.244	0.184	-1.120	-1.099	-1.101	-1.101	-1.096
				q_H	1.452	0.000	-1.273	-1.272	-1.276	-1.273	-1.267
	O_{eq}		singlet	q_M	1.226	0.118	-1.120	-1.101	-1.103	-1.100	-1.098
				q_H	1.501	0.000	-1.279	-1.278	-1.283	-1.280	-1.274
			triplet	q_M	1.218	0.184	-1.111	-1.084	-1.089	-1.091	-1.081
		GH		q_H	1.462	0.000	-1.258	-1.279	-1.276	-1.276	-1.275
				μ_M	0.562	0.167	-0.001	0.079	0.043	0.054	0.072
				μ_H	0.495	0.000	0.001	0.108	0.071	0.082	0.098

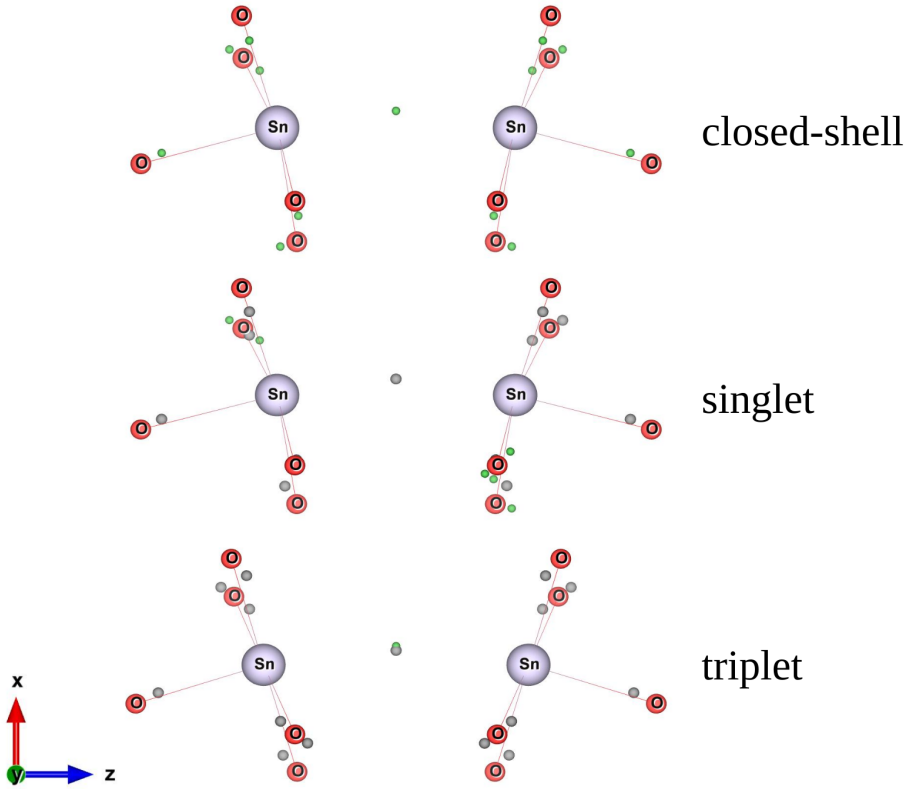

FIG. 1: Wannier centroid's representation of vacancy containing site. Oxygen and Tin atoms are labeled , and the spheres between them represents the centroid of the Wannier localization. The smaller one are characterized as alpha electrons and the other the beta ones.

TABLE IV: Bond lengths of oxygen atoms toward Sn and Cu in octahedral site and its defective counterpart (XX represent vacant atom), at O_{ap} as calculated at PBE0 level and GH method. The bond lengths are given in Åand the volume (D_{VOL}) is given in % tanking as reference the bulk volume.

Atom	Neighbor	D_{VOL}	O_{ap}1/XX	O_{ap}2	O_{eq}1	O_{eq}2	O_{eq}3	O_{eq}4
	bulk	ref	2.070	2.070	2.066	2.066	2.069	2.069
	no vacancy	-0.37	2.137	2.066	2.052	2.058	2.061	2.051
Sn	first neighbor	-0.15	1.778	1.969	2.033	2.026	2.038	2.026
	second neighbor	0.04	1.838	1.976	1.961	2.018	2.040	2.066
	third neighbor	0.09	2.153	1.978	2.052	2.065	2.009	1.968
	no vacancy	-0.37	1.945	1.945	2.071	2.072	1.959	1.960
Cu	first neighbor	-0.15	2.551	2.088	2.012	2.038	2.011	2.040
	second neighbor	0.04	2.034	2.043	2.048	2.069	2.253	2.170
	third neighbor	0.09	2.037	2.047	2.165	2.296	2.048	2.092

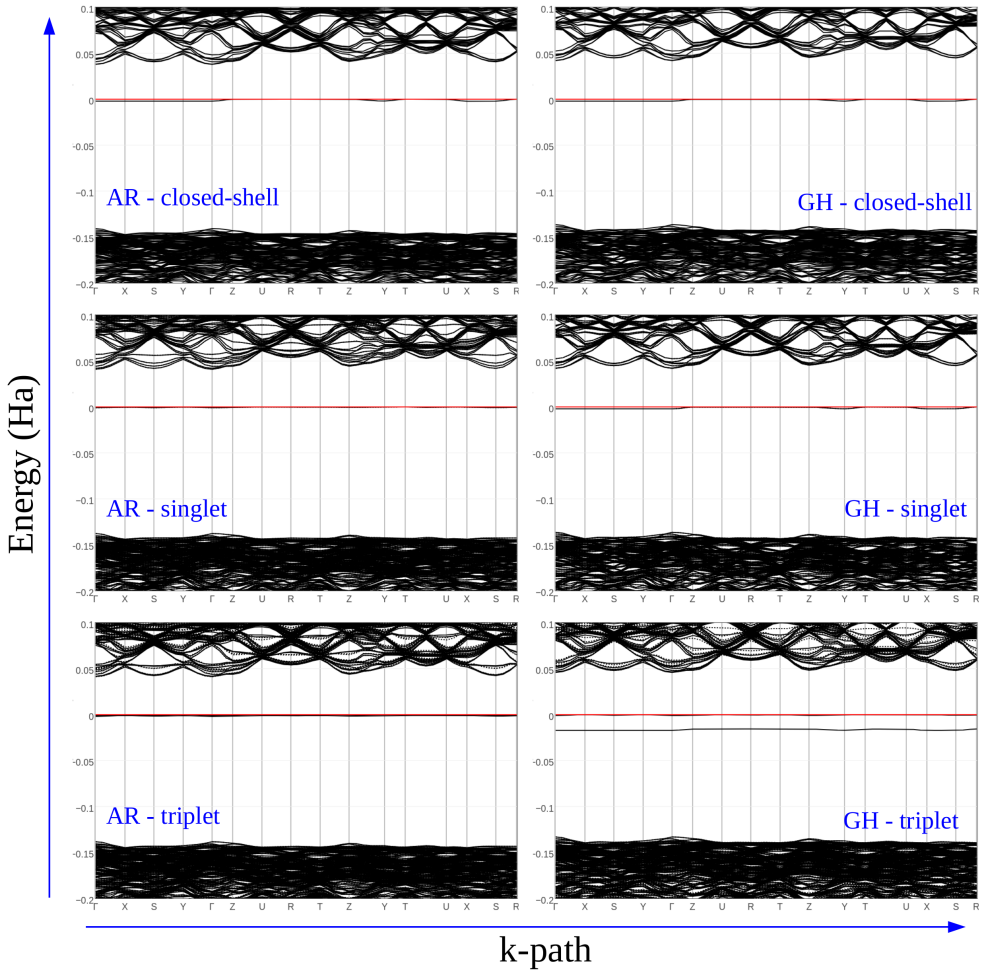

FIG. 2: Band structure of $CaTiO_3$ at PBE0 level for the three electronic configuration closed-shell, singlet and triplet. The methods **AR** and **GH** are placed into the left and right columns, respectively. Fermi energy are placed as a straight red line.

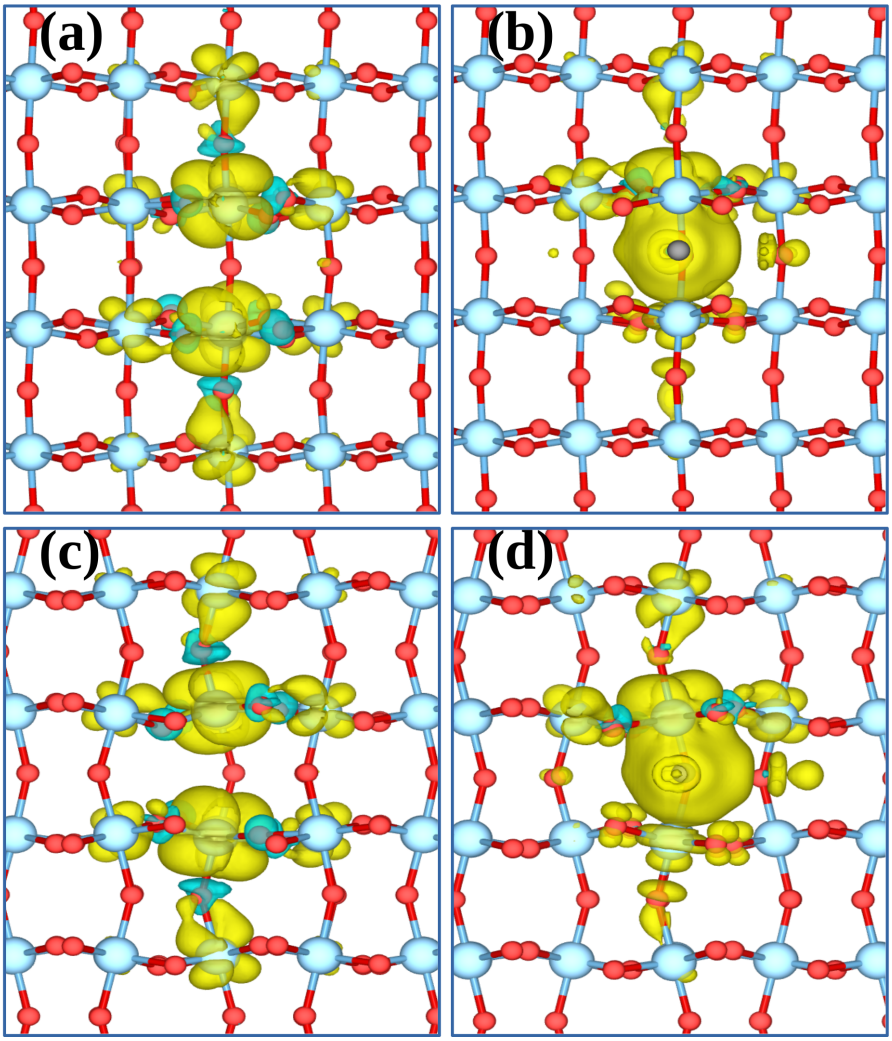

FIG. 3: Spin density 3D maps (cutoff 0.001 e/a_0^3) for the $CaTiO_3$ (a) and (c) are two views of the **AR** model and (b) and (d) are two views of the **GH** model. All calcium atoms have been removed for clarity.

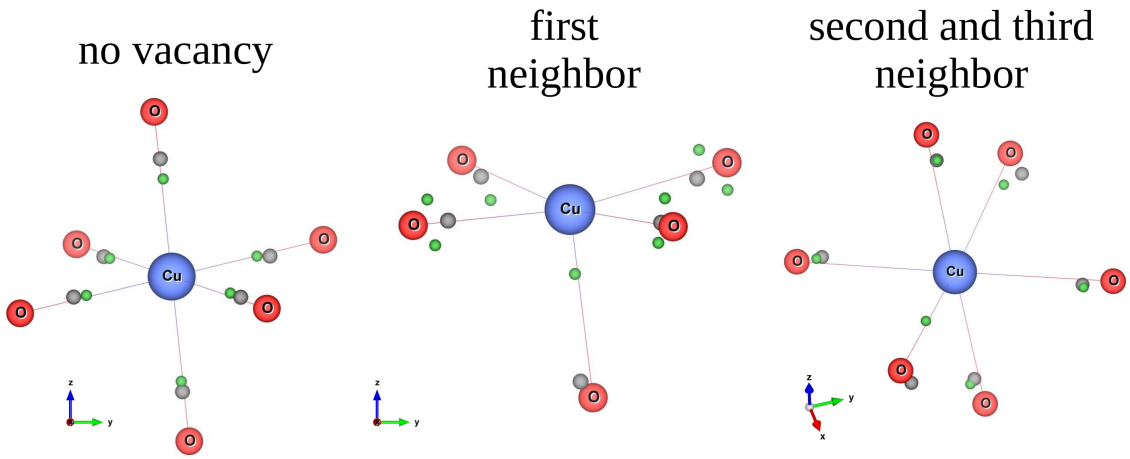

FIG. 4: Wannier centroid's representation of the doping site. Oxygen and Copper atoms are labeled, and the spheres between them represents the centroid of the Wannier localization. The smaller one are characterized as alpha electrons and the other the beta ones.

TABLE V: Atomic net charge (q) and spin density (μ) as calculated by both Mulliken (q_M and μ_M) and Hirshfeld (q_H and μ_H) of SnO_6 and CuO_6 "octahedral" sites and its defective sites or surrounds. Both quantities are given in |e|. The Sn atom is always a first neighbor of the vacancy, apart from the NV case in which it is neighbor of the doped site.

Atom	Cu Neighbor	Method	q/μ	Sn	$O_{ap}1$/XX	$O_{ap}2$	$O_{eq}1$	$O_{eq}2$	$O_{eq}3$	$O_{eq}4$
Bulk	-	-	q_M	1.762	-1.115	-1.115	-1.115	-1.115	-1.115	-1.115
			q_H	2.409	-1.355	-1.355	-1.351	-1.351	-1.351	-1.351
Sn	no vacancy	-	q_M	1.737	-0.945	-1.113	-1.116	-1.104	-1.110	-1.110
			q_H	2.376	-1.054	-1.353	-1.351	-1.338	-1.344	-1.345
	first neighbor	**AR**	q_M	1.546	-	-1.087	-1.078	-1.073	-1.072	-1.067
			q_H	2.275	-	-1.334	-1.325	-1.328	-1.322	-1.318
	first neighbor	**GH**	q_M	1.565	0.080	-1.081	-1.072	-1.071	-1.071	-1.069
			q_H	2.265	0.000	-1.334	-1.324	-1.325	-1.319	-1.316
	second neighbor	**AR**	q_M	1.495	-	-1.086	-1.039	-1.082	-1.078	-1.086
			q_H	2.230	-	-1.337	-1.246	-1.323	-1.333	-1.338
	second neighbor	**GH**	q_M	1.522	0.072	-1.083	-1.042	-1.078	-1.081	-1.086
			q_H	2.221	0.000	-1.337	-1.242	-1.322	-1.331	-1.335
	third neighbor	**AR**	q_M	1.489	-	-1.080	-1.080	-1.094	-1.067	-1.042
			q_H	2.230	-	-1.334	-1.347	-1.340	-1.315	-1.248
	third neighbor	**GH**	q_M	1.513	0.075	-1.076	-1.073	-1.094	-1.072	-1.046
			q_H	2.223	0.000	-1.334	-1.344	-1.341	-1.312	-1.245
Cu	no vacancy	-	q_M	0.889	-0.945	-0.949	-1.007	-1.007	-0.954	-0.953
			q_H	0.926	-1.054	-1.061	-1.150	-1.151	-1.066	-1.064
			μ_M	0.469	-0.026	0.012	0.231	0.228	0.034	0.003
			μ_H	0.519	-0.038	0.019	0.207	0.205	0.031	-0.004
	first neighbor	**AR**	q_M	0.689	-	-1.103	-1.068	-1.073	-1.064	-1.068
			q_H	0.668	-	-1.275	-1.220	-1.215	-1.211	-1.220
			μ_M	0.712	-	0.000	0.058	0.064	0.068	0.059
			μ_H	0.728	-	-0.002	0.055	0.059	0.062	0.056
	first neighbor	**GH**	q_M	0.720	0.080	-1.099	-1.069	-1.078	-1.068	-1.073
			q_H	0.661	0.000	-1.274	-1.218	-1.214	-1.208	-1.218
			μ_M	0.712	-0.003	0.000	0.059	0.064	0.068	0.059
			μ_H	0.727	0.000	-0.002	0.055	0.060	0.063	0.056
	second neighbor	**AR**	q_M	0.798	-1.092	-1.091	-1.093	-1.093	-1.039	-1.106
			q_H	0.747	-1.235	-1.235	-1.232	-1.239	-1.246	-1.288
			μ_M	0.758	0.053	0.053	0.051	0.048	0.001	0.000
			μ_H	0.766	0.051	0.052	0.049	0.047	-0.002	-0.002
	second neighbor	**GH**	q_M	0.798	-1.092	-1.091	-1.093	-1.094	-1.042	-1.106
			q_H	0.746	-1.234	-1.234	-1.232	-1.239	-1.242	-1.288
			μ_M	0.757	0.053	0.053	0.051	0.048	0.001	0.000
			μ_H	0.766	0.051	0.052	0.049	0.047	-0.002	-0.002
	third neighbor	**AR**	q_M	0.792	-1.092	-1.088	-1.108	-1.042	-1.086	-1.098
			q_H	0.742	-1.235	-1.231	-1.283	-1.248	-1.233	-1.243
			μ_M	0.755	0.055	0.055	0.000	0.001	0.054	0.046
			μ_H	0.764	0.053	0.053	-0.002	-0.002	0.052	0.046
	third neighbor	**GH**	q_M	0.792	-1.092	-1.087	-1.108	-1.046	-1.087	-1.098
			q_H	0.741	-1.234	-1.228	-1.283	-1.245	-1.233	-1.243
			μ_M	0.755	0.055	0.055	0.000	0.001	0.054	0.046
			μ_H	0.763	0.053	0.053	-0.002	-0.002	0.052	0.046

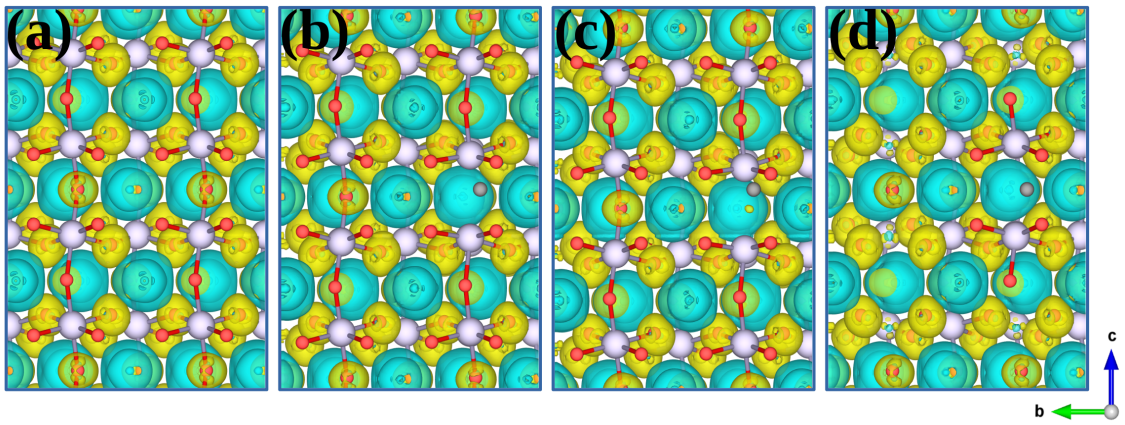

FIG. 5: CaSnO3 3D interaction densities (difference between the electron density of the interacting system and the superposition of atomic non-interacting densities) with a cutoff 0.015 e/a_0^3 (a) Pristine System (b) Restricted (c) Singlet (d) Triplet. The Calcium atoms are omitted for a better view. The grey small ball presents the "ghost" atom, a.k.a. vacant atom.