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First Generation Antipsychotic Haloperidol: Optical Absorption Measurement and Structural, Electronic, and Optical Properties of its Anhydrous Monoclinic Crystal by First-Principle Approaches

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TABLE S1: Lattice parameters (LP) in (Å), unit cell volume in (Å3) and unit cell angle α (degree) for the anhydrous monoclini c haloperidol crystal. The LDA, GGA and GGA+TS calculation results were obtained using 830, 940 e 1100 eV cutoff energy. Their deviations Δ in comparison with experimental data 4 are also shown.

C. Level	*a*(Å)	Δ*a* (Å)	*b*(Å)	Δ*b*(Å)	*c*(Å)	Δ*c*(Å)	V(Å^3)	ΔV(Å^3)	*α*(deg)	Δ*α* (deg)	β(deg)	Δβ(deg)	γ(deg)	Δγ(deg)
LDA_{830eV}	7.51	-0.31	8.64	-0.36	26.78	-1.57	1687.85	-224.38	90.00	–	103.53	-2.81	90.00	–
LDA_{940eV}	7.51	-0.31	8.64	-0.36	26.78	-1.57	1687.85	-224.38	90.00	–	103.53	-2.81	90.00	–
LDA_{1100eV}	7.51	-0.31	8.64	-0.36	26.78	-1.57	1687.85	-224.38	90.00	–	103.54	-2.80	90.00	–
GGA_{830eV}	8.35	0.53	9.50	0.50	31.52	3.17	2336.61	424.38	90.00	–	110.77	4.43	90.00	–
GGA_{940eV}	8.35	0.53	9.50	0.50	31.52	3.17	2336.61	424.38	90.00	–	110.77	4.43	90.00	–
GGA_{1100eV}	8.35	0.53	9.50	0.50	31.52	3.17	2336.61	424.38	90.00	–	110.77	4.43	90.00	–
$GGA+TS_{830eV}$	7.75	-0.06	8.90	-0.10	27.69	-0.66	1845.25	-66.99	90.00	–	104.48	-1.86	90.00	–
$GGA+TS_{940eV}$	7.75	-0.06	8.90	-0.10	27.69	-0.66	1845.25	-66.99	90.00	–	104.48	-1.86	90.00	–
$GGA+TS_{1100eV}$	7.75	-0.06	8.90	-0.10	27.69	-0.66	1845.25	-66.99	90.00	–	104.48	-1.86	90.00	–
Exp	7.82	–	9.00	–	28.34	–	1912.23	–	90.00	–	106.34	–	90.00	–

TABLE S2: Atomic fractional coordinates (x_{GTS}, y_{GTS}, z_{GTS}) obtained using the GGA+TS exchange-correlation functional and a plane wave basis cutoff energy of 940 eV for the haloperidol crystal. The experimental values (x_{exp}, y_{exp}, z_{exp}) of Reed and Schaefer [1] are also shown for comparison.

Atom	X_{G-TS}	Y_{G-TS}	Z_{G-TS}	X_{exp}	Y_{exp}	Z_{exp}
Cl	0.775069	0.472008	0.463044	0.7799 (3)	0.4799 (2)	0.4625 (1)
F	-1.39655	0.573469	-0.02811	-1.3913 (5)	0.5558 (5)	-0.0277 (1)
O1	0.014219	0.697652	0.308364	0.0229 (4)	0.7050 (4)	0.3079 (1)
O2	-0.73429	0.605662	0.158232	-0.7452 (5)	0.6054 (5)	0.1607 (1)
N	-0.21201	0.426271	0.220546	-0.2119 (6)	0.4373 (4)	0.2233 (2)
C1	0.568642	0.485404	0.418648	0.5761 (8)	0.4926 (7)	0.4181 (2)
C2	0.535952	0.394934	0.375955	0.5417 (8)	0.4090 7)	0.3766 (2)
C3	0.375987	0.413008	0.339359	0.3845 (7)	0.4272 (6)	0.3401 (2)
C4	0.249331	0.520478	0.344499	0.2562 (7)	0.5291 (6)	0.3445 (2)
C5	0.284541	0.605613	0.388833	0.2932 (8)	0.6097 (7)	0.3878 (2)
C6	0.442692	0.58909	0.426091	0.4510 (9)	0.5933 (8)	0.4245 (2)
C7	0.075559	0.548203	0.304143	0.0938(7)	0.5533 (6)	0.3042 (2)
C8	-0.07154	0.442111	0.312615	-0.0635 (7)	0.4518 (6)	0.3128 (2)
C9	-0.24384	0.451335	0.271049	-0.2363 (7)	0.4622 (6)	0.2721 (2)
C10	-0.0808	0.537769	0.211734	-0.0804 (7)	0.5427 (5)	0.2144 (2)
C11	0.097405	0.522829	0.250496	0.0985 (7)	0.5282 (6)	0.2528 (2)
C12	-0.37853	0.442111	0.179855	-0.3791 (7)	0.4548 (6)	0.1838 (2)
C13	-0.53123	0.340964	0.186184	-0.5299 (7)	0.3541 (6)	0.1894 (2)
C14	-0.69509	0.344691	0.141374	-0.6897 (7)	0.3536 (6	0.1436 (2)
C15	-0.78893	0.495332	0.131821	-0.7941 (8)	0.4972 (7)	0.1337 (2)
C16	-0.95387	0.508977	0.089869	-0.9541 (7)	0.5065 (7)	0.0914 (2)
C17	-1.02673	0.388679	0.058194	-1.0181 (8)	0.3894 (7)	0.0603 (2)
C18	-1.17816	0.409174	0.018958	-1.1671 (9)	0.4041 (8)	0.0205 (2)
C19	-1.25436	0.55127	0.011932	-1.2505 (9)	0.5404 (10)	0 0128 (2)
C20	-1.19009	0.672442	0.043159	-1.1928 (10)	0.6572 (9)	0.0430 (3)
C21	-1.03859	0.649771	0.081944	-1.0451 (9)	0.6407 (7)	0.0818 (2)

TABLE S3: Haloperidol bond lengths and angles in the unit cell: GGA+TS 940 eV calculated and experimental values of Reed and Schaefer [1].

Bond	$(A\text{-}B)_{G\text{-}TS}$	$(A\text{-}C)_{G\text{-}TS}$	$[B\text{-}A\text{-}C]_{G\text{-}TS}$	$(A\text{-}B)_{exp}$	$(A\text{-}C)_{exp}$	$[B\text{-}A\text{-}C]_{exp}$
C2-C1-C6	1.39	1.39	121.28	1.36	1.38	120.12
C2-C1- Cl1	1.39	1.76	119.22	1.36	1.73	120.66
C6-C1- Cl1	1.39	1.76	119.47	1.38	1.73	119.17
C1-C2-C3	1.39	1.4	118.8	1.36	1.38	120.2
C2-C3-C4	1.4	1.4	121.56	1.38	1.39	121.7
C3-C4-C5	1.4	1.4	117.82	1.39	1.38	116.68
C3-C4-C7	1.4	1.54	123.11	1.39	1.47	121.11
C5-C4-C7	1.4	1.54	119.07	1.38	1.47	122.17
C4-C5-C6	1.4	1.39	121.7	1.38	1.38	122.14
C5-C6-C1	1.39	1.39	118.74	1.38	1.38	119.12
C4-C7-C8	1.54	1.54	109.9	1.47	1.6	109.26
C4-C7-C11	1.54	1.54	112.41	1.47	1.48	119.15
C4-C7- O1	1.54	1.43	109.93	1.47	1.49	109.84
C8-C7-C11	1.54	1.54	108.42	1.6	1.48	107.11
C8-C7- O1	1.54	1.43	106.58	1.6	1.49	101.23
C11-C7- O1	1.54	1.43	109.42	1.48	1.49	108.73
C7-C8-C9	1.54	1.53	113.28	1.6	1.51	114.02
C8-C9-N1	1.53	1.49	111.88	1.51	1.47	112.65
C11-C10-N1	1.52	1.48	111.44	1.52	1.47	111.8
C10-C11-C7	1.52	1.54	111.03	1.52	1.48	114.78
C13-C12-N1	1.53	1.49	114.11	1.53	1.47	113.78
C12-C13-C14	1.53	1.53	113.87	1.53	1.53	112.53
C13-C14-C15	1.53	1.52	115.04	1.53	1.47	113.88
C14-C15-C16	1.52	1.5	119.02	1.47	1.52	118.52
C14-C15- O2	1.52	1.23	121.58	1.47	1.22	123.72
C16-C15- O2	1.5	1.23	119.38	1.52	1.22	117.25
C15-C16-C17	1.5	1.41	123.25	1.52	1.37	122.89
C15-C16-C21	1.5	1.41	117.85	1.52	1.39	119.21
C17-C16-C21	1.41	1.41	118.9	1.37	1.39	117.82
C16-C17-C18	1.41	1.39	120.63	1.37	1.38	121.45
C17-C18-C19	1.39	1.39	118.26	1.38	1.38	117.88
C18-C19-C20	1.39	1.39	123.12	1.38	1.35	122.25
C18-C19- F1	1.39	1.36	118.3	1.38	1.36	117.43
C20-C19- F1	1.39	1.36	118.57	1.35	1.36	120.28
C19-C20-C21	1.39	1.39	117.67	1.35	1.36	118.94
C16-C21-C20	1.41	1.39	121.37	1.39	1.36	121.65
C10-N1-C12	1.48	1.49	108.35	1.47	1.47	108.38
C10-N1-C9	1.48	1.49	109.39	1.47	1.47	110.3
C12-N1-C9	1.49	1.49	111.89	1.47	1.47	112.23

TABLE S4: Atomic coordinates of isolated Haloperidol molecule

Atom	x	y	z	Atom	x	y	z
C1	11.767	0.069	22.389	F1	-2.949	-0.557	13.789
C2	11.530	0.863	21.269	H27	12.261	1.600	20.938
C3	10.337	0.692	20.563	H28	10.170	1.316	19.686
C4	9.387	-0.264	20.950	H29	8.918	-1.763	22.416
C5	9.645	-1.016	22.105	H30	11.012	-1.465	23.715
C6	10.823	-0.857	22.833	H31	6.768	0.171	21.752
C7	8.084	-0.514	20.178	H32	7.351	1.458	20.687
C8	6.979	0.425	20.702	H33	5.201	-0.645	20.059
C9	5.684	0.339	19.898	H34	4.998	1.111	20.265
C10	6.901	-0.429	17.949	H35	7.022	-0.260	16.873
C11	8.241	-0.285	18.662	H36	6.508	-1.455	18.077
C12	4.662	0.410	17.657	H37	8.961	-1.001	18.245
C13	3.521	1.317	18.120	H38	8.633	0.722	18.459
C14	2.303	1.311	17.191	H39	4.326	-0.642	17.687
C15	1.573	-0.015	17.089	H40	4.918	0.639	16.610
C16	0.342	-0.098	16.242	H41	3.188	1.019	19.124
C17	-0.163	0.994	15.514	H42	3.885	2.353	18.195
C18	-1.290	0.582	14.707	H43	1.567	2.048	17.555
C19	-1.896	-0.356	14.640	H44	2.583	1.634	16.176
C20	-1.458	-1.493	15.375	H45	0.337	1.962	15.547
C21	-0.330	-1.332	16.168	H46	-1.670	1.679	14.117
O1	7.630	-1.847	20.411	H47	-1.973	-2.450	15.107
O2	1.956	-1.013	17.701	H48	0.059	-2.171	16.741
Cl1	13.304	0.207	23.227	H49	8.217	-2.475	19.886

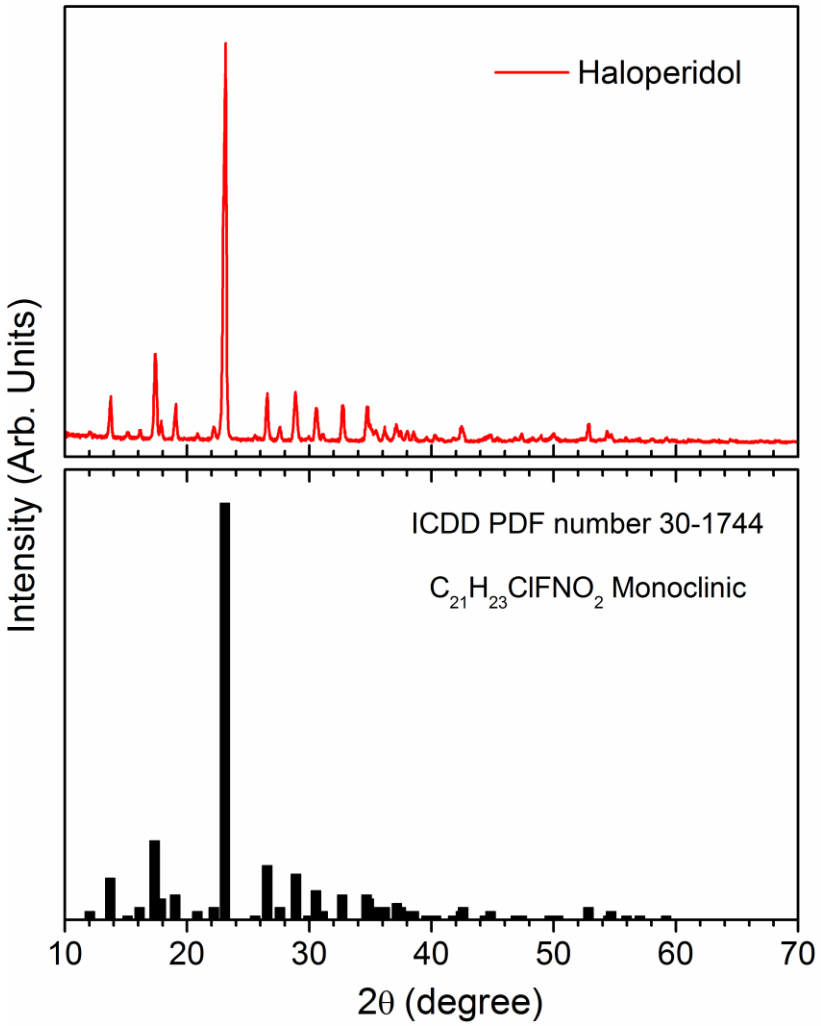

FIGURE S1: X-ray diffraction data of haloperidol sample.

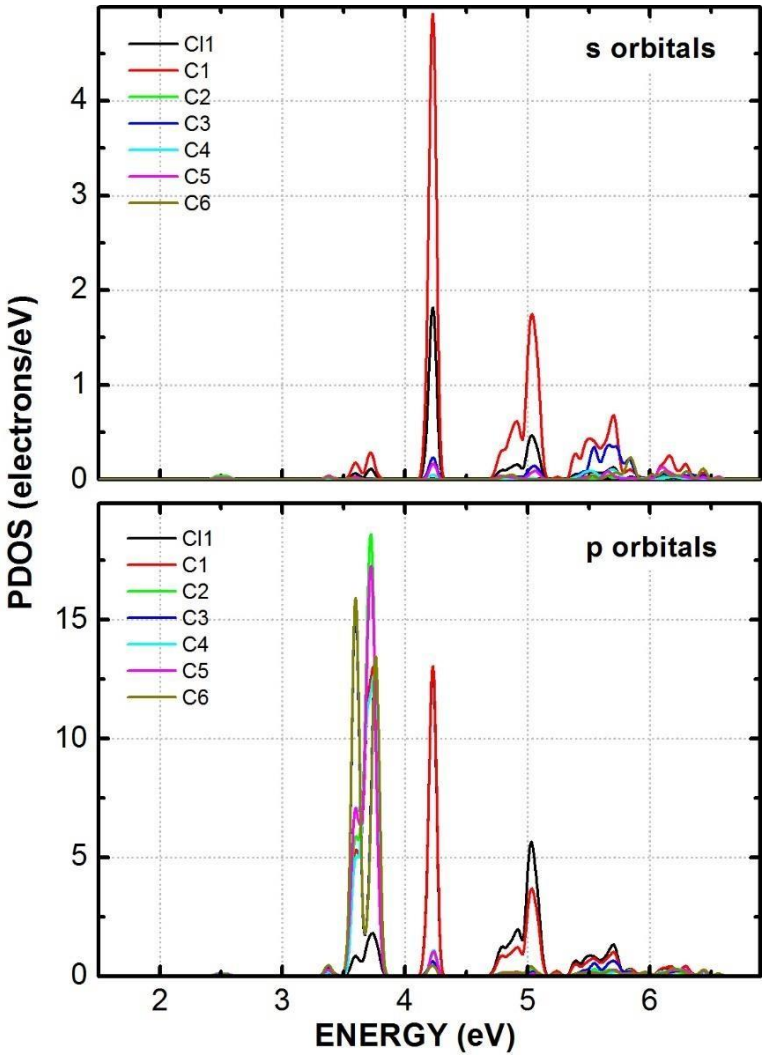

FIGURE S2: Partial density of states of haloperidol 4-clorophenyl fragment (region i) showing the s state and p state contributions of each atom at the conduction band (energy range between 1.5 and 6.9 eV).

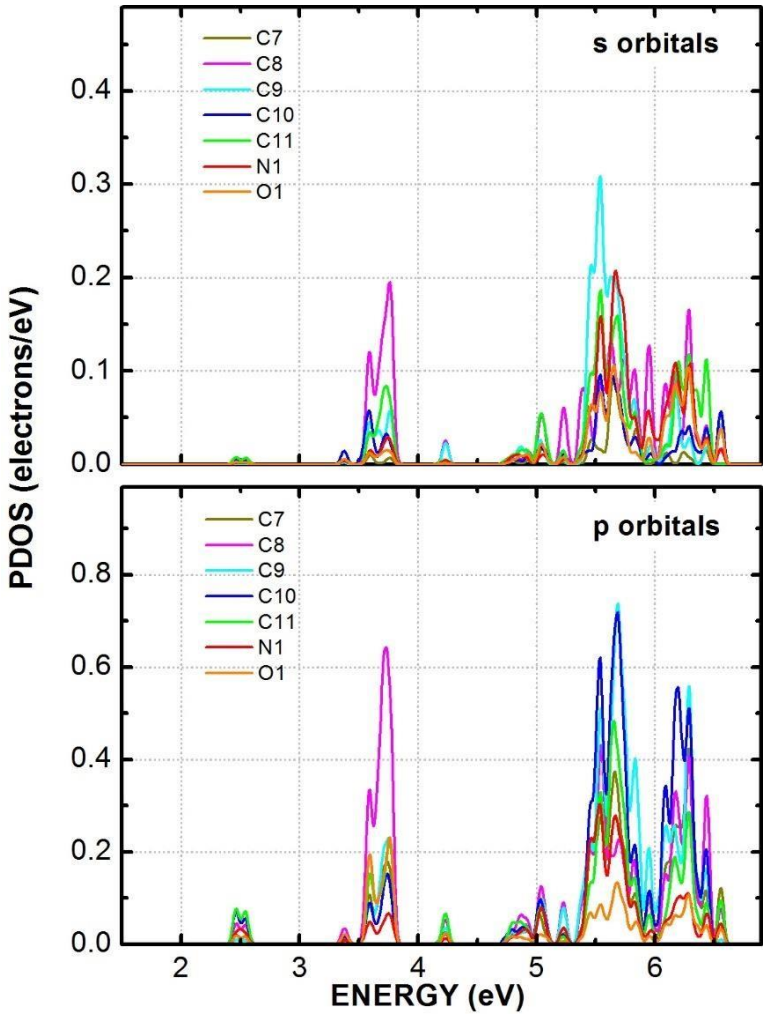

FIGURE S3: Partial density of states of haloperidol 4-hydroxypiperidin-1-yl fragment (region ii) showing the s state and p state contributions of each atom at the conduction band (energy range between 1.5 and 6.9 eV).

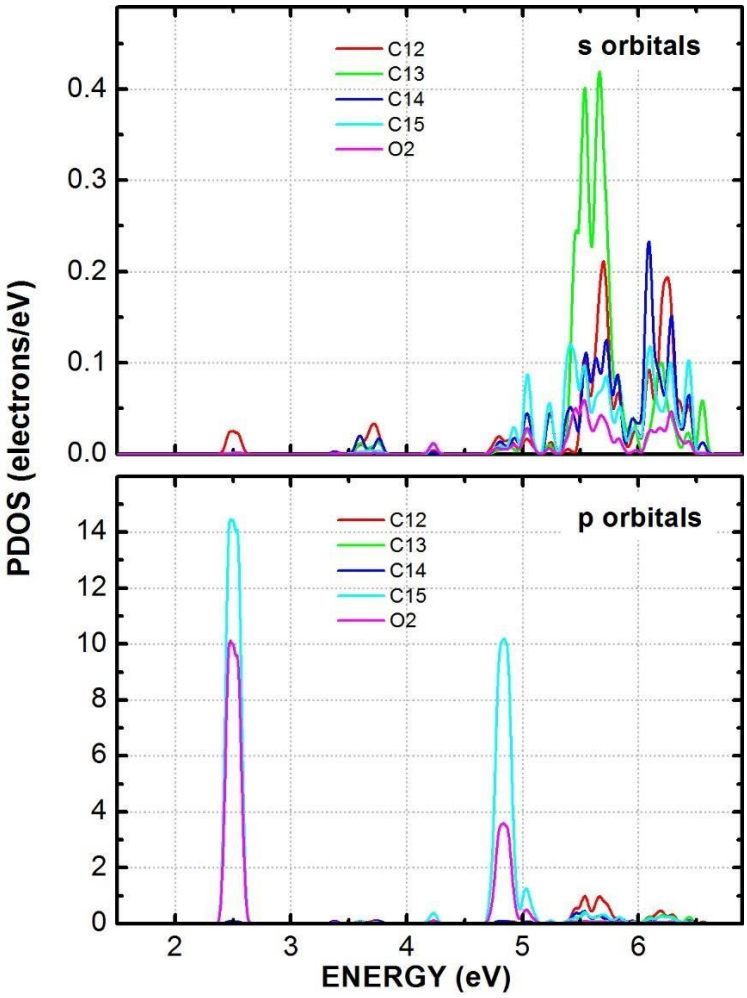

FIGURE S4: Partial density of states of haloperidol butan-1-one fragment (region iii) showing the s state and p state contributions of each atom at the conduction band (energy range between 1.5 and 6.9 eV).

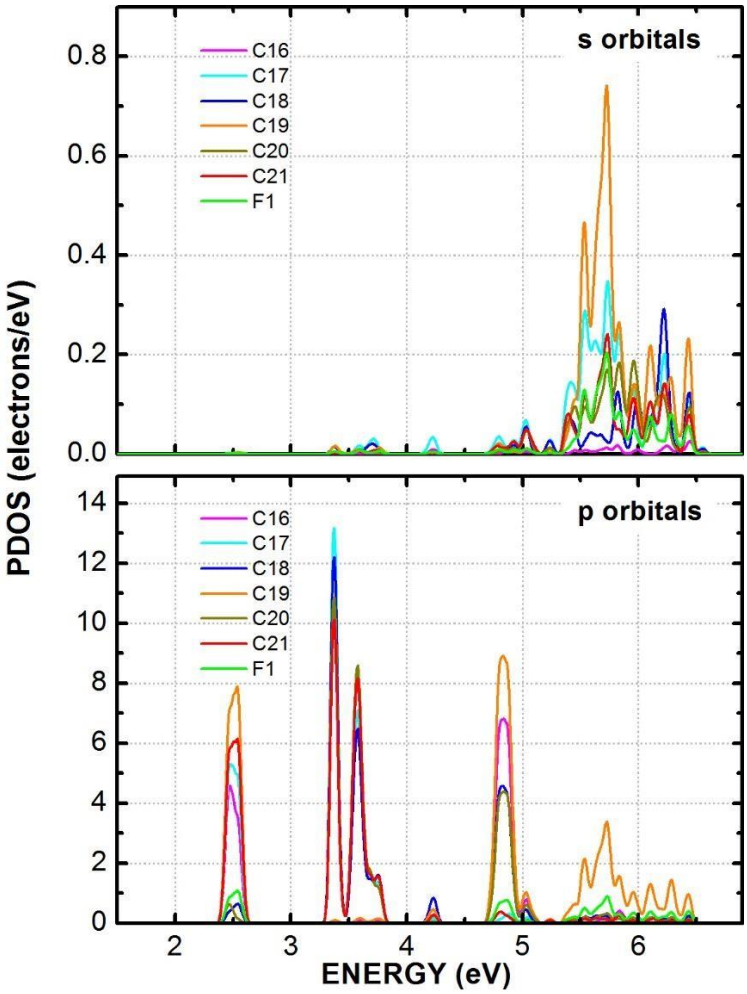

FIGURE S5: Partial density of states of haloperidol 4-fluorophenyl fragment (region iv) showing the s state and p state contributions of each atom at the conduction band (energy range between 1.5 and 6.9 eV).

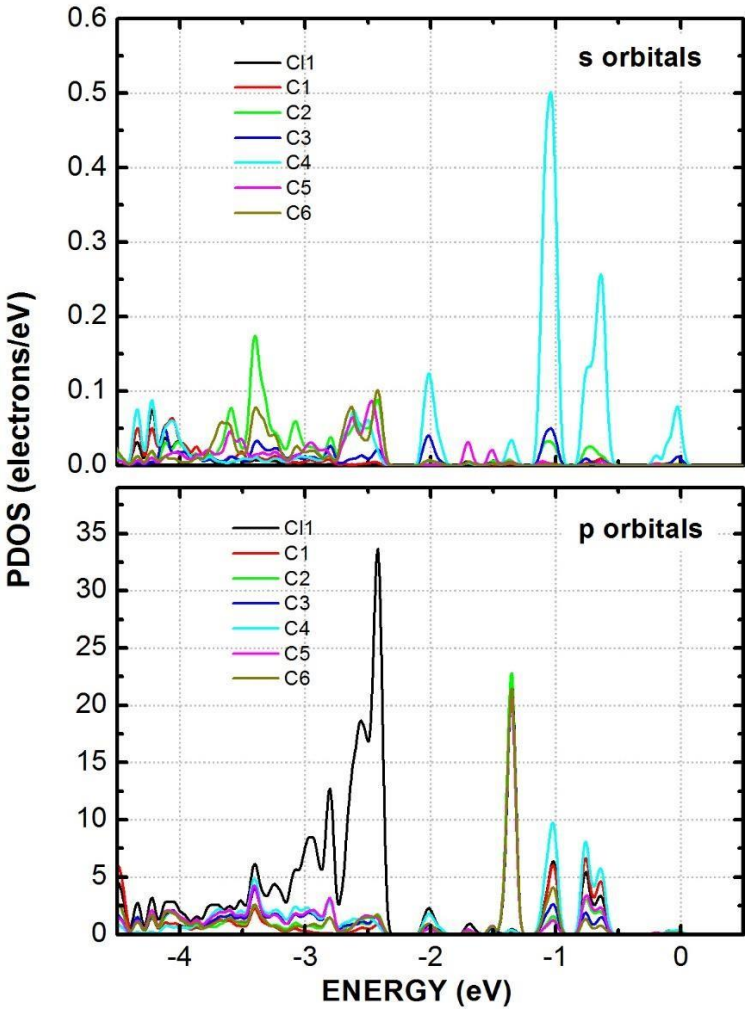

FIGURE S6: Partial density of states of haloperidol 4-clorophenyl fragment (region i) showing the s state and p state contributions of each atom at the valence band (energy range between -4.5 and 0.0 eV).

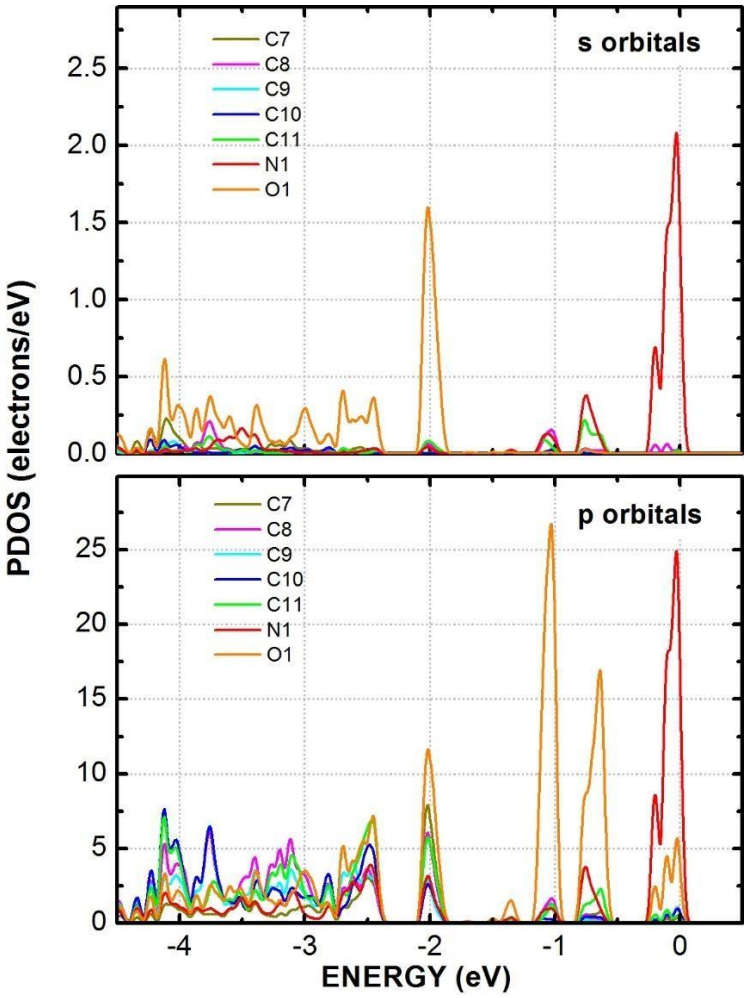

FIGURE S7: Partial density of states of haloperidol 4-hydroxypiperidin-1-yl fragment (region ii) showing the s state and p state contributions of each atom at the valence band (energy range between -4.5 and 0.0 eV).

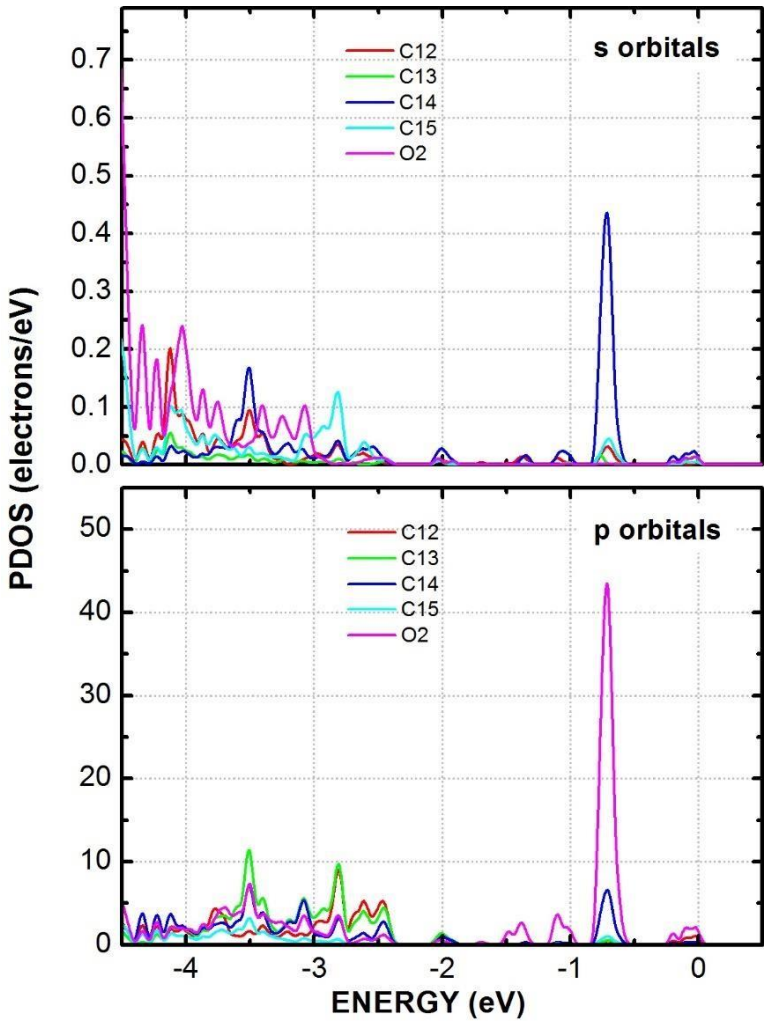

FIGURE S8: Partial density of states of haloperidol butan-1-one fragment (region iii) showing the s state and p state contributions of each atom at the valence band (energy range between -4.5 and 0.0 eV).

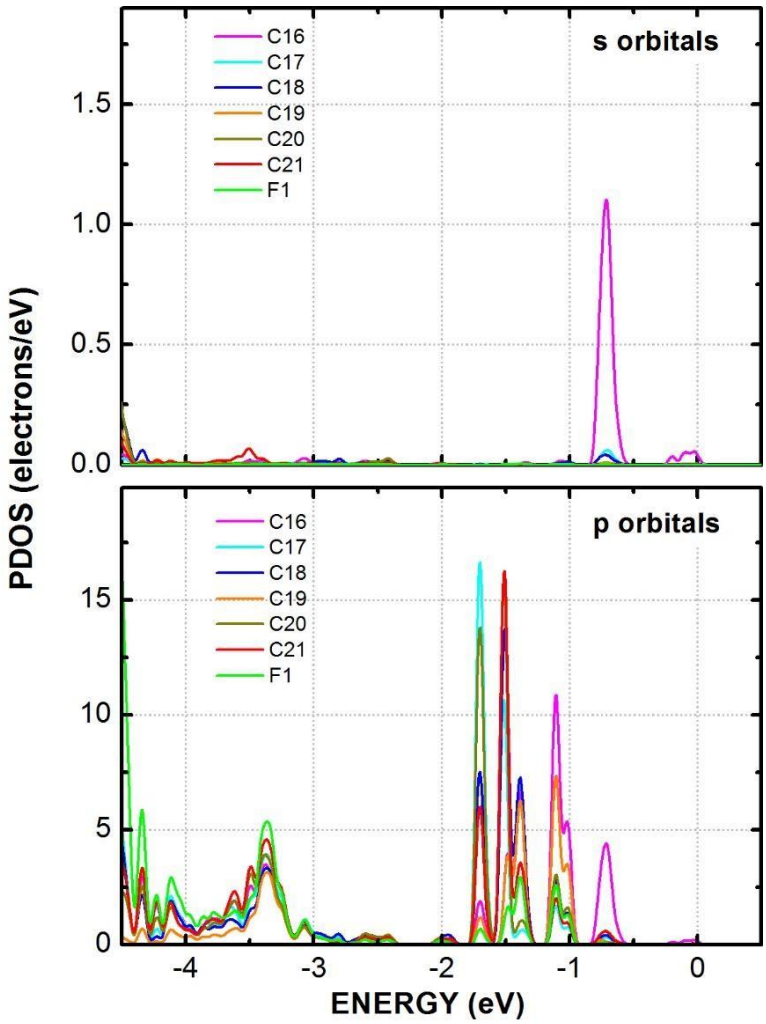

FIGURE S9: Partial density of states of haloperidol 4-fluorophenyl fragment (region iv) showing the s state and p state contributions of each atom at the valence band (energy range between -4.5 and 0.0 eV).

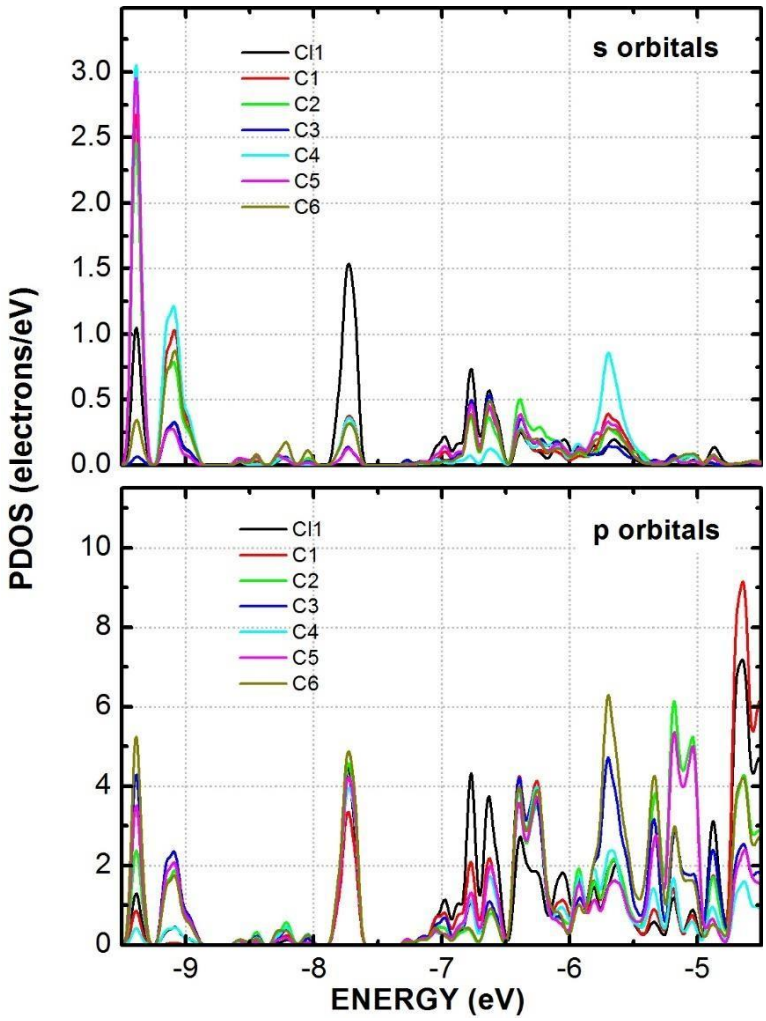

FIGURE S10: Partial density of states of haloperidol 4-clorophenyl fragment (region i) showing the s state and p state contributions of each atom at the valence band (energy range between -9.5 and -4.5 eV).

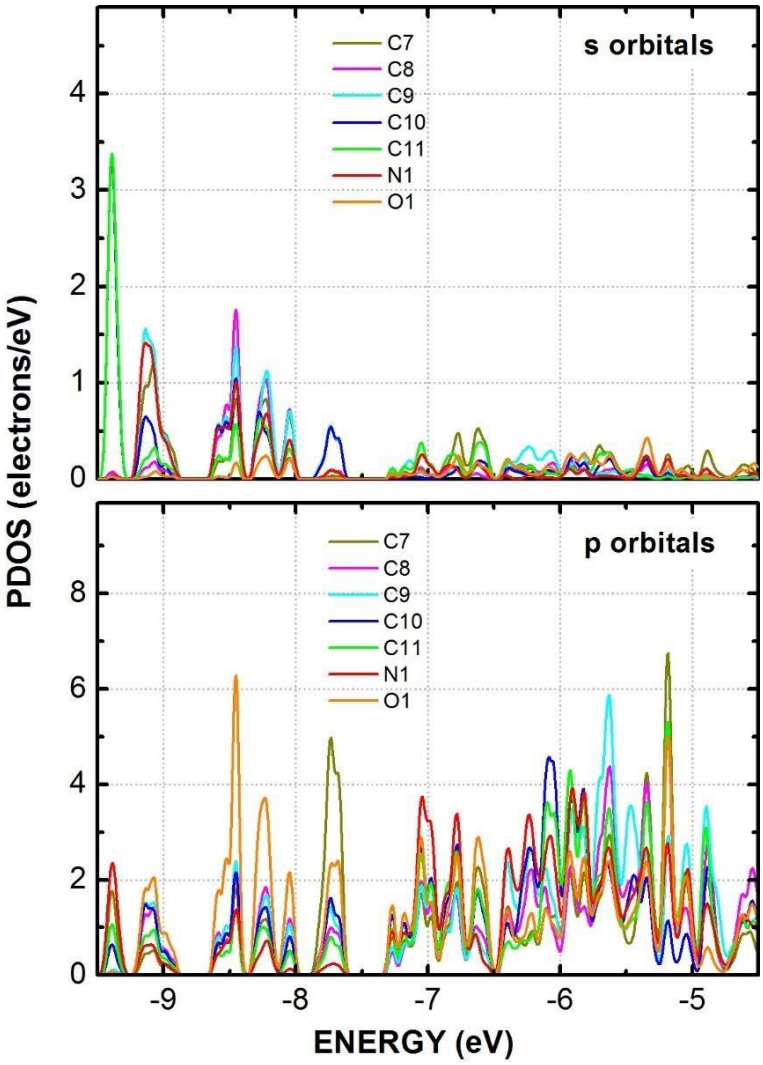

FIGURE S11: Partial density of states of haloperidol 4-hydroxypiperidin-1-yl fragment (region ii) showing the s state and p state contributions of each atom at the valence band (energy range between -9.5 and -4.5 eV).

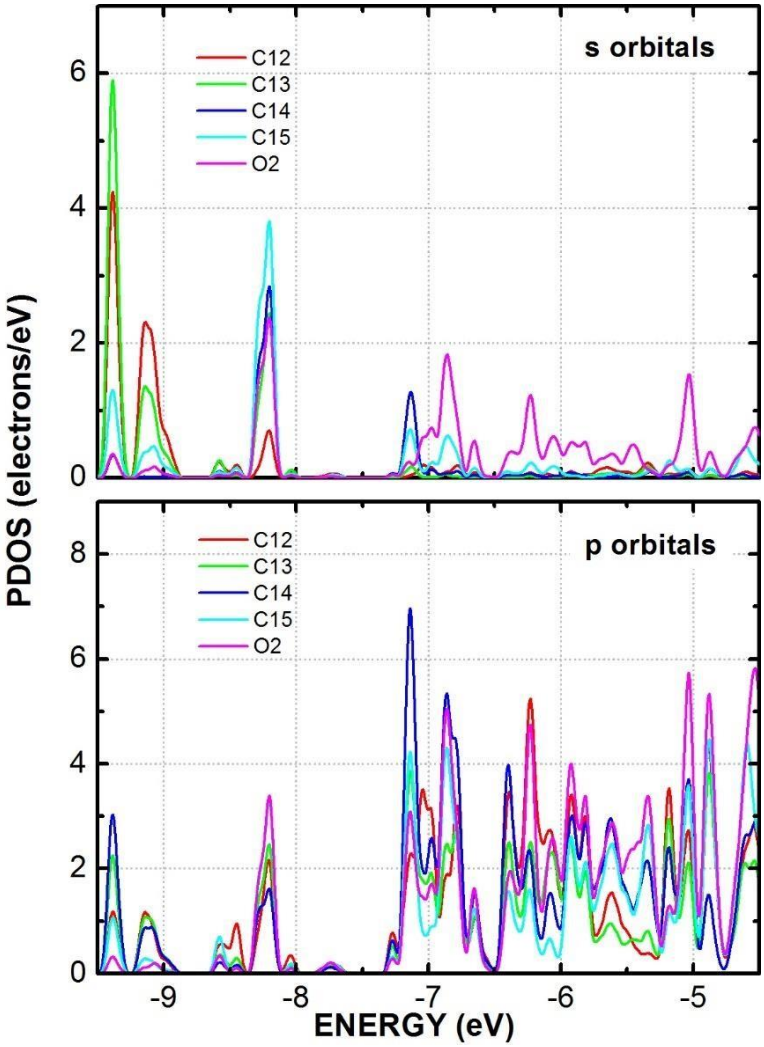

FIGURE S12: Partial density of states of haloperidol butan-1-one fragment (region iii) showing the s state and p state contributions of each atom at the valence band (energy range between -9.5 and -4.5 eV).

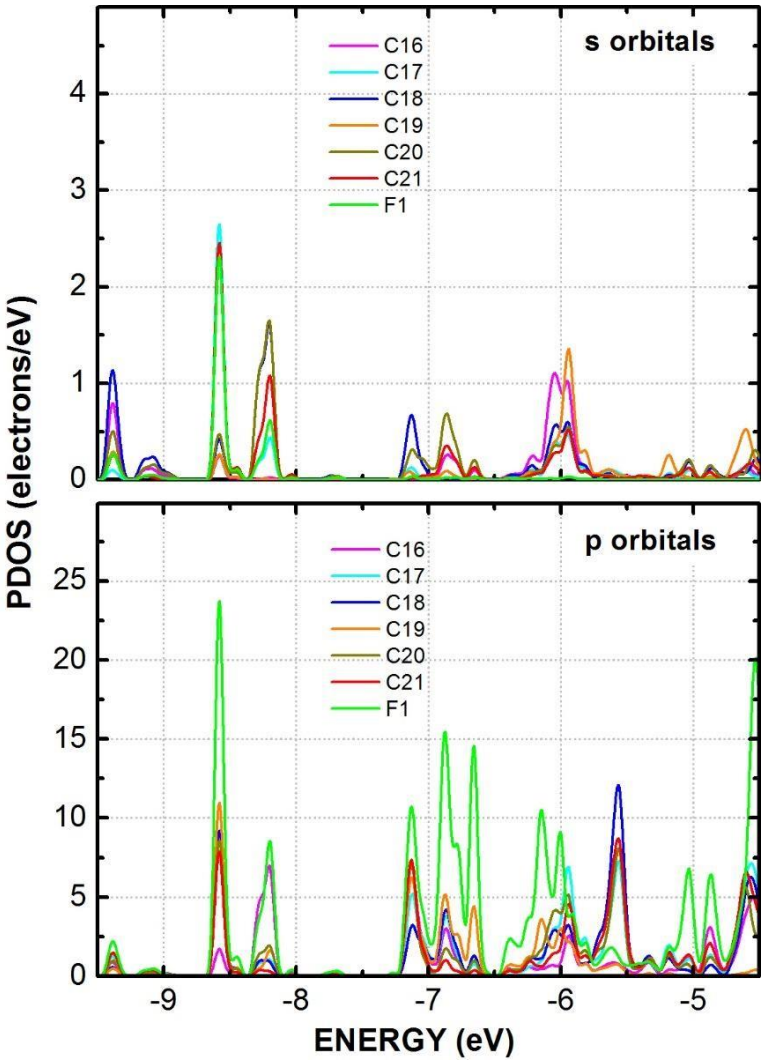

FIGURE S13: Partial density of states of haloperidol 4-fluorophenyl fragment (region iv) showing the s state and p state contributions of each atom at the valence band (energy range between -9.5 and -4.5 eV).

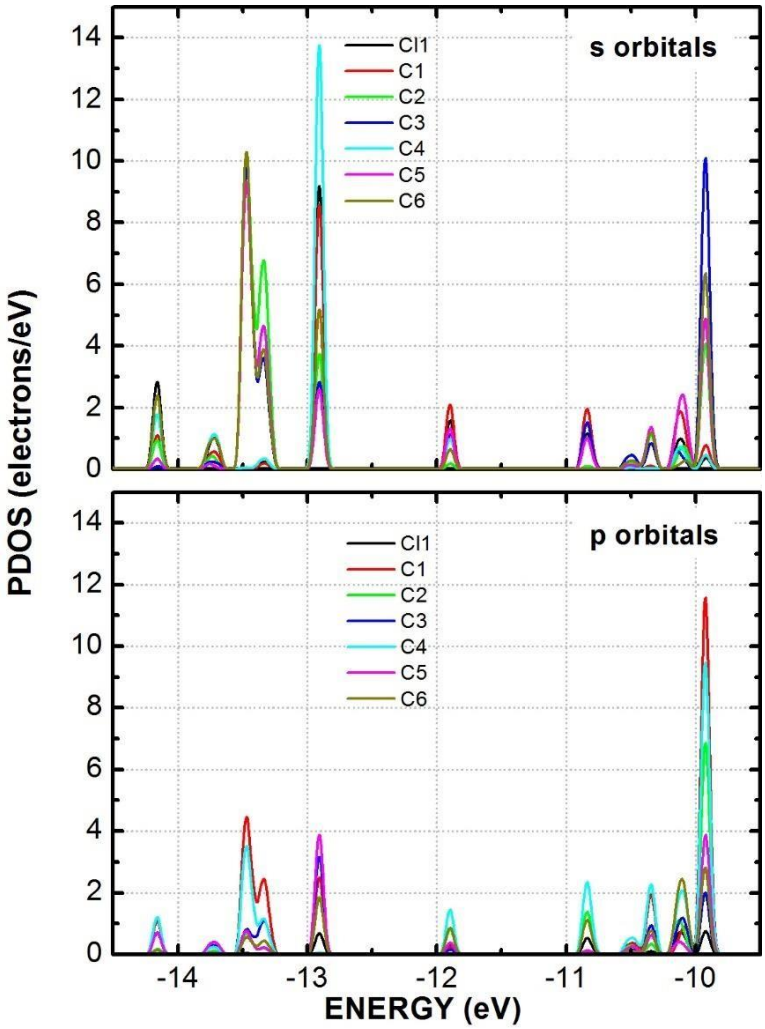

FIGURE S14: Partial density of states of haloperidol 4-clorophenyl fragment (region i) showing the s state and p state contributions of each atom at the valence band (energy range between -14.5 and -9.5 eV).

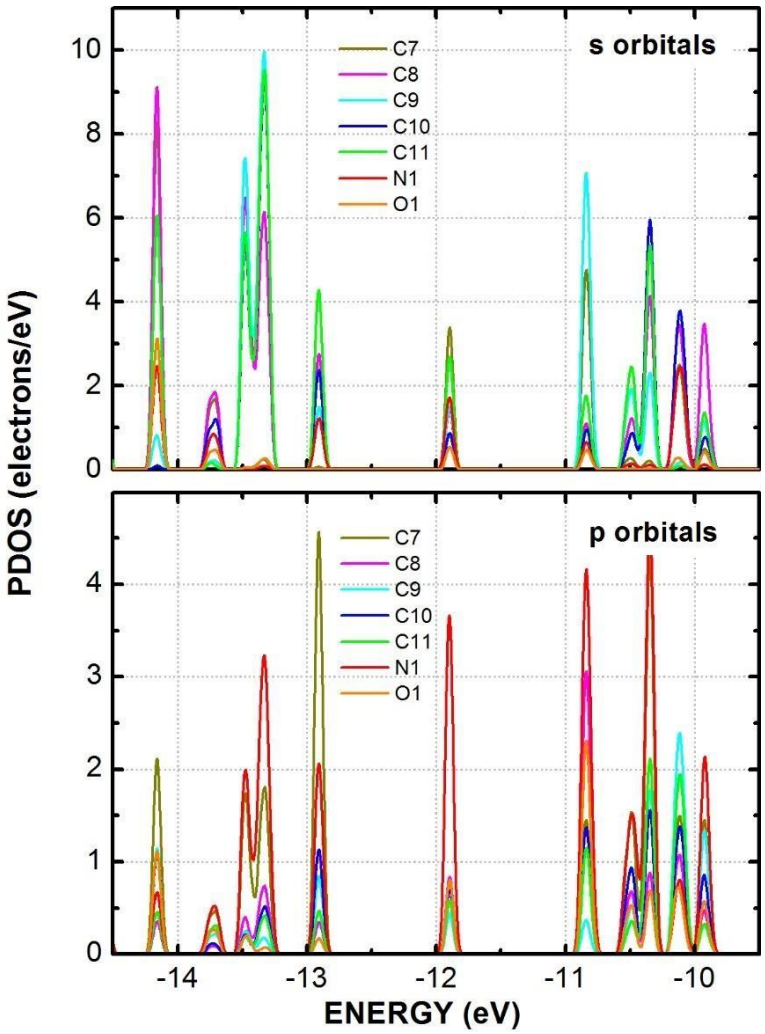

FIGURE S15: Partial density of states of haloperidol 4-hydroxypiperidin-1-yl fragment (region ii) showing the s state and p state contributions of each atom at the valence band (energy range between -14.5 and -9.5 eV).

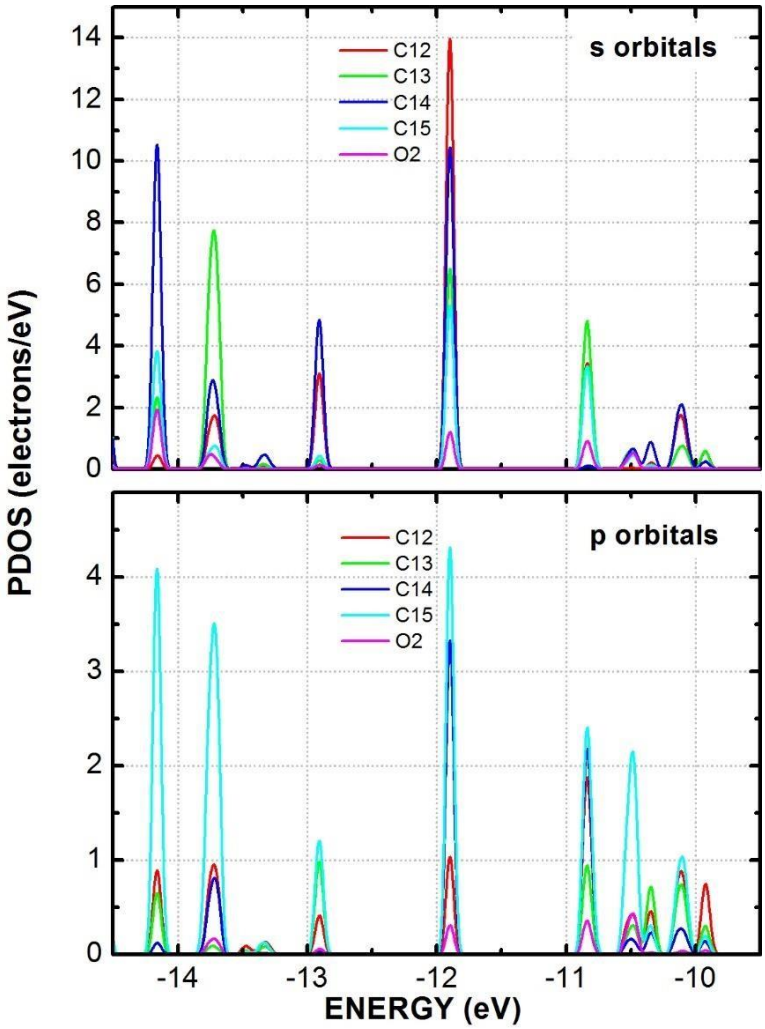

FIGURE S16: Partial density of states of haloperidol butan-1-one fragment (region iii) showing the s state and p state contributions of each atom at the valence band (energy range between -14.5 and -9.5 eV).

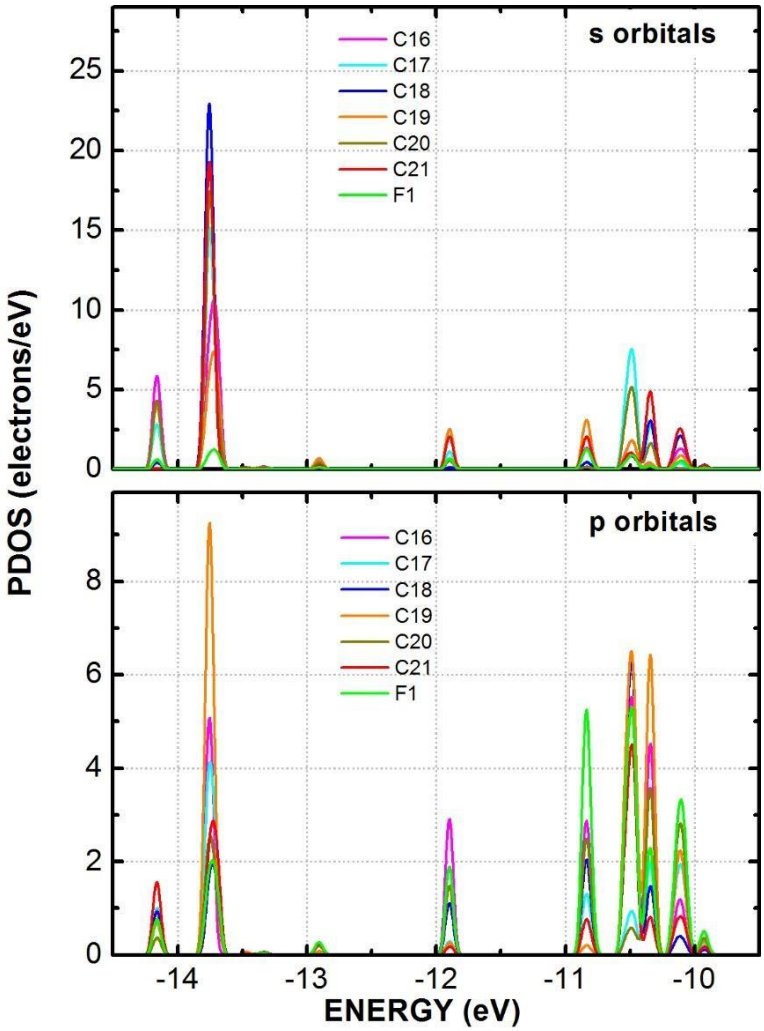

FIGURE S17: Partial density of states of haloperidol 4-fluorophenyl fragment (region iv) showing the s state and p state contributions of each atom at the valence band (energy range between -14.5 and -9.5 eV).

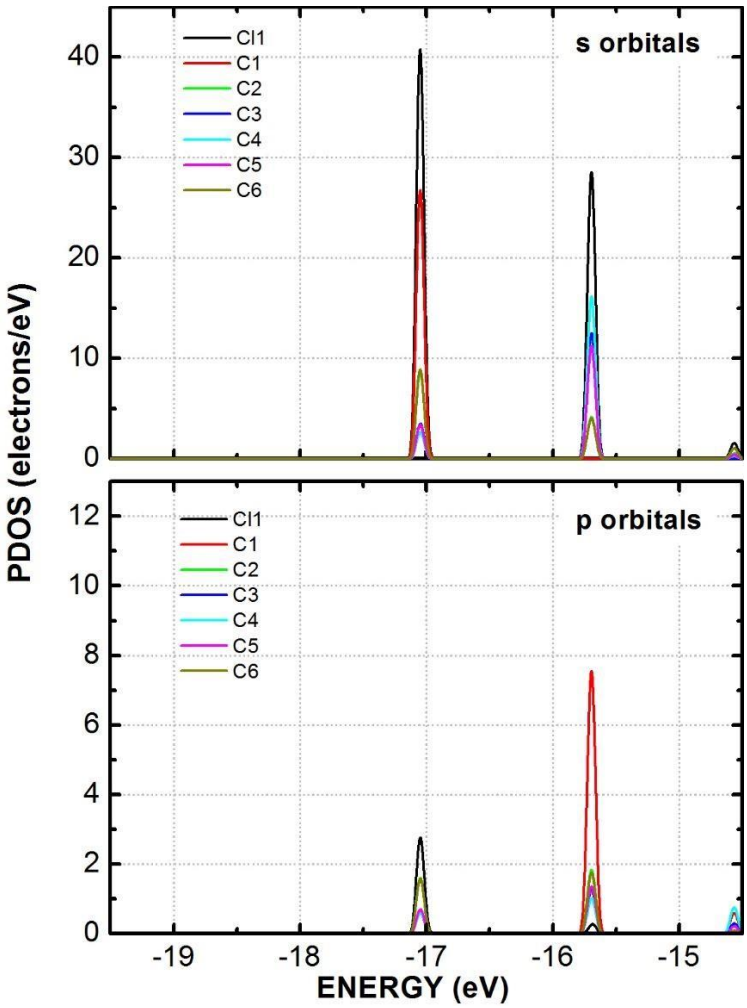

FIGURE S18: Partial density of states of haloperidol 4-clorophenyl fragment (region i) showing the s state and p state contributions of each atom at the valence band (energy range between -19.5 and -14.5 eV).

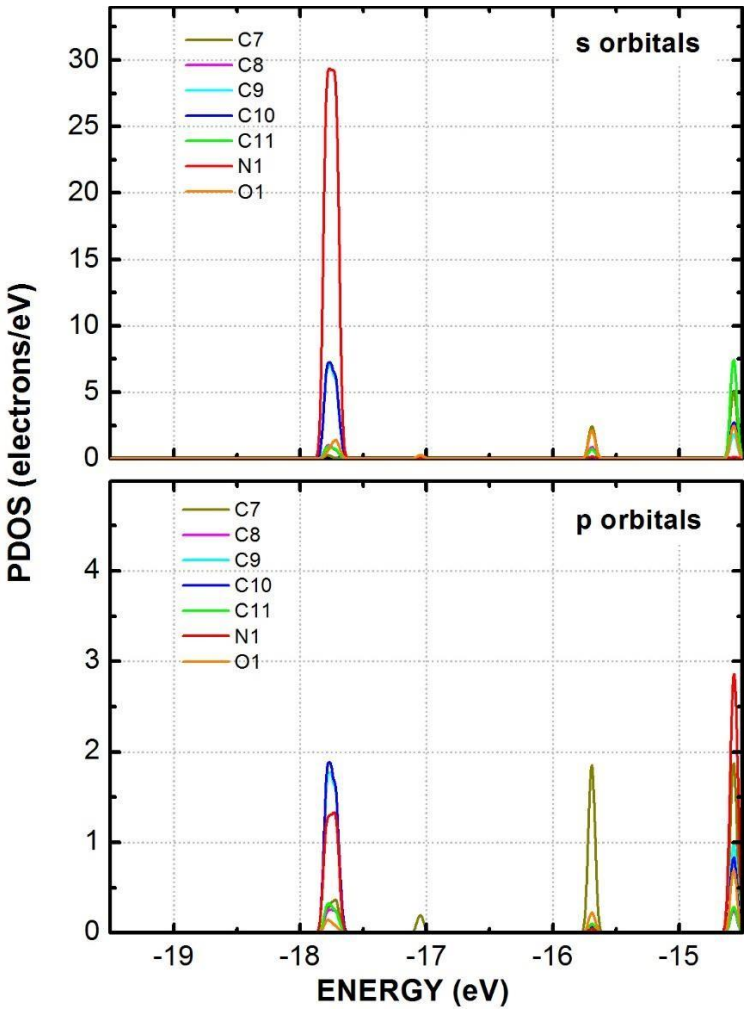

FIGURE S19: Partial density of states of haloperidol 4-hydroxypiperidin-1-yl fragment (region ii) showing the s state and p state contributions of each atom at the valence band (energy range between -19.5 and -14.5 eV).

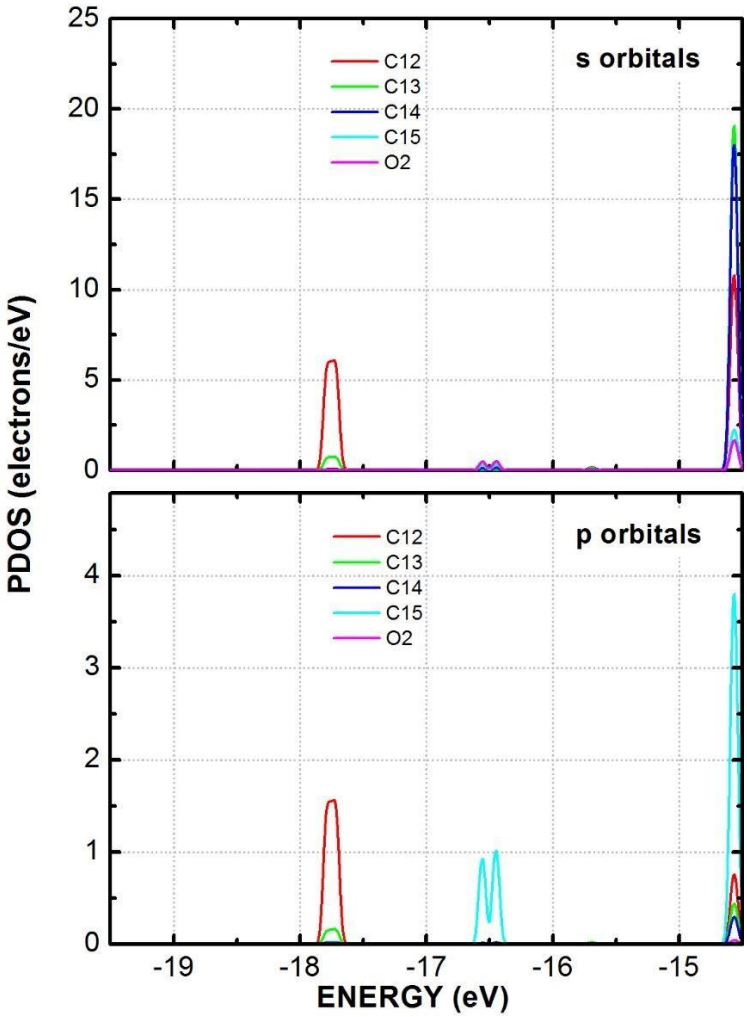

FIGURE S20: Partial density of states of haloperidol butan-1-one fragment (region iii) showing the s state and p state contributions of each atom at the valence band (energy range between -19.5 and -14.5 eV).

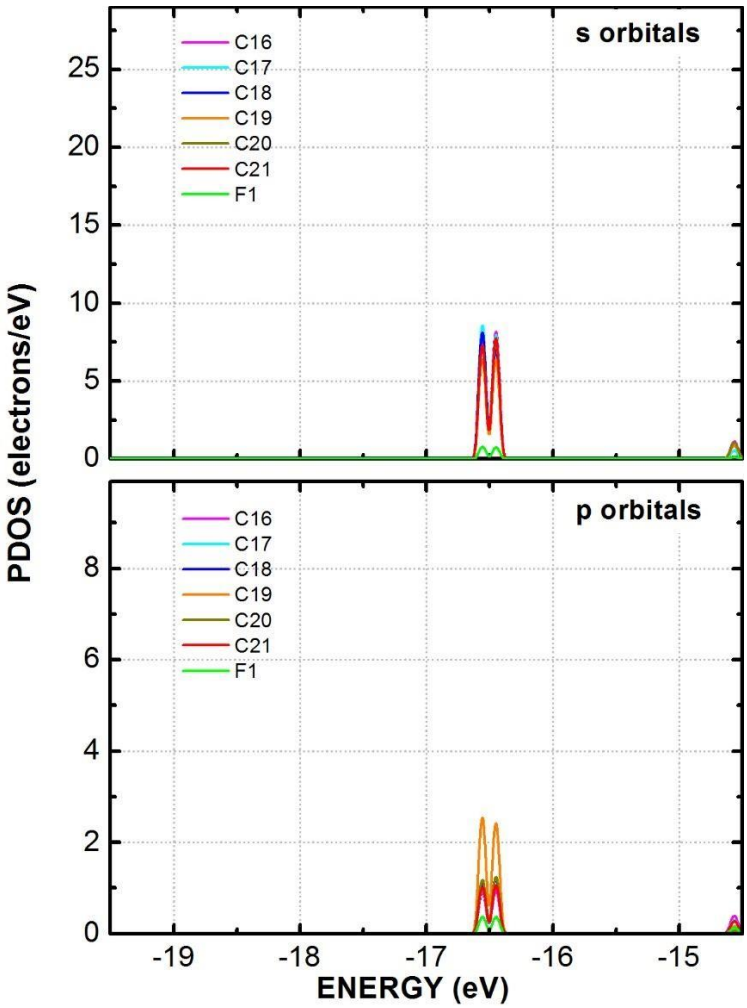

FIGURE S21: Partial density of states of haloperidol 4-fluorophenyl fragment (region iv) showing the s state and p state contributions of each atom at the valence band (energy range between -19.5 and -14.5 eV).

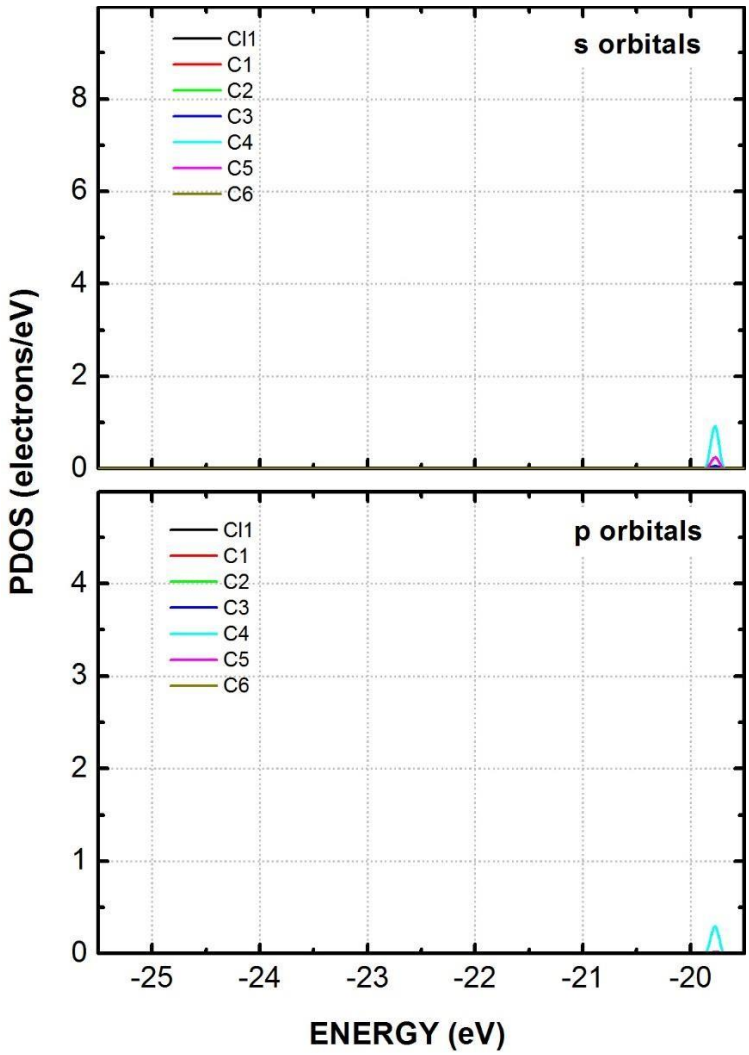

FIGURE S22: Partial density of states of haloperidol 4-clorophenyl fragment (region i) showing the s state and p state contributions of each atom at the valence band (energy range between -25.5 and -19.5 eV).

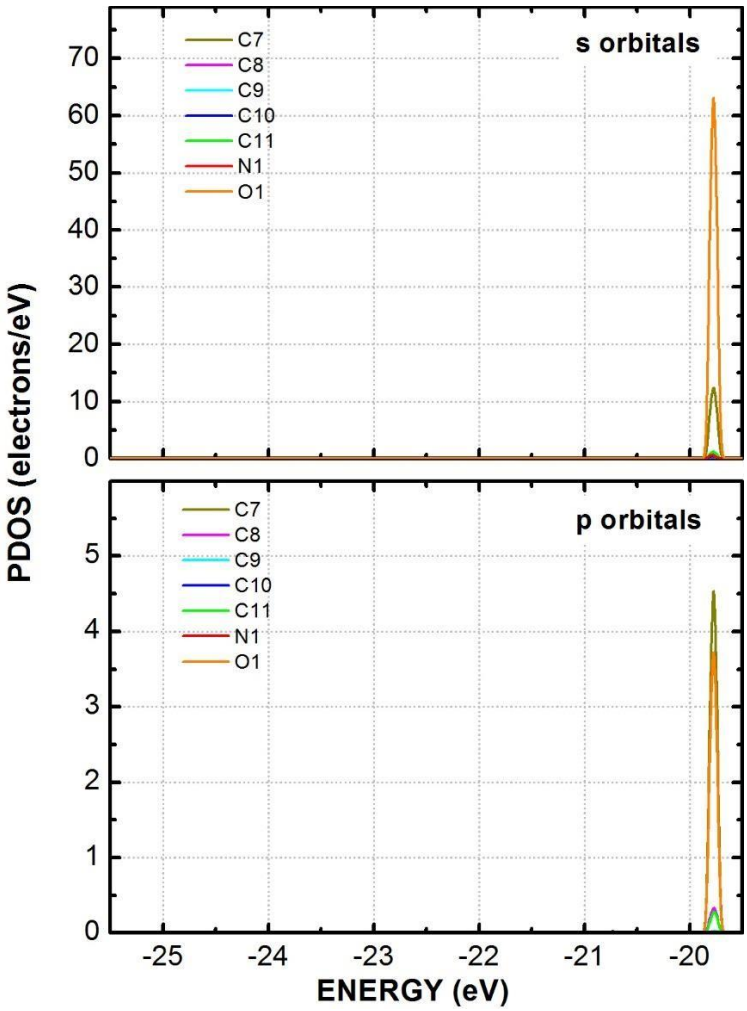

FIGURE S23: Partial density of states of haloperidol 4-hydroxypiperidin-1-yl fragment (region ii) showing the s state and p state contributions of each atom at the valence band (energy range between -25.5 and -19.5 eV).

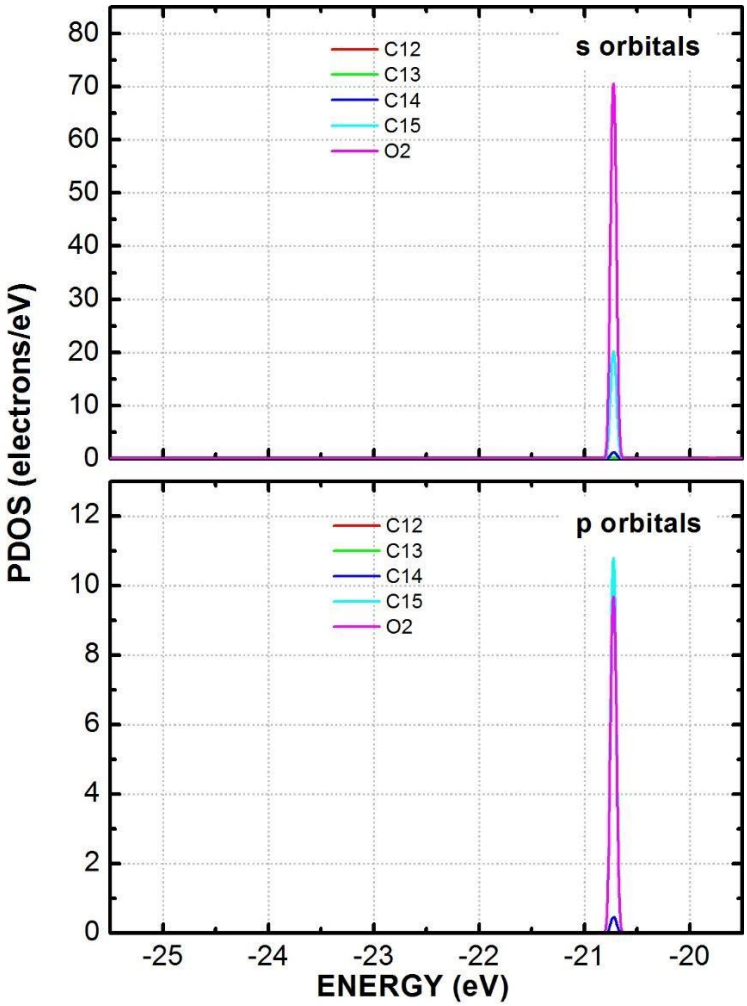

FIGURE S24: Partial density of states of haloperidol butan-1-one fragment (region iii) showing the s state and p state contributions of each atom at the valence band (energy range between -25.5 and -19.5 eV).

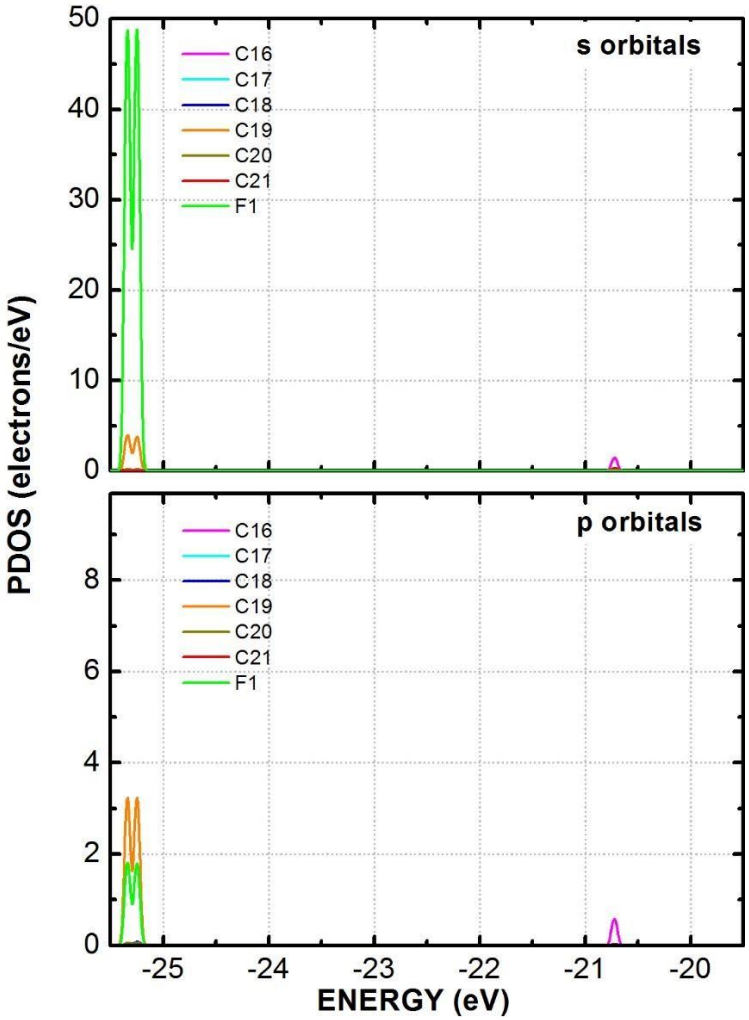

FIGURE S25: Partial density of states of haloperidol 4-fluorophenyl fragment (region iv) showing the s state and p state contributions of each atom at the valence band (energy range between -25.5 and -19.5 eV).

References

1 L. L. Reed and J. P. Schaefer, *Acta Crystallogr. Sect. B*, 1973, **29**, 1886–1890.