Supplementary Information: Symmetry and reactivity of π-systems in electric and magnetic fields: a perspective from conceptual DFT

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S1 Electron densities of $[H_2CO]^-$ anion and density difference plots

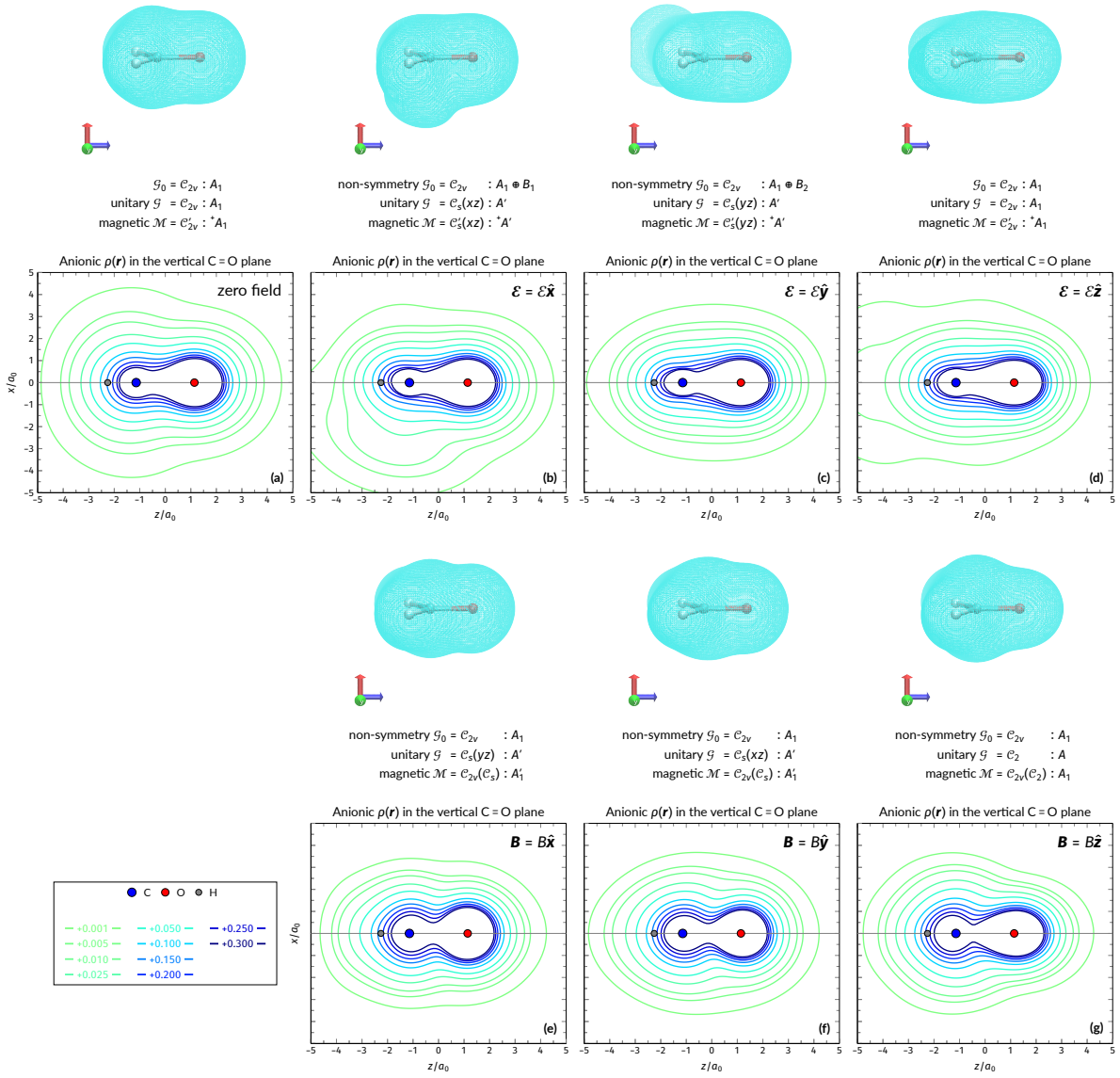
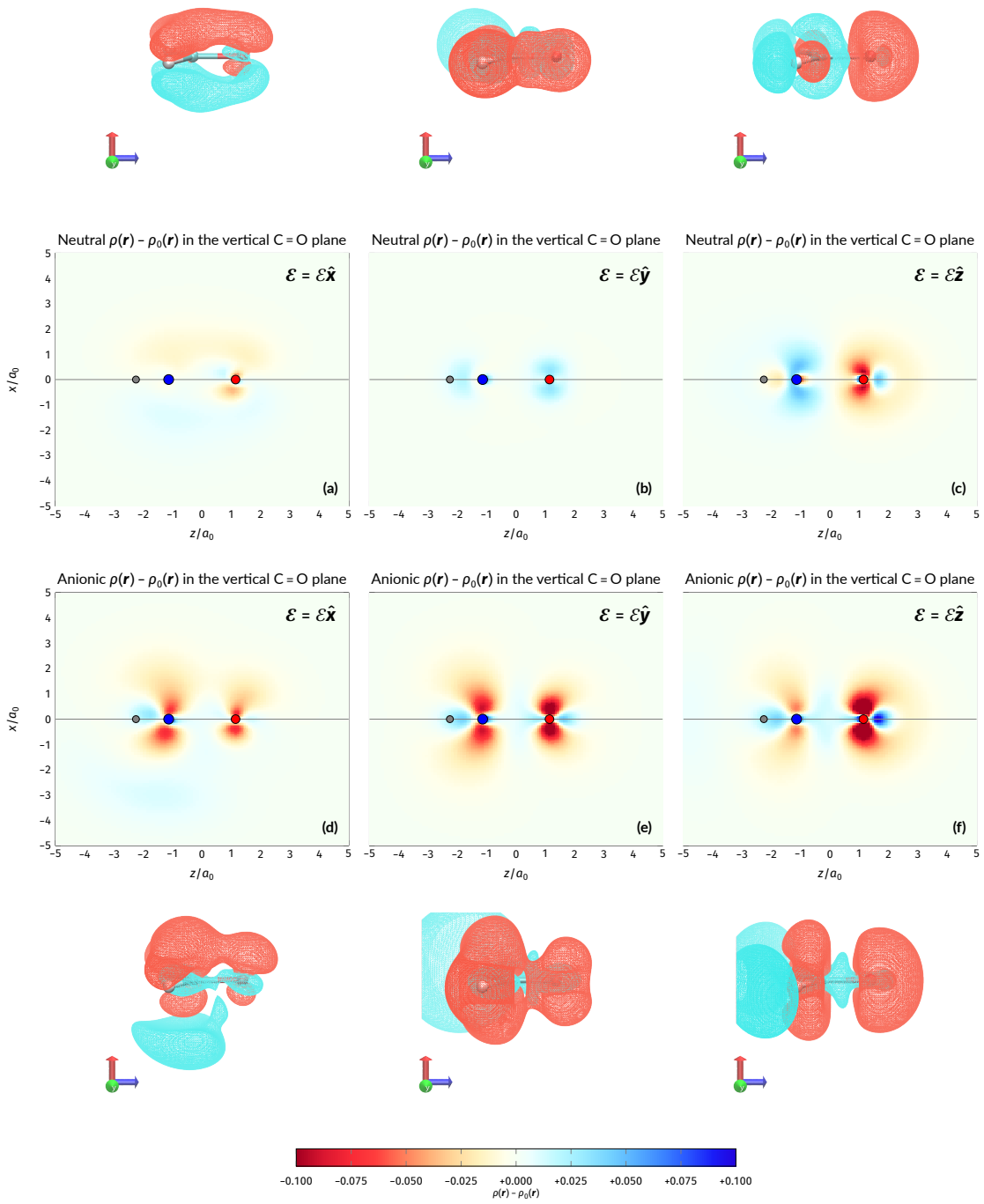


Figure S1: Contour plots of the electron density $\rho(\mathbf{r})$ of the $[H_2CO]^-$ anion in various external-field configurations. Above each plot are the three-dimensional isosurface of the corresponding electron density at isovalue $\rho(\mathbf{r}) = 0.01$ and the representations spanned by $\rho(\mathbf{r})$ and its symmetry partners in various groups as determined by QSym^2 (see also Appendix B in the main text for relevant character tables). Magnetic symmetries in $\mathcal{M}$ are given in terms of its irreducible representations since electron densities are real-valued (*cf.* Section 2.3.3.2 in the main text). All electron densities were calculated at the r^{2}SCAN0/cc-pVTZ level. The electric field strength $\mathcal{E}$ is set at 0.1 a.u. and the magnetic field strength B at $1.0B_0$.



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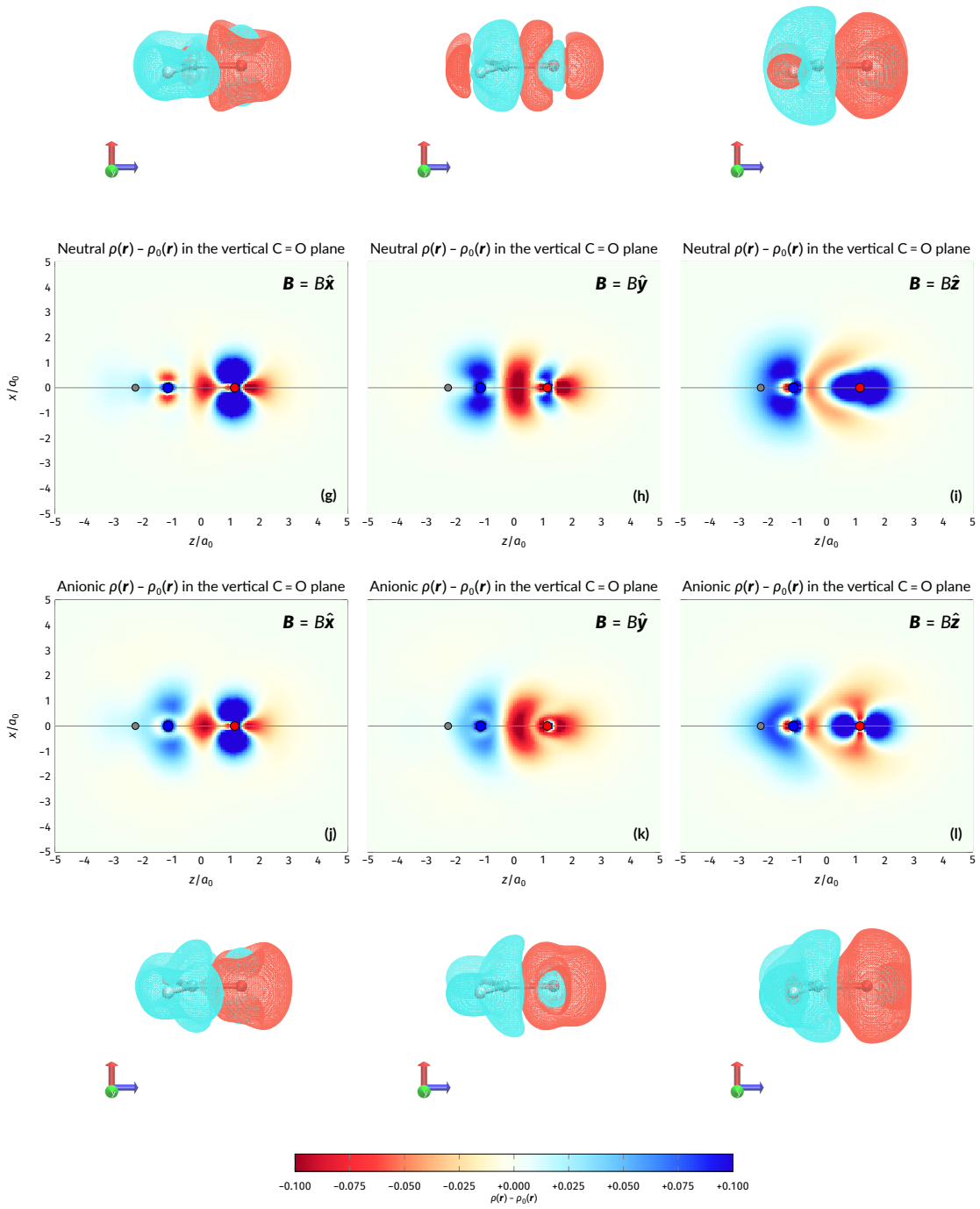

Figure S2: Density difference plots in various external-field configurations. Each plot shows the difference $\rho(\mathbf{r}) - \rho_0(\mathbf{r})$ in the vertical C=O plane with $\rho(\mathbf{r})$ the density of either the neutral species or the anionic one in the given field, and $\rho_0(\mathbf{r})$ the corresponding density at zero field. Each plot is also accompanied by an isosurface of the density difference shown at $|\rho(\mathbf{r}) - \rho_0(\mathbf{r})| = 0.005$.

S2 Analysis results for HFCO

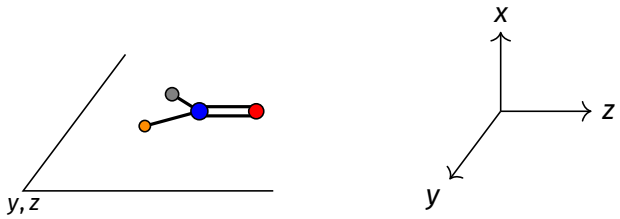

Figure S3: Geometrical arrangement of HFCO in all calculations. The molecule lies in the yz-plane with the C=O bond aligning with the z-axis. H: grey, C: blue, O: red, F: orange.

S2.1 Symmetry constraints on electric dipole moments

Table S1: Symmetry groups and allowed electric dipole components $\boldsymbol{\mu}$ of HFCO in external electric or magnetic fields. The allowed electric dipole components are those that are not constrained to vanish by the corresponding symmetry group. The geometrical arrangement of the HFCO molecule is given in Figure S3. $\mathcal{G}$ gives the unitary symmetry group of the molecule-plus-field system and $\mathcal{M}$ the magnetic symmetry group (*cf.* Section 2.2.1 in the main text). In the absence of an external magnetic field, $\mathcal{M}$ is a grey group as denoted by the dash [Equation (24) in the main text]. Character tables for all groups as generated by QSym^2 are given in Appendix B in the main text. Note that in the $\mathbf{B} = B\hat{\mathbf{x}}$ case, the system has no magnetic group due to the lack of time-reversed symmetry operations.

Field	$\mathcal{G}$	Allowed $\boldsymbol{\mu}$	$\mathcal{M}$	Allowed $\boldsymbol{\mu}$
$\mathbf{0}$	$\mathcal{C}_s(yz)$	μ_y, μ_z	$\mathcal{C}_s'(yz)$	μ_y, μ_z
$\boldsymbol{\mathcal{E}} = \mathcal{E}\hat{\mathbf{x}}$ (perpendicular)	$\mathcal{C}_1$	μ_x, μ_y, μ_z	$\mathcal{C}_1'$	μ_x, μ_y, μ_z
$\boldsymbol{\mathcal{E}} = \mathcal{E}\hat{\mathbf{y}}$ (in-plane)	$\mathcal{C}_s(yz)$	μ_y, μ_z	$\mathcal{C}_s'(yz)$	μ_y, μ_z
$\boldsymbol{\mathcal{E}} = \mathcal{E}\hat{\mathbf{z}}$ (parallel)	$\mathcal{C}_s(yz)$	μ_y, μ_z	$\mathcal{C}_s'(yz)$	μ_y, μ_z
$\mathbf{B} = B\hat{\mathbf{x}}$ (perpendicular)	$\mathcal{C}_s(yz)$	μ_y, μ_z	-	-
$\mathbf{B} = B\hat{\mathbf{y}}$ (in-plane)	$\mathcal{C}_1$	μ_x, μ_y, μ_z	$\mathcal{C}_s(yz)(\mathcal{C}_1)$	μ_y, μ_z
$\mathbf{B} = B\hat{\mathbf{z}}$ (parallel)	$\mathcal{C}_1$	μ_x, μ_y, μ_z	$\mathcal{C}_s(yz)(\mathcal{C}_1)$	μ_y, μ_z

S2.2 Calculated electric dipole moments

Table S2: Electric dipole moment components (in atomic units) for HFCO calculated using the r^{2}SCAN0 and cTPSS exchange-correlation functionals in 6-31G** and cc-pVTZ basis sets. The electric field strength $\boldsymbol{\mathcal{E}}$ is set at 0.1 a.u. and the magnetic field strength B at 1.0 B_0.

(a) r^{2}SCAN0

Field	6-31G**			cc-pVTZ		
	μ_x	μ_y	μ_z	μ_x	μ_y	μ_z
$\mathbf{0}$	0.000 000 000	−0.504 153 451	−0.667 099 400	0.000 000 000	−0.539 087 871	−0.656 739 980
$\boldsymbol{\mathcal{E}} = \mathcal{E}\hat{\mathbf{x}}$ (perpendicular)	+0.843 025 900	−0.510 258 110	−0.651 623 250	+1.102 638 225	−0.529 875 366	−0.632 962 909
$\boldsymbol{\mathcal{E}} = \mathcal{E}\hat{\mathbf{y}}$ (in-plane)	0.000 000 000	+1.071 912 414	−0.657 722 470	0.000 000 000	+1.480 133 793	−0.514 399 955
$\boldsymbol{\mathcal{E}} = \mathcal{E}\hat{\mathbf{z}}$ (parallel)	0.000 000 000	−0.465 176 676	+1.280 146 850	0.000 000 000	−0.385 131 630	+1.677 359 970
$\mathbf{B} = B\hat{\mathbf{x}}$ (perpendicular)	0.000 000 000	+0.827 268 771	−0.695 147 257	0.000 000 000	+0.709 136 583	−0.656 474 226
$\mathbf{B} = B\hat{\mathbf{y}}$ (in-plane)	0.000 000 000	+0.528 252 893	−0.696 304 097	0.000 000 000	+0.690 315 439	−0.620 750 521
$\mathbf{B} = B\hat{\mathbf{z}}$ (parallel)	0.000 000 000	+0.858 643 144	+1.496 848 359	0.000 000 000	+1.027 873 856	+0.732 919 497

(b) cTPSS

Field	6-31G**			cc-pVTZ		
	μ_x	μ_y	μ_z	μ_x	μ_y	μ_z
$\mathbf{0}$	0.000 000 000	−0.441 160 192	−0.623 589 127	0.000 000 000	−0.484 270 157	−0.610 392 342
$\boldsymbol{\mathcal{E}} = \mathcal{E}\hat{\mathbf{x}}$ (perpendicular)	+0.861 566 295	−0.445 529 227	−0.610 584 021	+1.137 158 616	−0.473 134 059	−0.588 167 436
$\boldsymbol{\mathcal{E}} = \mathcal{E}\hat{\mathbf{y}}$ (in-plane)	0.000 000 000	+1.244 473 360	−0.602 723 699	0.000 000 000	+1.805 587 942	−0.364 885 680
$\boldsymbol{\mathcal{E}} = \mathcal{E}\hat{\mathbf{z}}$ (parallel)	0.000 000 000	−0.389 846 305	+1.387 953 299	0.000 000 000	−0.239 660 695	+1.911 552 802
$\mathbf{B} = B\hat{\mathbf{x}}$ (perpendicular)	0.000 000 000	+0.559 299 281	−0.306 997 213	0.000 000 000	+0.606 192 147	−0.239 076 175
$\mathbf{B} = B\hat{\mathbf{y}}$ (in-plane)	0.000 000 000	+0.526 191 952	−0.682 964 369	0.000 000 000	+0.669 392 535	−0.578 657 826
$\mathbf{B} = B\hat{\mathbf{z}}$ (parallel)	0.000 000 000	+0.718 812 883	+1.276 925 684	0.000 000 000	+0.879 825 148	+0.798 810 909

S2.3 Fukui functions

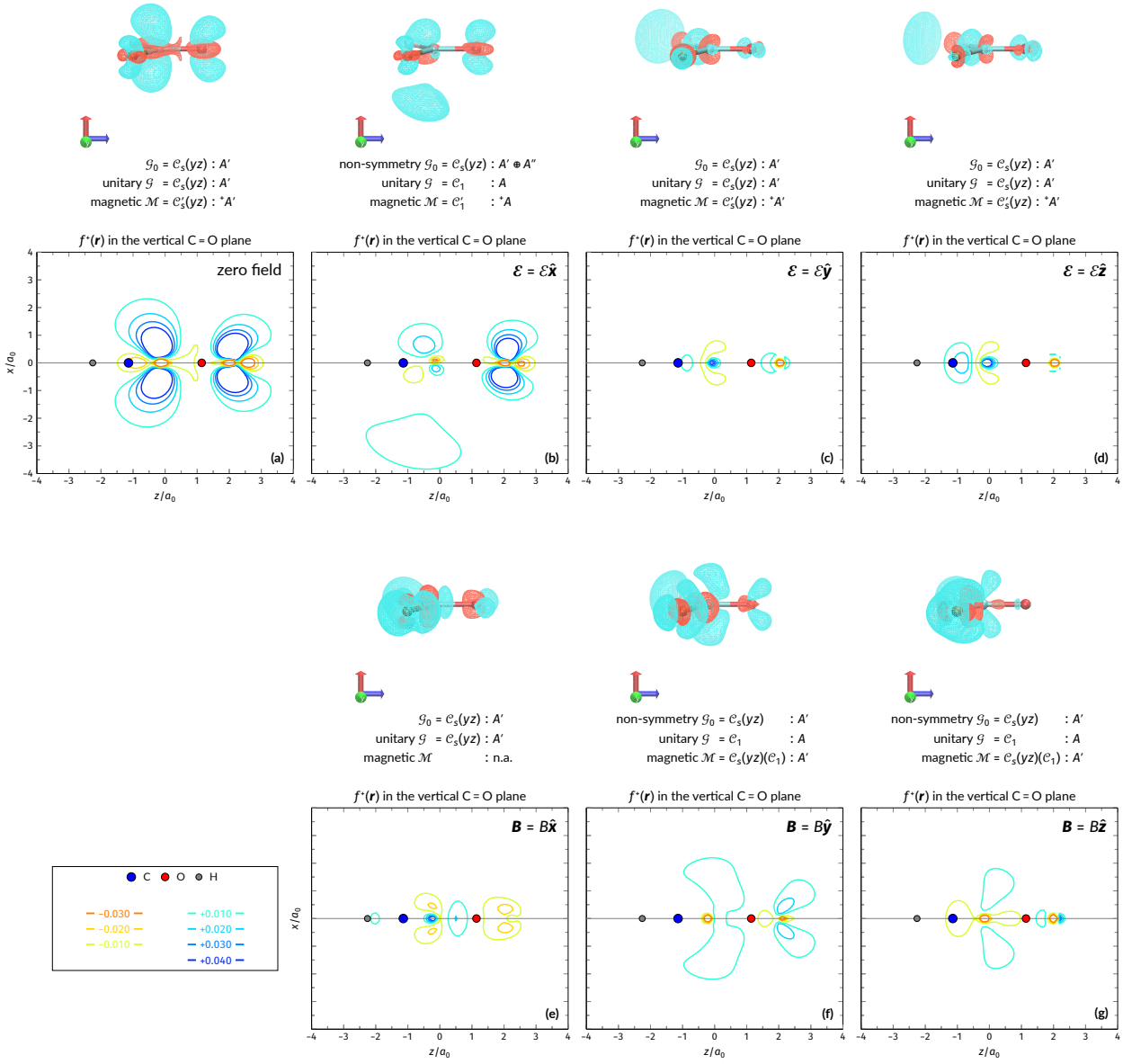

Figure S4: Contour plots of the Fukui function for nucleophilic attack, $f^+(\mathbf{r})$, of HFCO in various external-field configurations. Above each plot are the three-dimensional isosurface of the corresponding Fukui function at isovalue $f^+(\mathbf{r}) = 0.01$ and the representations spanned by $f^+(\mathbf{r})$ and its symmetry partners in various groups as determined by QSym^2 (see also Appendix B in the main text for relevant character tables). Magnetic symmetries in $\mathcal{M}$ are given in terms of its irreducible representations since Fukui functions are real-valued (*cf.* Section 2.3.3.2 in the main text). Positive regions (blue) indicate sites in the system that are favourable for nucleophilic attack. All Fukui functions were calculated using the finite-difference approach [Equation (22) in the main text] at the r^{2}SCAN0/cc-pVTZ level. The electric field strength $\mathcal{E}$ is set at 0.1 a.u. and the magnetic field strength B at $1.0B_0$.