CHEMPHYSCHEM

Supporting Information

Critique of the multipath nuclear spin-spin coupling concept for ^1J(C,C) based on models of electronic current induced by ^{13}C nuclear magnetic dipoles in ethane, cyclopropane, and bicyclobutane

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Supporting information. Captions for the figures

Fig. 3:

From top to bottom, streamlines and modulus of the electron current density induced via the Fermi interaction by two magnetic dipoles, at C1 and C2, and spin-spin coupling density for staggered ethane. The position of the nuclei is marked by crosses. The perturbing dipole at C1 is perpendicular to the plane of the plot, pointing outward. On the left, the vector field has $C_{2h}(C_s)$ magnetic symmetry, and the perturbing dipole at C2 is antiparallel to that at C1. This arrangement is consistent with the sign of the experimental coupling constant. On the right, the vector field has C_{2h} magnetic symmetry, and the perturbing dipole at C2 is parallel to that at C1. The modulus of the current density is represented by the contour maps B and E, in which the values of the solid lines increase in steps of 0.01 c from the 0-contour, up to 0.1 au. Maps C and F represent the Fermi coupling density via contours and corresponding three-dimensional perspective view. In the contour map C, the values of the dashed (solid) lines increase (decrease) in steps of 5×10^{-4} au from the 0-contour. Contours from 0.2 au to 1.0 au, in

steps of 0.2 au, were added to ease the visualisation. Values greater (smaller) than 5.0 (-5.0) au have been cut. Maps C and F show that the coupling path passes through the C-C bond, confirming the results of Figure 2a.

Fig. 4:

From top to bottom, streamlines and modulus of the electron current density induced via the Fermi interaction by two magnetic dipoles, at C1 and C2, and spin-spin coupling density for cyclopropane in the plane of the carbon nuclei. The position of the nuclei is marked by crosses. The perturbing dipole at C1 is perpendicular to the plane of the plot, pointing outward. On the left, the vector field has C_{2v} magnetic symmetry, and the perturbing dipole at C2 is antiparallel to that at C1 (this arrangement is consistent with the sign of the experimental coupling constant). On the right, the vector field has $C_{2v}(C_s)$ magnetic symmetry, and the perturbing dipole at C2 is parallel to that at C1. In the contour maps B and E, the values of the solid lines increase in steps of 0.01 c from the 0-contour, up to 0.1 au. Maps C and F represent the Fermi coupling density via contours and corresponding three-dimensional perspective view. In the contour map C, the values of the dashed (solid) lines increase (decrease) in steps of 5×10^{-4} au from the 0-contour. Contours from 0.2 au to 1.0 au, in steps of 0.2 au,

were added to ease the visualisation. Values greater (smaller) than 5.0 (-5.0) au have been cut.

Fig. 5:

From top to bottom, streamlines and modulus of the electron current density induced via the Fermi interaction by a magnetic dipole at C1, and spin-spin coupling density for bicyclobutane. The plot plane contains three carbon atoms (C1 and C2 are the spin-coupled bridgehead carbon nuclei). Plotting conventions are the same as in Fig. 3. Map 5a confirms that carbon C2 lies in between the two α vortices in the vicinity of a saddle point of the vector field shown in Figure 1e. Map 5c is fully consistent with map 2c, proving that the coupling path goes essentially through the C1-C2 bond, as discussed in the text.

Fig. 6:

From top to bottom, streamlines and modulus of the electron current density induced via the Fermi interaction by two magnetic dipoles, at C1 and C2, and spin-spin coupling density for bicyclobutane. The plotting conventions are the same as in previous figures, and the position of the nuclei is the same as in Fig. 5. The perturbing dipole at C1 is perpendicular to the plane of the plot, pointing outward. In the maps D and E on the right,

the perturbing dipole at C2 is parallel to that at C1 (this arrangement is consistent with the sign of the experimental coupling constant). In the maps A and B on the left, the perturbing dipole at C2 is antiparallel to that at C1. Maps C and F represent the Fermi coupling density via contours and corresponding three-dimensional perspective view. These plots confirm the validity of the reductionist model discussed in the text to rationalize CC couplings. In particular, map F shows very clearly that through-space effects are negligible, compare for the height of the spikes nearby the coupled C1 and C2 nuclei with that in the proximity of C3.

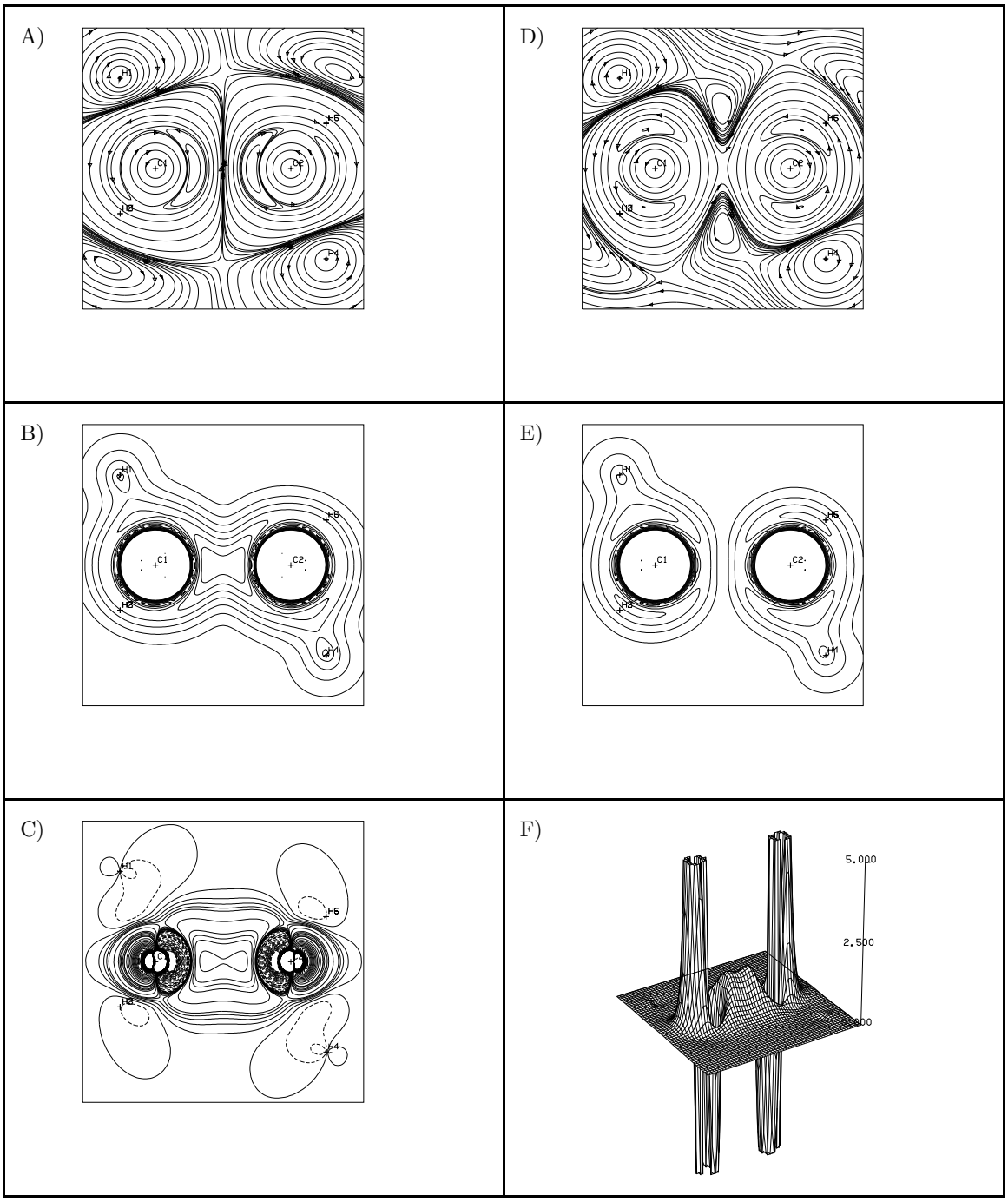

A)
H1
H5
C1
C2
H3
H4
D)
H1
H5
C1
C2
H3
H4
B)
H1
H5
C1
C2
H3
H4
E)
H1
H5
C1
C2
H3
H4
C)
H1
H5
C1
C2
H3
H4
F)
5.000
2.500

Figure 3:

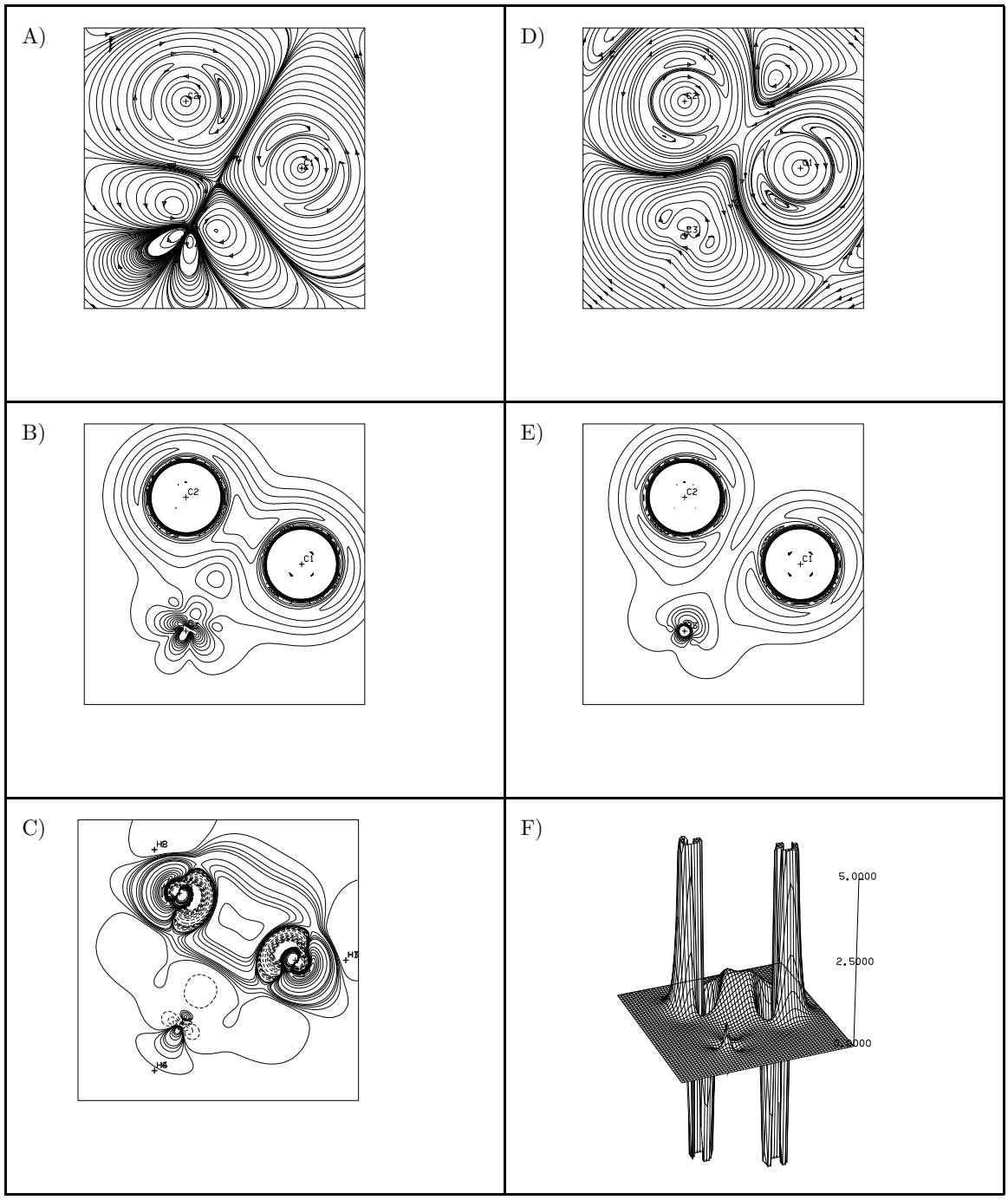
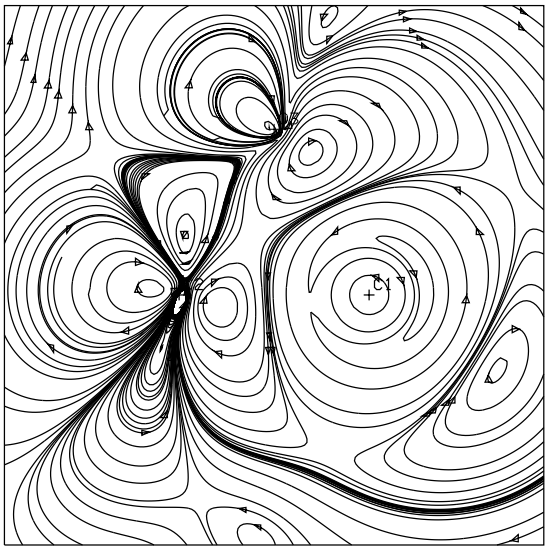
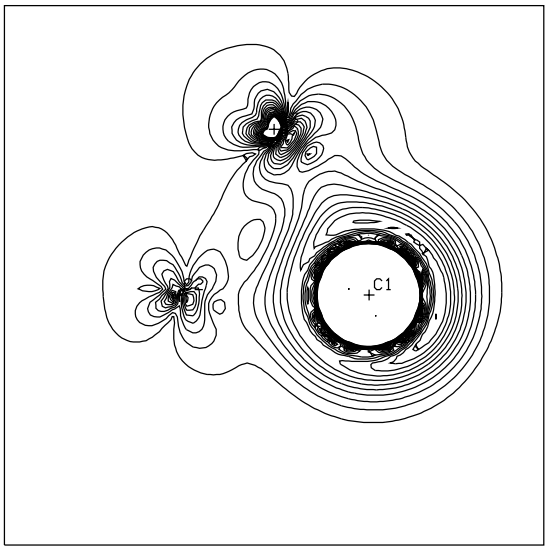


Figure 4:

a)



b)



c)

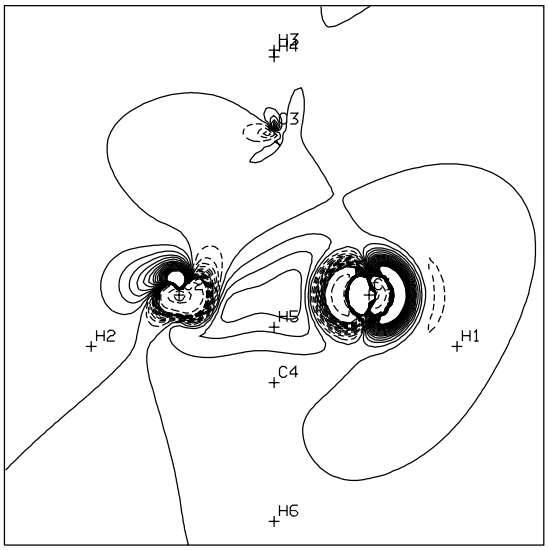


Figure 5:

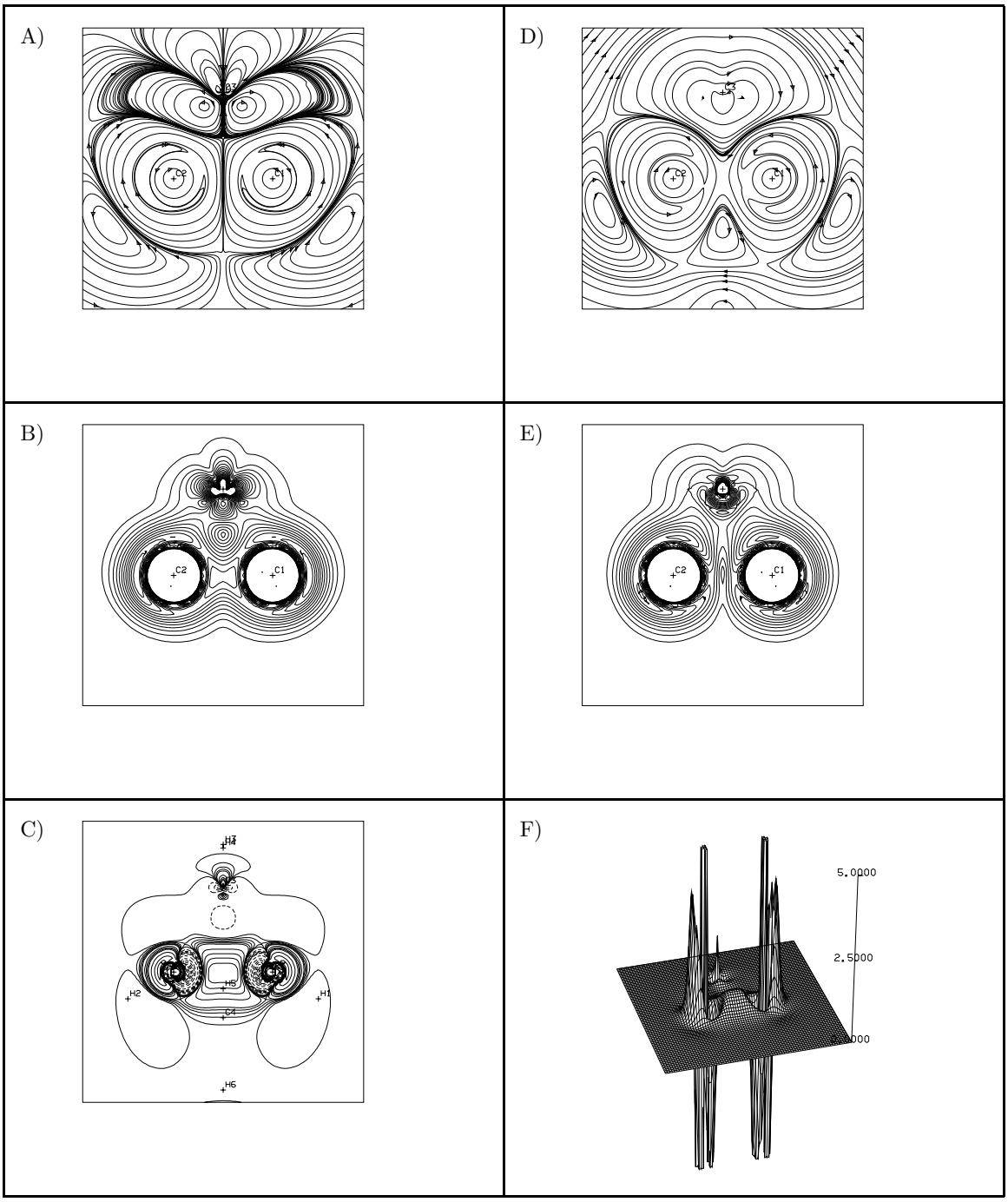


Figure 6: