Supporting Information: Revealing Non-Covalent Interactions

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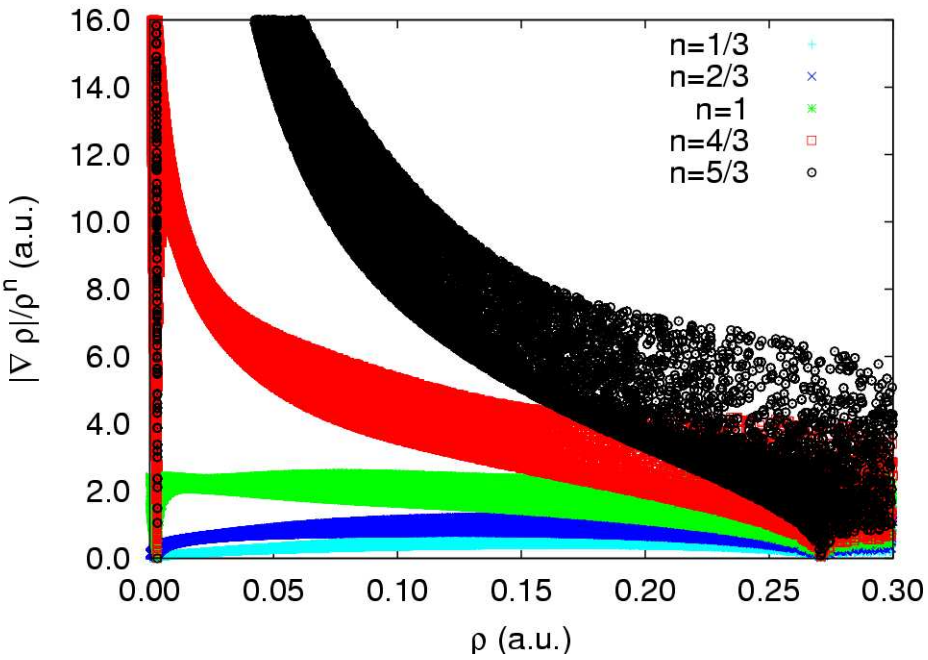
1 Other Density-Gradient Ratios

Figure S1: Plots of the ratio $|\nabla\rho|/\rho^n, n = \{\frac{1}{3}, \frac{2}{3}, 1, \frac{4}{3}, \frac{5}{3}\}$ versus ρ for the methane dimer. The data was obtained by evaluating B3LYP/631G* density and gradient values on a cuboid grid with a 0.1 au increment.

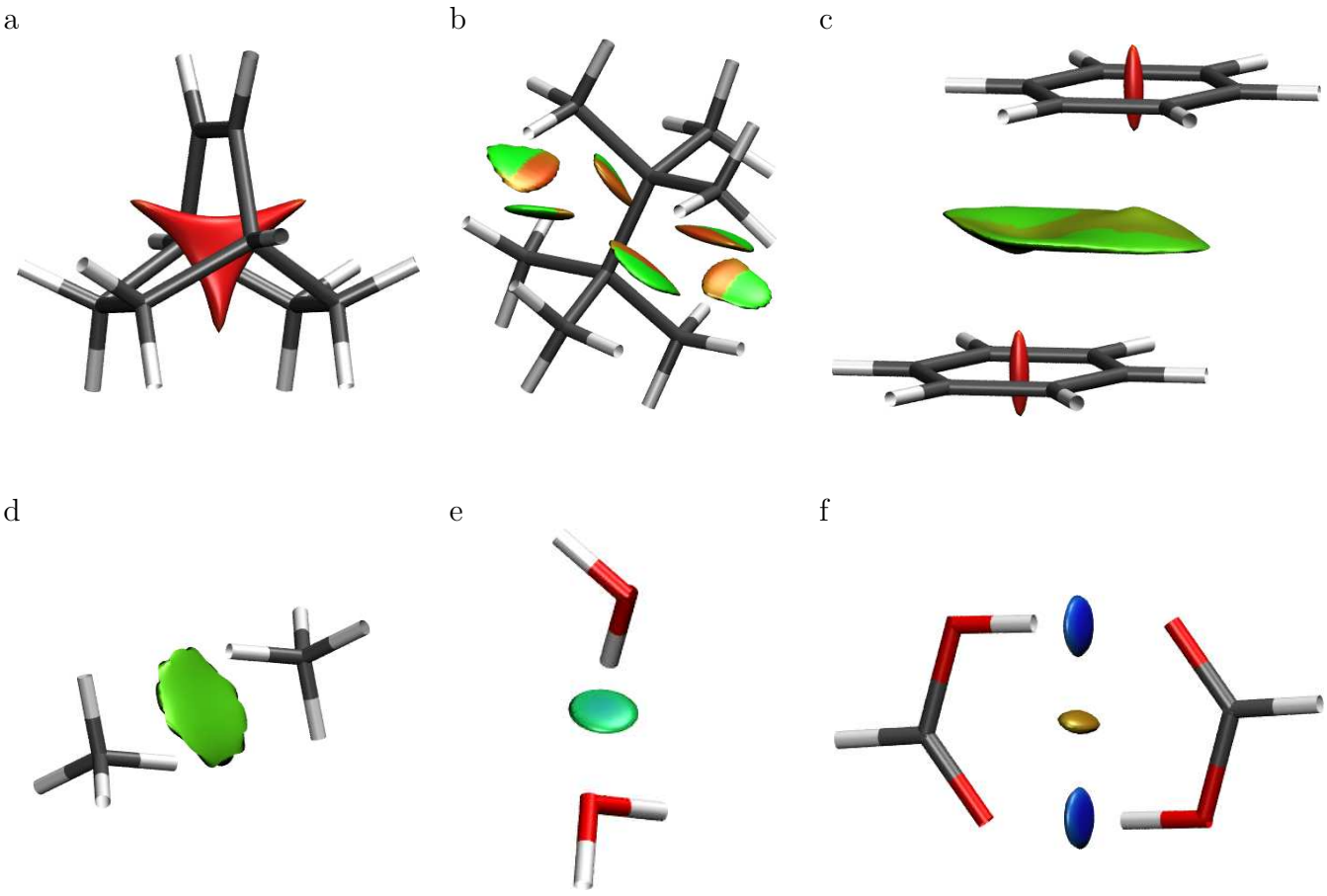


The behavior of several $|\nabla\rho|/\rho^n$ ratios ($n = \{\frac{1}{3}, \frac{2}{3}, 1, \frac{4}{3}, \frac{5}{3}\}$) is shown in Figure S1 for low density regions of the methane dimer. The reduced gradient ($n = \frac{4}{3}$) has large, positive values in density tails and low values, approaching zero, for non-covalent interactions. Now consider the behavior of the $|\nabla\rho|/\rho^n$ ratio for other exponents. If there are low powers of the density in the denominator, the ratio approaches zero for both exponential tails and non-covalent interactions. If high powers of the density are used, the ratio assumes very large values in both situations (although it will still be zero exactly at a critical point). The 4/3 power used in the reduced gradient is not the only

one that can isolate non-covalent interactions, but there is a relatively small range of acceptable values. In particular, Fig. S1 shows that the local speed ($\frac{|\nabla\rho|}{\rho}$) [Bohorquez, H. J.; Boyd, R. J. *J. Chem. Phys.* **2008**, *129*, 024110.] can also be used to identify non-covalent interactions. However, it is not as discriminatory as the reduced gradient since it approaches a constant for the density tail regions.

2 MP2 results

Figure S2: MP2/6-311++G** gradient isosurfaces with $s = 0.5$ au for (a) bicyclo[2,2,2]octene, (b) branched octane, and the homomolecular dimers of (c) benzene, (d) methane, (e) water, and (f) formic acid. The surfaces are colored on a blue-green-red scale according to values of sign(λ_2)ρ, ranging from -0.04 to 0.02 au. Blue indicates strong attractive interactions and red indicates strong non-bonded overlap.



3 S22 results

Figure S3: B3LYP/6-31G* gradient isosurfaces with $s = 0.5$ au for the complexes of the s22 intermolecular interaction test set. The surfaces are colored on a blue-green-red scale according to values of sign$(\lambda_2)\rho$, ranging from -0.04 to 0.02 au. Blue indicates strong attractive interactions and red indicates strong non-bonded overlap.

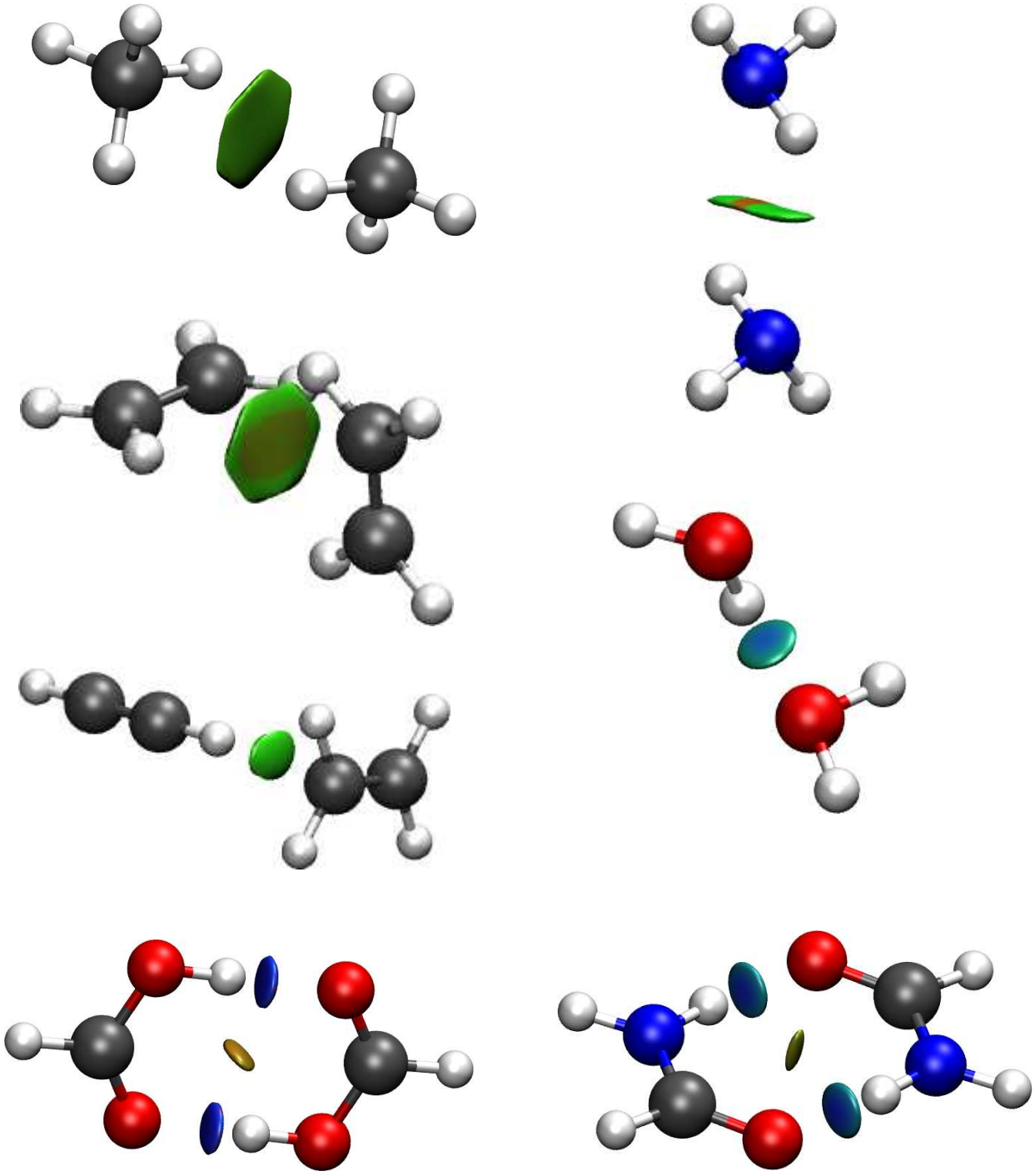
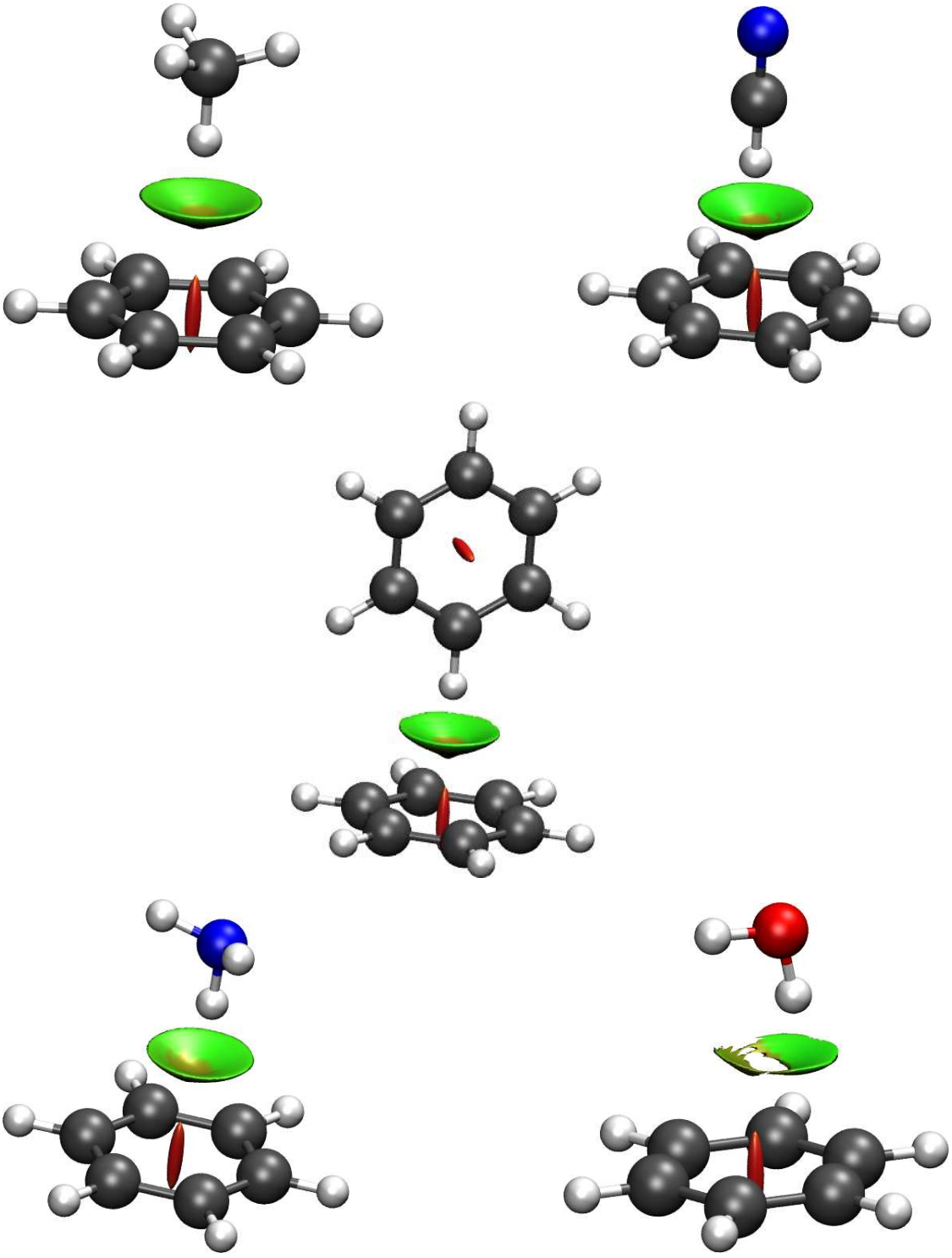


Figure S3 continued: B3LYP/6-31G* gradient isosurfaces with $s = 0.5$ au for the complexes of the s22 intermolecular interaction test set. The surfaces are colored on a blue-green-red scale according to values of sign(λ_2)ρ, ranging from -0.04 to 0.02 au. Blue indicates strong attractive interactions and red indicates strong non-bonded overlap.



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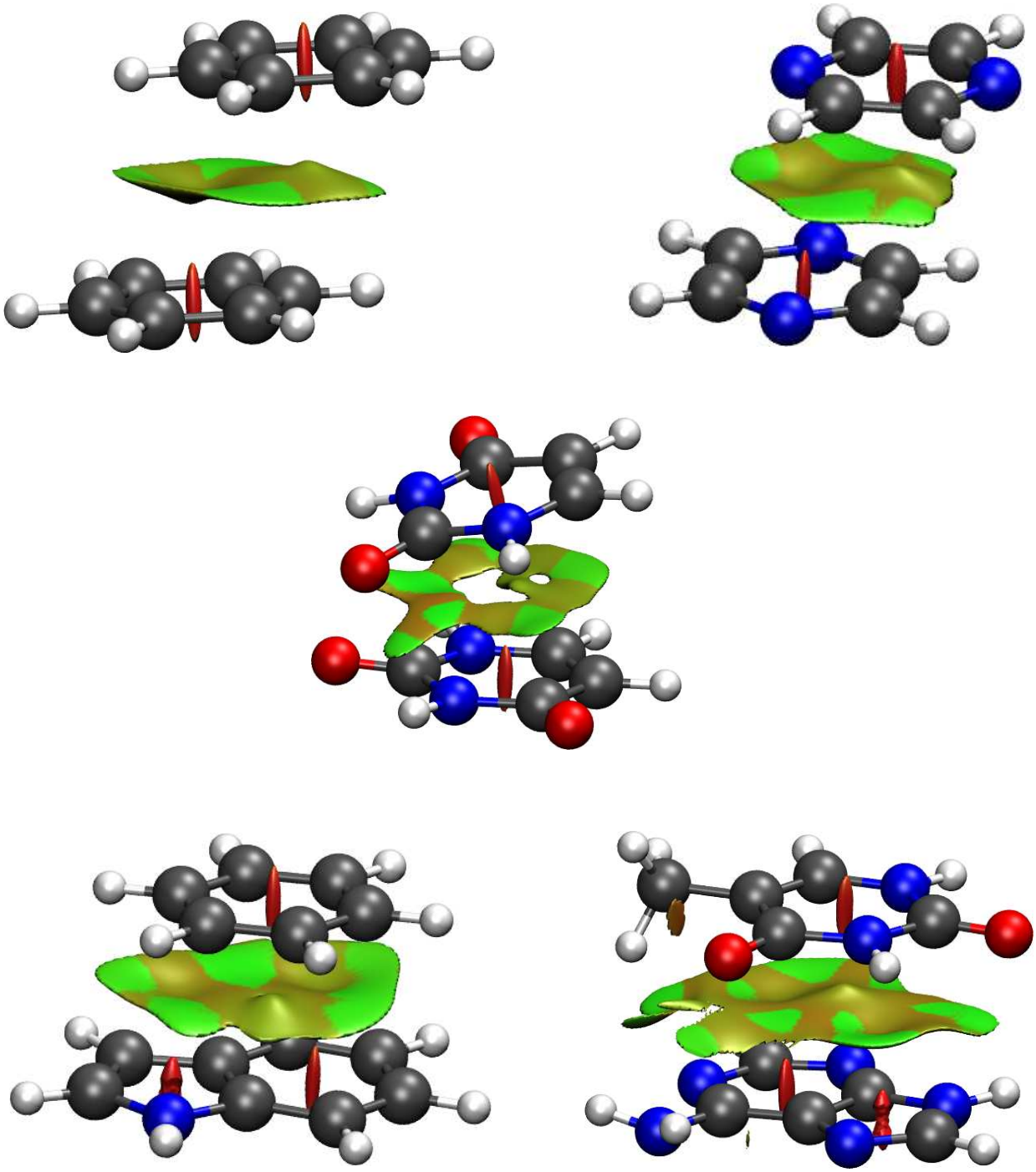
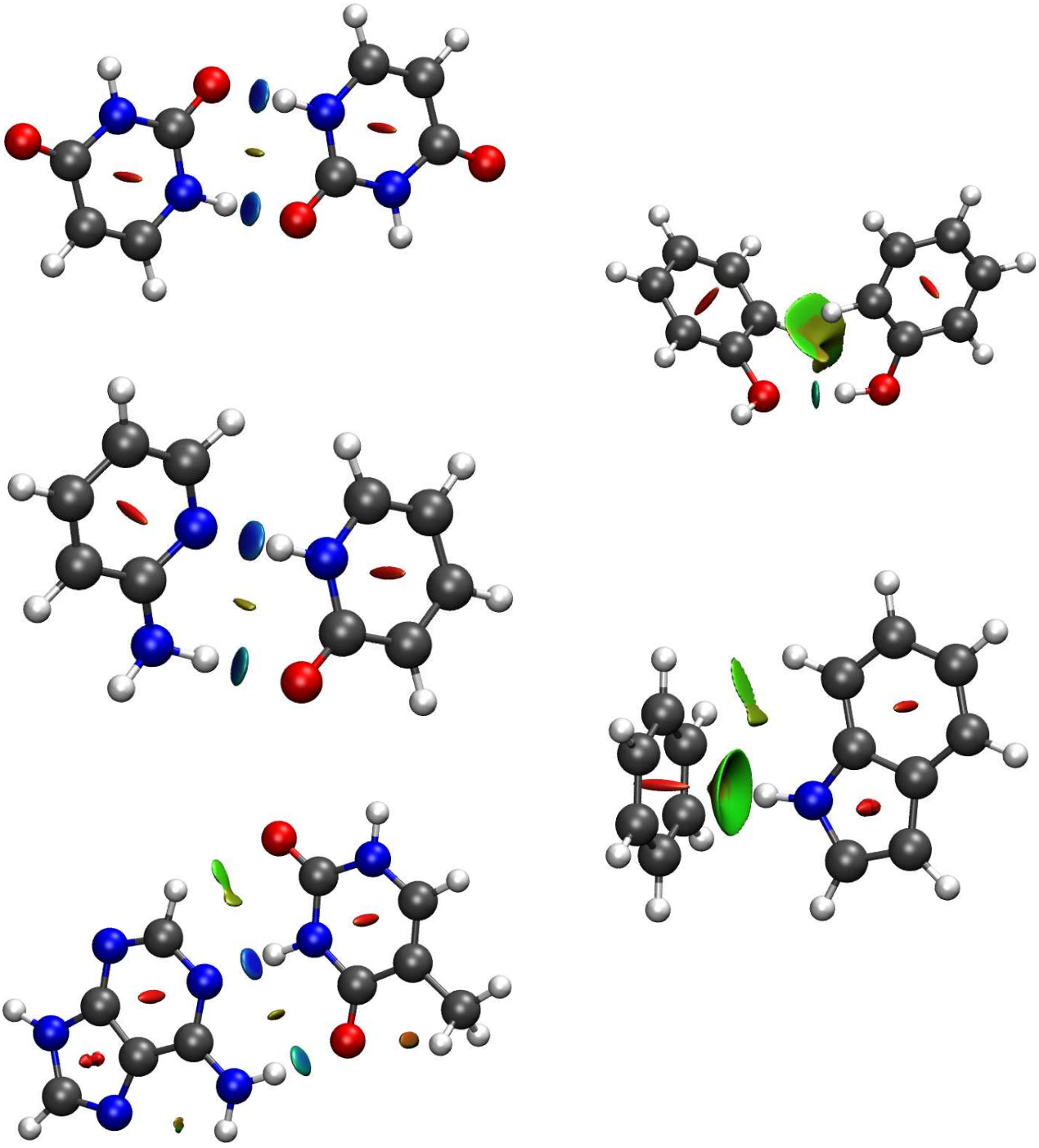
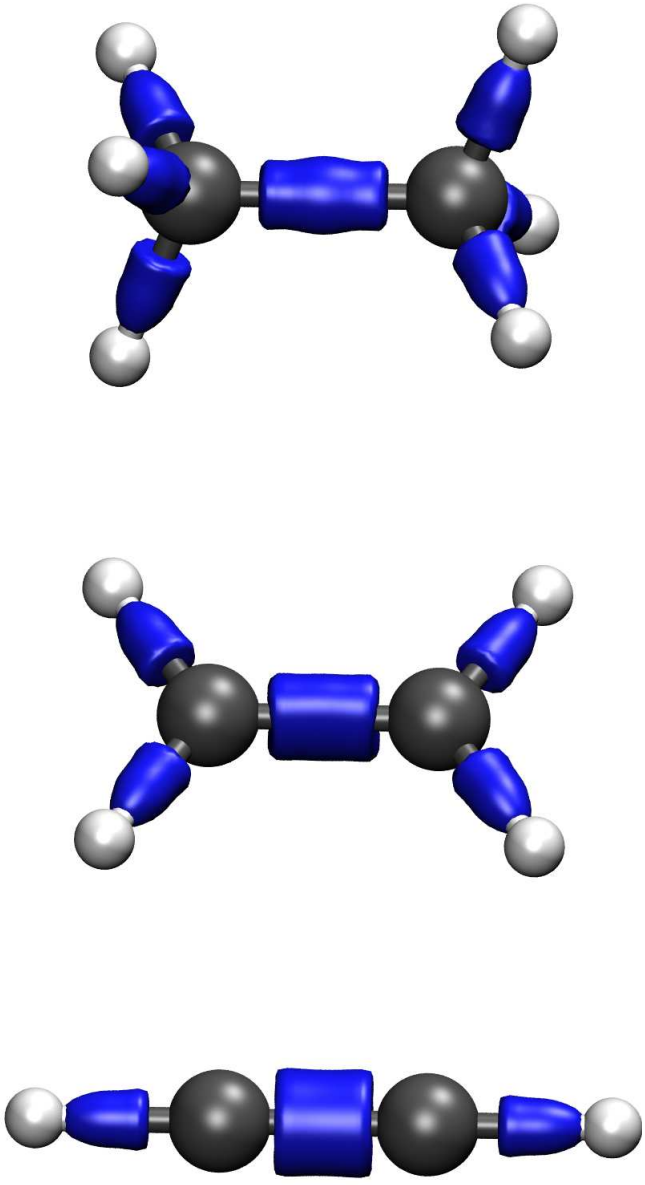


Figure S3 continued: B3LYP/6-31G* gradient isosurfaces with $s = 0.5$ au for the complexes of the s22 intermolecular interaction test set. The surfaces are colored on a blue-green-red scale according to values of sign(λ_2)ρ, ranging from -0.04 to 0.02 au. Blue indicates strong attractive interactions and red indicates strong non-bonded overlap.



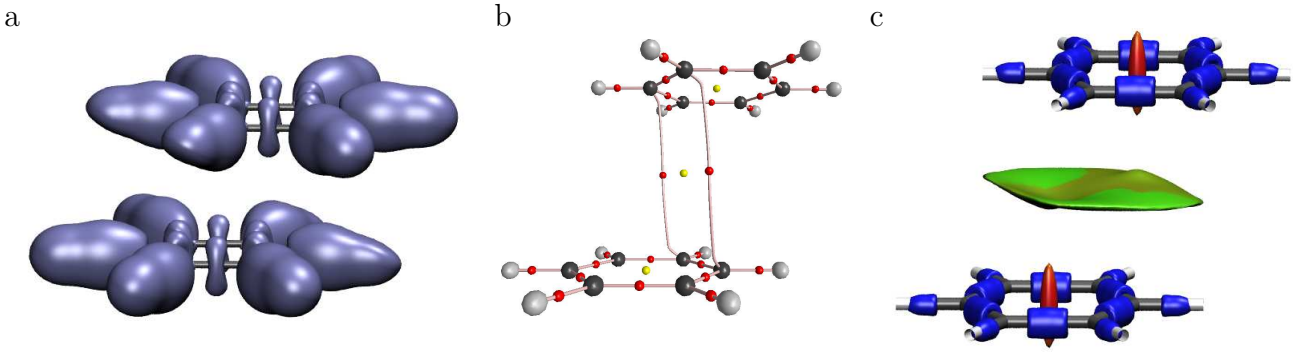
4 Covalent Bonding

Figure S4: B3LYP/6-31G* gradient isosurfaces with $s = 0.2$ au for ethane, ethylene, and acetylene. The surfaces are colored on a blue-green-red scale according to values of sign(λ_2)ρ, ranging from -0.5 to 0.0 au. Blue indicates strong attractive interactions.



5 Comparison with ELF and AIM

Figure S5: The ELF= 0.9 au isosurface for benzene dimer (a) and the AIM molecular graph showing critical points and bond paths (b). An overlay of the $s = 0.6$ au, $\rho < 0.5$ au and $s = 0.2$, $\rho < 0.4$ isosurfaces (c) displays both non-covalent interactions and covalent bonds, colored on a blue-green-red scale according to values of sign$(\lambda_2)\rho$, ranging from -0.04 to 0.02 au. All results were obtained from the B3LYP/6-31G* electron density.



6 Atomic-Density Parameters

Table S1: Parameterized exponents (ζ) and coefficients (c) of sphericalized atomic densities, in atomic units.

Atom	c_1	ζ_1	c_2	ζ_2	c_3	ζ_3
H	0.2815	0.5288	–	–	–	–
He	2.437	0.3379	–	–	–	–
Li	11.84	0.1912	0.06332	0.9992	–	–
Be	31.34	0.1390	0.3694	0.6945	–	–
B	67.82	0.1059	0.8527	0.5300	–	–
C	120.2	0.0884	1.172	0.5480	–	–
N	190.9	0.0767	2.247	0.4532	–	–
O	289.5	0.0669	2.879	0.3974	–	–
F	406.3	0.0608	3.049	0.3994	–	–
Ne	561.3	0.0549	6.984	0.3447	–	–
Na	760.8	0.0496	22.42	0.2511	0.06358	1.0236
Mg	1016	0.0449	37.17	0.2150	0.3331	0.7753
Al	1319	0.0411	57.95	0.1874	0.8878	0.5962
Si	1658	0.0382	87.16	0.1654	0.7888	0.6995
P	2042	0.0358	115.7	0.1509	1.465	0.5851
S	2501	0.0335	158.0	0.1369	2.170	0.5149
Cl	3024	0.0315	205.5	0.1259	3.369	0.4974
Ar	3625	0.0296	260.0	0.1168	5.211	0.4412

7 Computations using the Promolecular Density

Approximate promolecular densities were constructed (by summing exponential atomic densities) for branched octane, bicyclo[2,2,2]octene, and the homomolecular dimers of methane, benzene, water, and formic acid. It should be noted that, in order to generate the isosurfaces for bicyclo[2,2,2]octene, branched octane, and benzene dimer, lower cut-offs on the gradient (0.25-0.35 au) and higher cut-offs on the density (0.08-0.09 au) were required. This is to be expected, since the approximate promolecular densities used to generate these isosurfaces cannot adjust to alleviate Pauli repulsion in the manner of self-consistent DFT electron densities.

Figure S6: Gradient isosurfaces obtained using approximate promolecular densities. The bounds on the density and reduced gradient values (in au) are $s^{pro} = 0.35$, $\rho^{pro} < 0.05$ for branched octane, $s^{pro} =< 0.25$, $\rho^{pro} < 0.09$ for bicyclo[2,2,2]octene and benzene dimer, $s^{pro} = 0.6$, $\rho^{pro} < 0.05$ for the methane and water dimers, and $s^{pro} = 0.5$, $\rho^{pro} < 0.065$ for formic acid dimer. The surfaces are colored on a blue-green-red scale according to values of sign$(\lambda_2)\rho^{pro}$, ranging from -0.06 to 0.05 au. Blue indicates strong attractive interactions and red indicates strong non-bonded overlap.