Probing Aromaticity and Non-Covalent Interactions with Single-Exponential Decay Detector (SEDD)

Piotr de Silva

Department of Physical Chemistry
University of Geneva

Paris, June 26th, 2013

Background: Non-Additive Kinetic Potential

- The non-additive kinetic potential appears in subsystem DFT and Frozen Density Embedding Theory (FDET).
- A Kohn-Sham equation for the embedded system needs to be solved.
- The interaction with the environment is represented by the embedding potential.
- The key component is the non-additive kinetic potential $v_t^{nad}[\rho_A, \rho_B](\mathbf{r})$.

$$v_t^{nad}[\rho_A, \rho_B](\mathbf{r}) = \frac{\delta T_s^{nad}[\rho_A, \rho_B]}{\delta \rho_A(\mathbf{r})} = \left.\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})}\right|_{\rho=\rho_A+\rho_B} - \left.\frac{\delta T_s[\rho]}{\delta \rho(\mathbf{r})}\right|_{\rho=\rho_A}$$

Approximate Functionals

- The exact kinetic functional $T_s[\rho]$ is known for HEG (Thomas-Fermi) and two-electron systems (von Weizsäcker).
- In practice, TF or GGAs are used for $T_s^{nad}[\rho_A, \rho_B]$ and $v_t^{nad}[\rho_A, \rho_B]$.
- If $\rho_A \to 0$ and $\int \rho_B d\mathbf{r} = 2$, then $v_t^{nad}[\rho_A, \rho_B] \to v_t[\rho_B] = \frac{1}{8}\frac{|\nabla\rho_B|^2}{\rho_B^2} - \frac{1}{4}\frac{\nabla^2\rho_B}{\rho_B}$.
- Switching to von Weizsäcker may be beneficial in regions where ρ_B is a two-electron density, which is not penetrated by ρ_A.
- Two-electron densities correspond to localized electron pairs.

Electron Localizability

- Localized electron pairs are revealed by ELF.
- Local measure of Pauli repulsion.
- Orbitals are needed to evaluate the kinetic energy density.
- Electron density is sufficient to fully describe a many-electron system.
- It's available experimentally.

Electron Localizability

- Localized electron pairs are revealed by ELF.
- Local measure of Pauli repulsion.
- Orbitals are needed to evaluate the kinetic energy density.
- Electron density is sufficient to fully describe a many-electron system.
- It's available experimentally.

Objective

Define a dimensionless scalar field revealing the fragments of space with an increased electron localization, that would depend only on the electron density and its derivatives up to the second order.

Single-Exponential Decay Detector (SEDD)

Ansatz

- Localized electrons do not overlap in space with others.
- Localized pairs can be described with a single orbital.
- Locally, electron density behaves exponentially:

$$\rho(\mathbf{r}) \sim e^{-\lambda|\mathbf{r}-\mathbf{r_0}|}.$$

At nuclear cusps	$\lambda = \lambda(Z)$
Far from the molecule	$\lambda = \lambda(IP)$
At density critical points	$\lambda = 0$

Single-Exponential Decay Detector (SEDD)

$$\nabla \left[\left(\frac{\nabla \rho}{\rho} \right)^2 \right] = 0 \qquad \text{wherever the density is single-exponential}$$

Single-Exponential Decay Detector (SEDD)

$$\nabla\left[\left(\frac{\nabla\rho}{\rho}\right)^2\right] = 0 \qquad \text{wherever the density is single-exponential}$$

$$\xi = \left(\frac{\nabla\left[\left(\frac{\nabla\rho}{\rho}\right)^2\right]}{\rho}\right)^2 \qquad \text{dimensionless, scalar field}$$

$\xi = 0$ wherever the density is single-exponential, except for the asymptotic region, where $\xi \to \infty$.

Single-Exponential Decay Detector (SEDD)

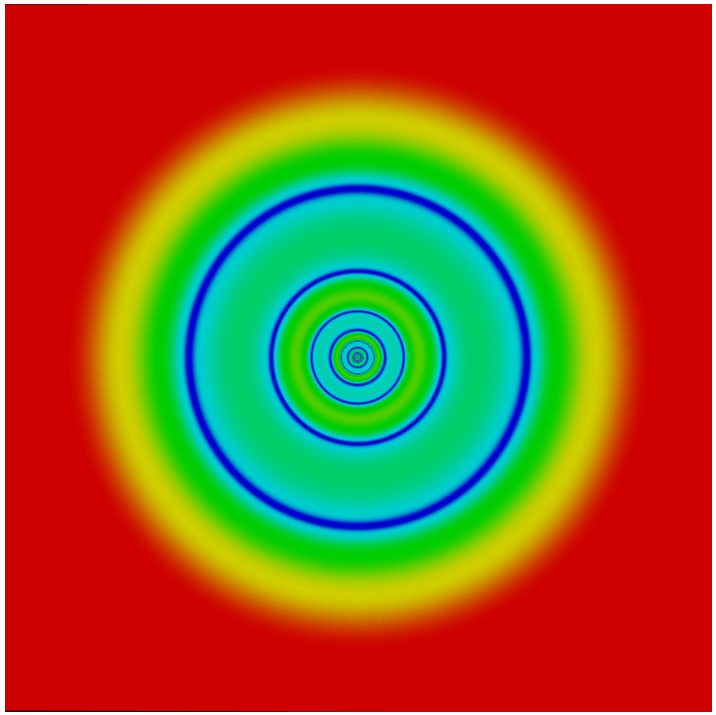
$$\nabla\left[\left(\frac{\nabla\rho}{\rho}\right)^2\right] = 0 \qquad \text{wherever the density is single-exponential}$$

$$\xi = \left(\frac{\nabla\left[\left(\frac{\nabla\rho}{\rho}\right)^2\right]}{\rho}\right)^2 \qquad \text{dimensionless, scalar field}$$

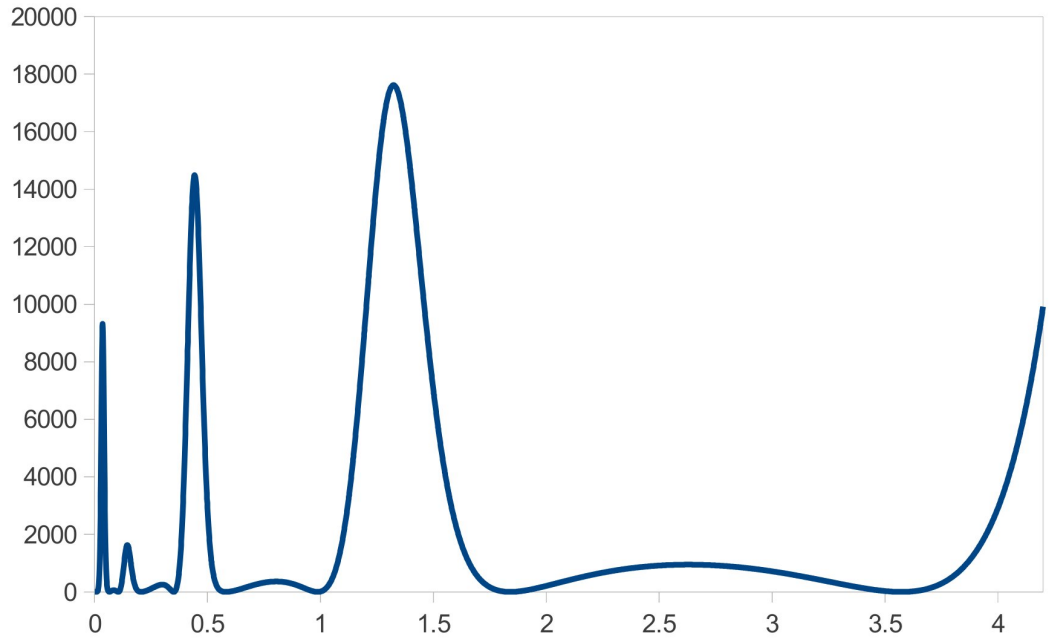
$\xi = 0$ wherever the density is single-exponential, except for the asymptotic region, where $\xi \to \infty$.

$$SEDD(\mathbf{r}) = \ln(\xi)$$

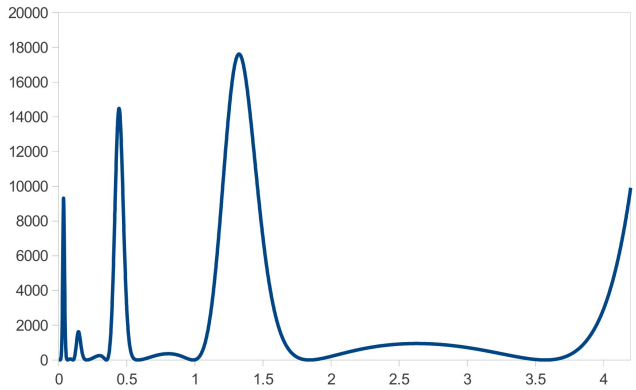
Xenone - Shell structure



Xenone - Shell structure



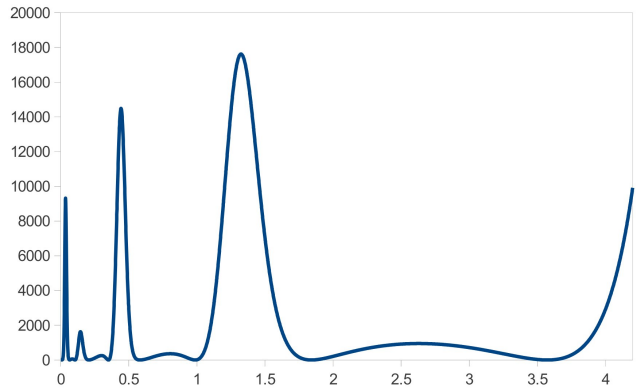
Xenone - Shell structure



	SEDD
K	1.9
L	8.4
M	17.2
N	18.0
O	8.5

Table : Number of electrons in shells.

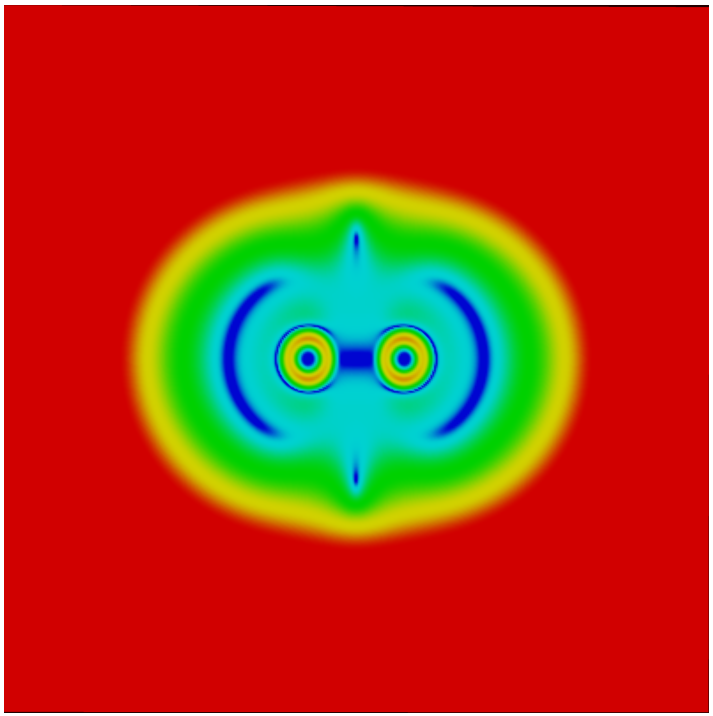
Xenone - Shell structure

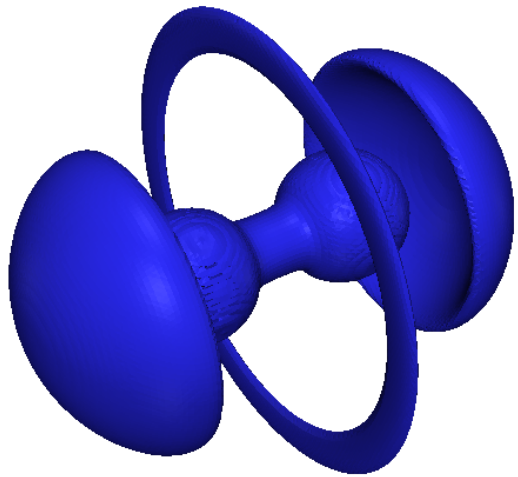


	SEDD	ELF
K	1.9	2.2
L	8.4	8.9
M	17.2	17.0
N	18.0	17.6
O	8.5	8.2

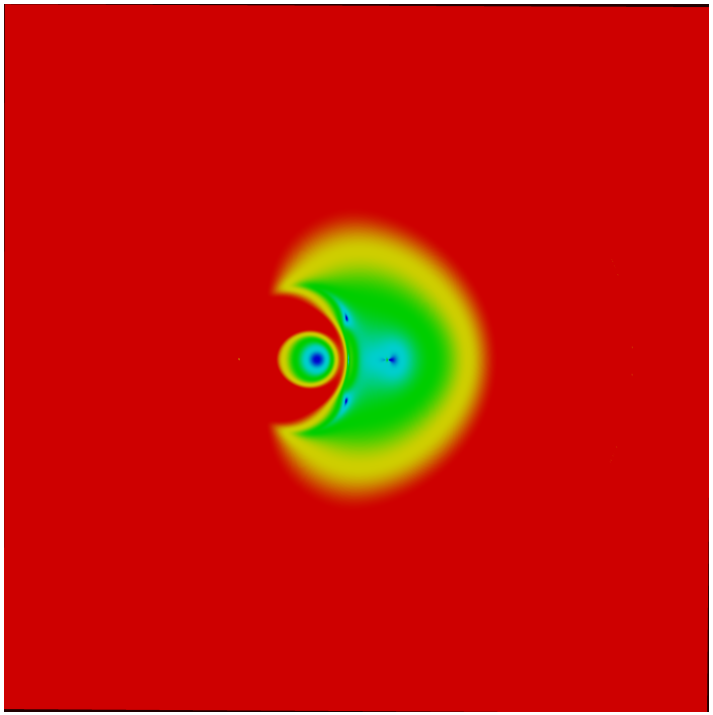
Table : Number of electrons in shells.

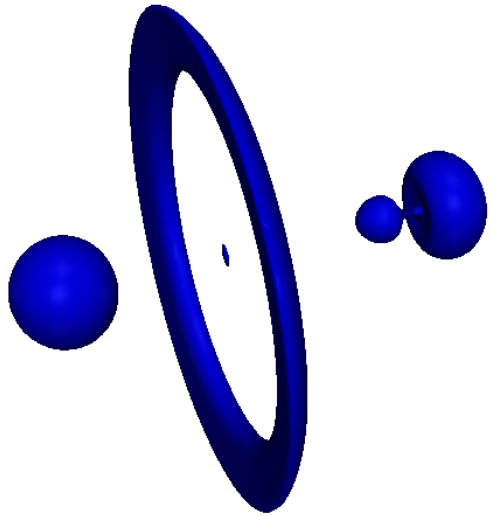
N_2



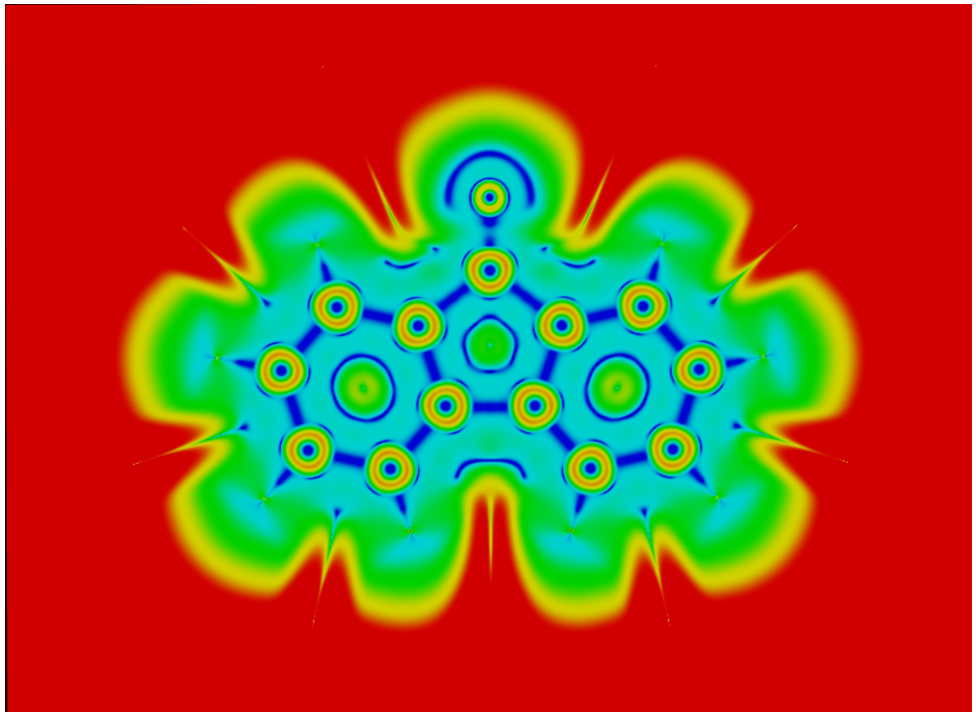


LiH



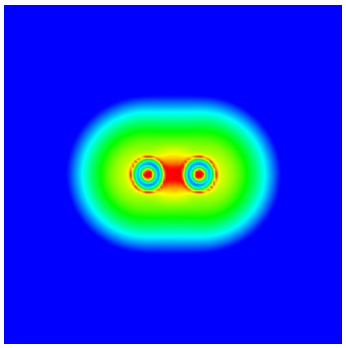


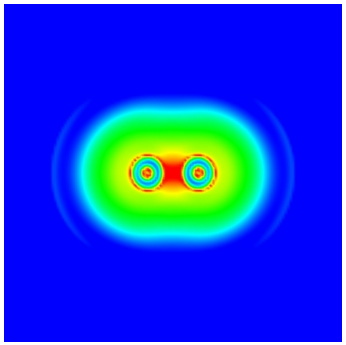
Fluorenone



Basis set dependence: N_2

STOs

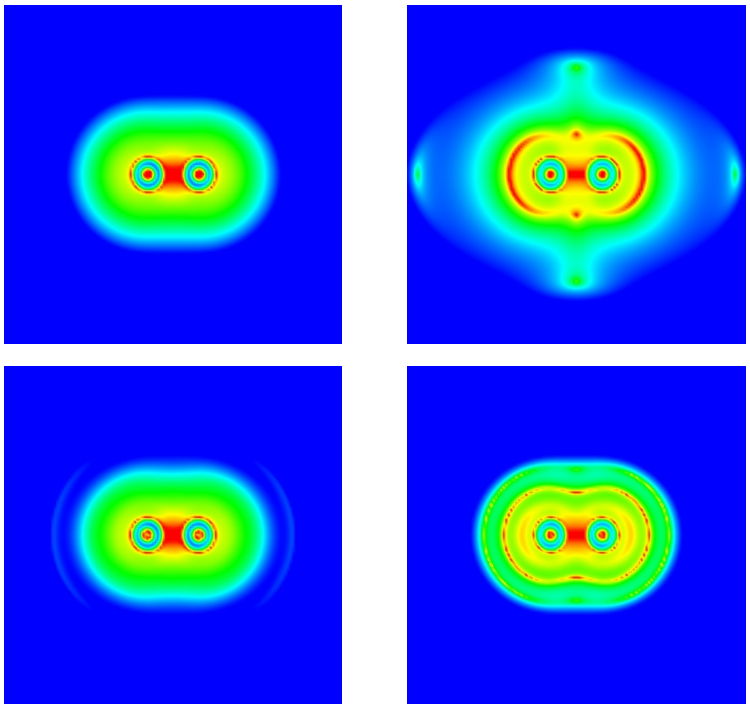




GTOs

Basis set dependence: N_2

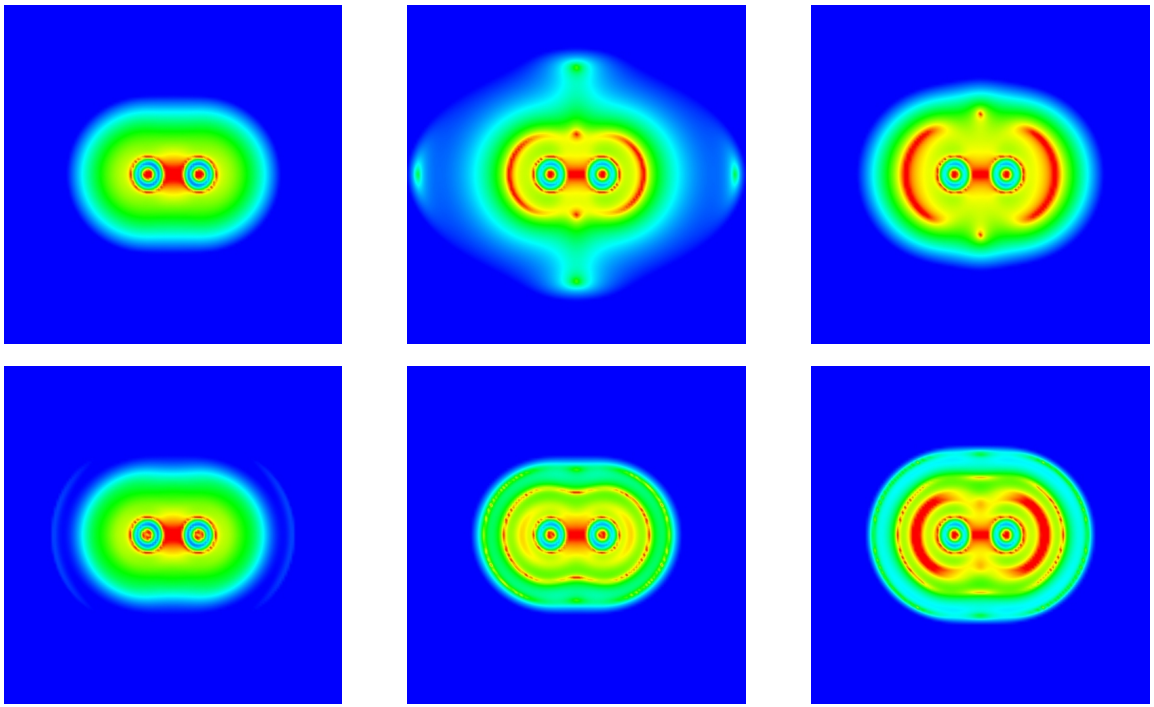
STOs



GTOs

Basis set dependence: N_2

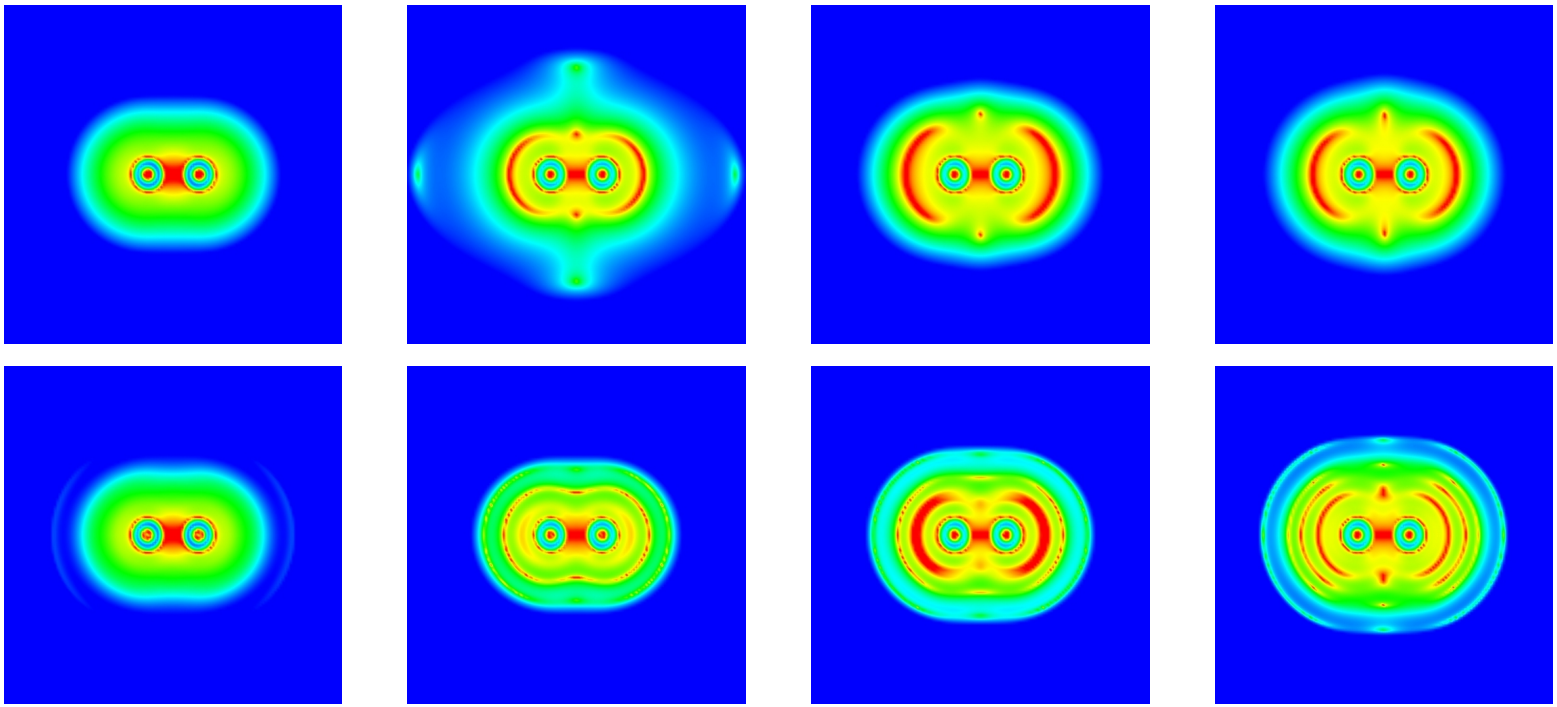
STOs



GTOs

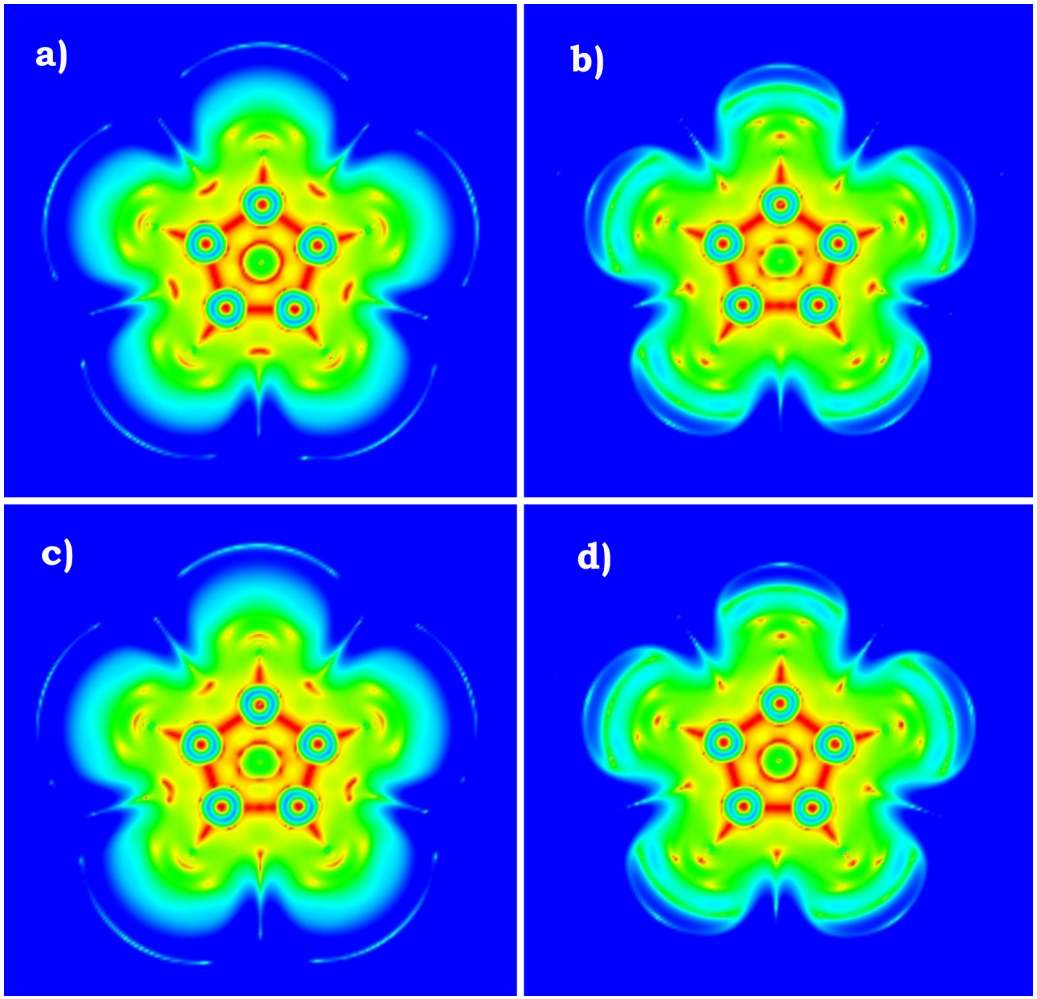
Basis set dependence: N_2

STOs

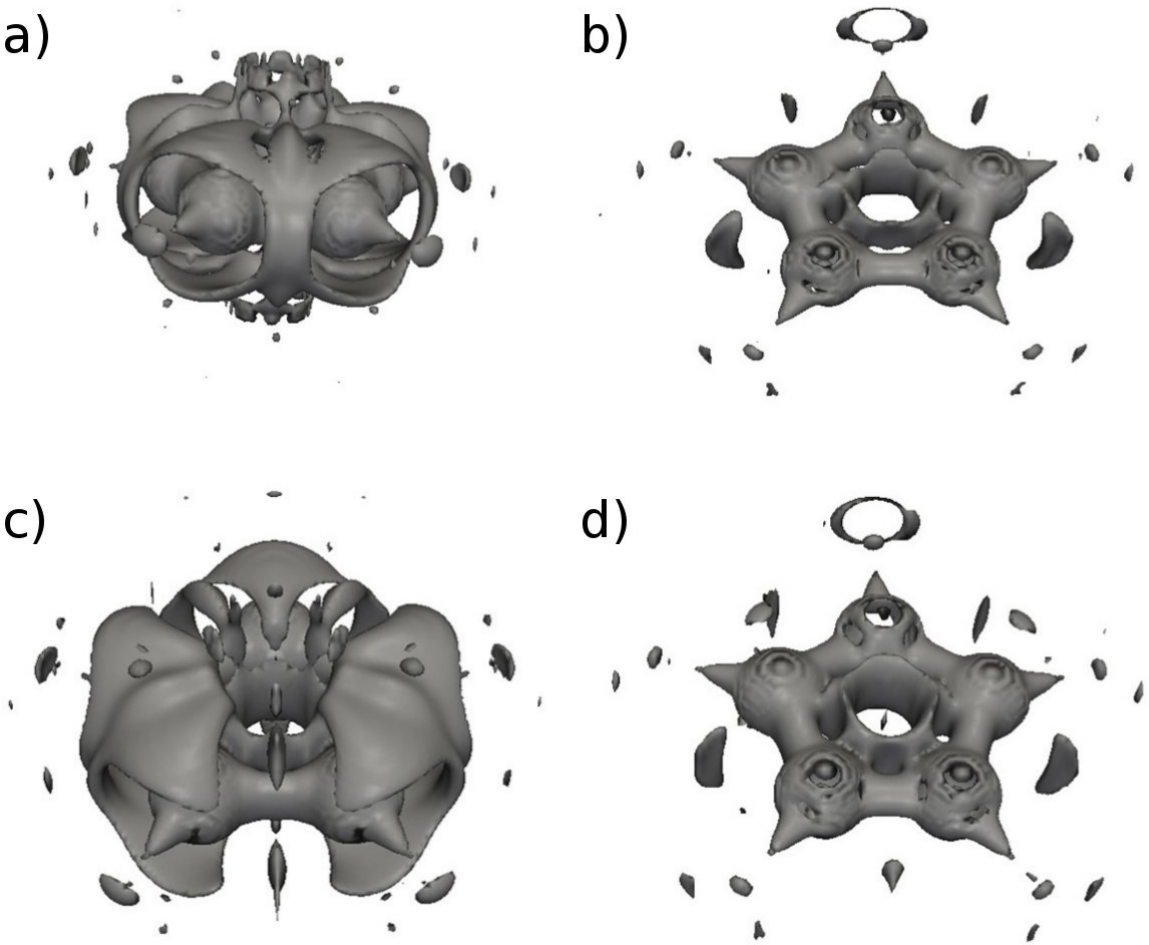


GTOs

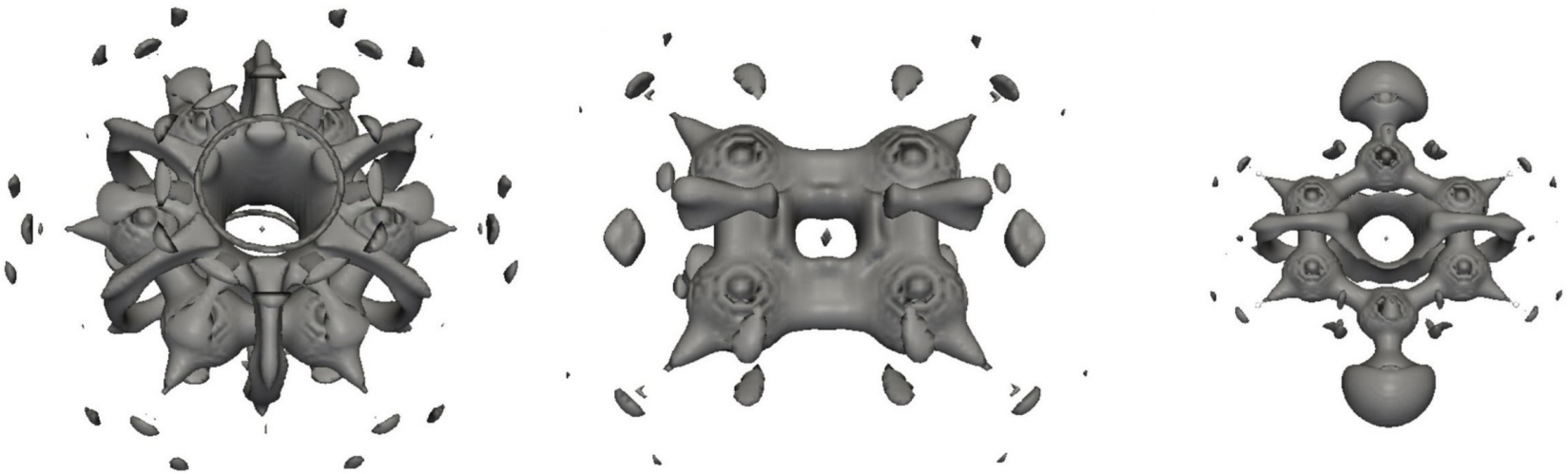
Aromaticity



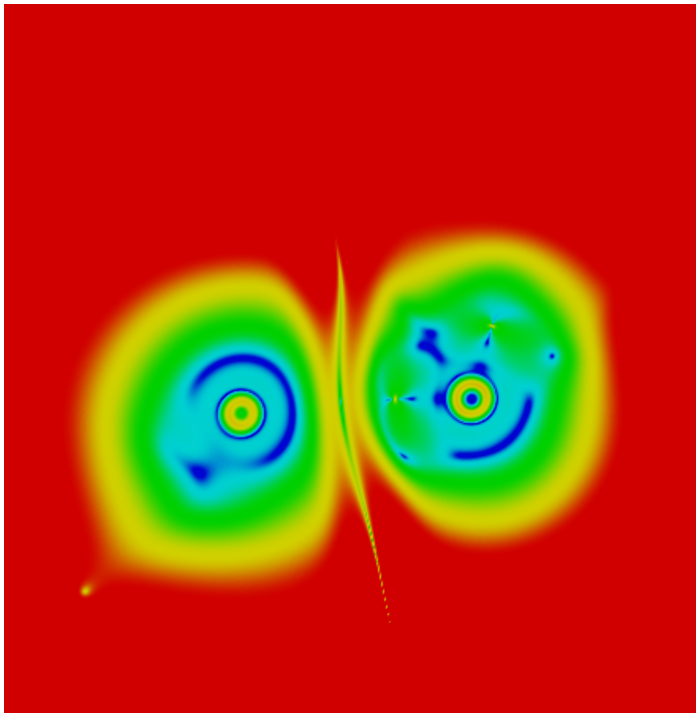
Aromaticity

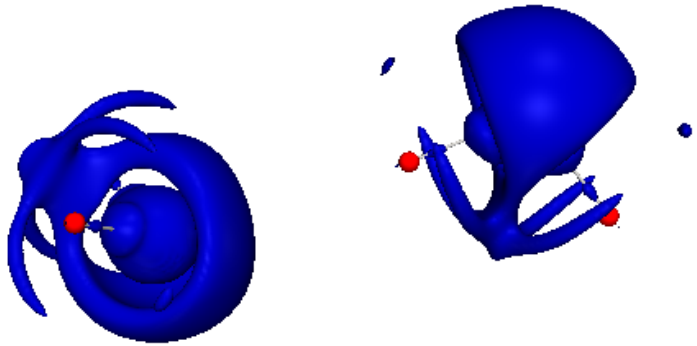


Aromaticity



Non-Covalent Interactions: Water dimer

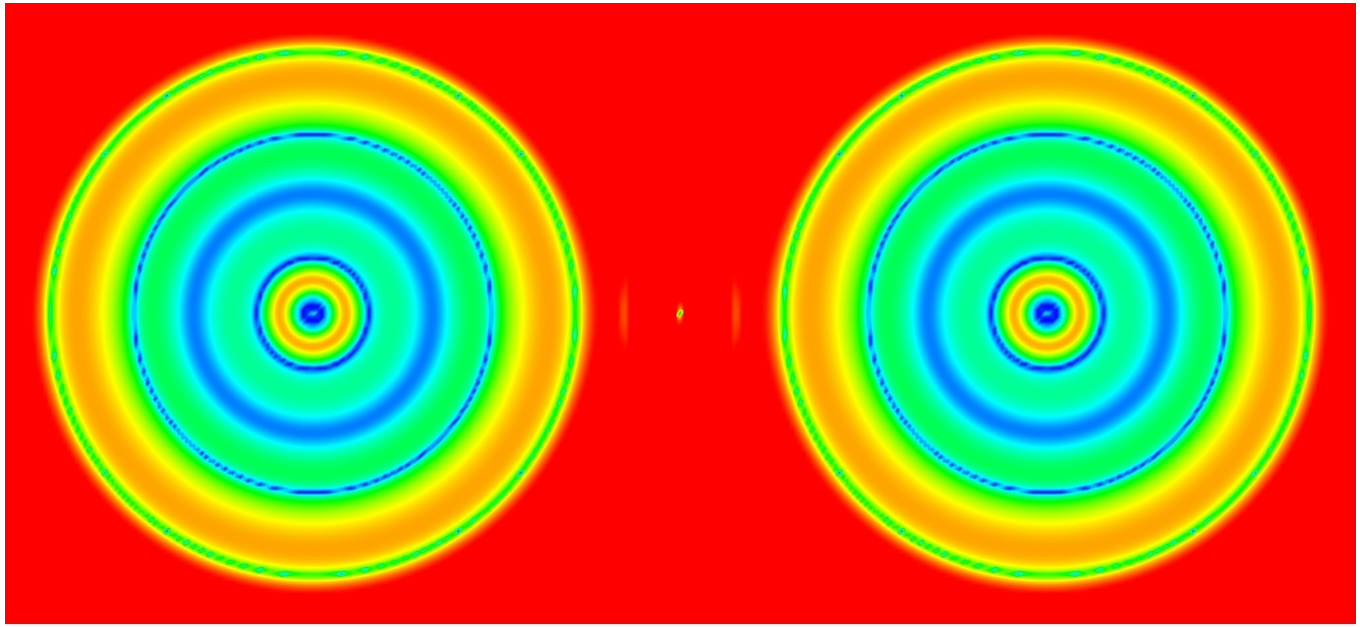




Bond formation: N_2

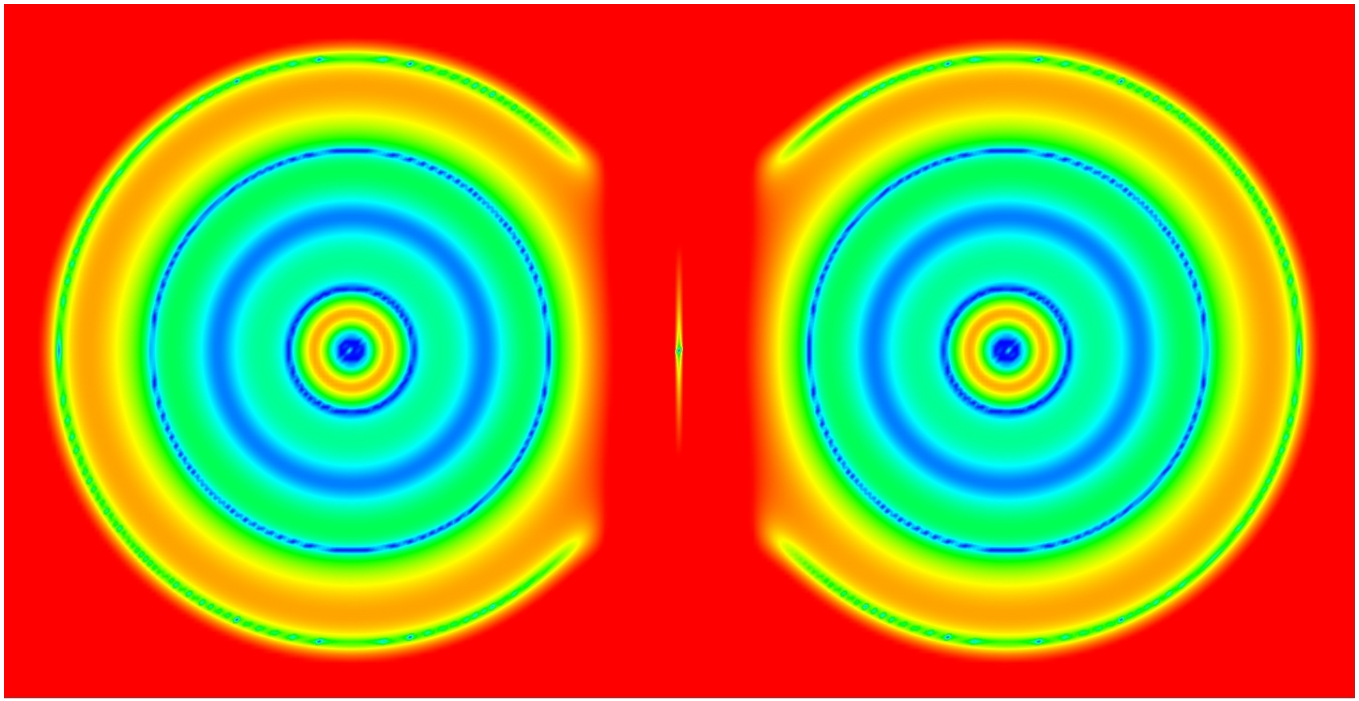
Distance: $10\mathring{A}$

Bond formation: N_2



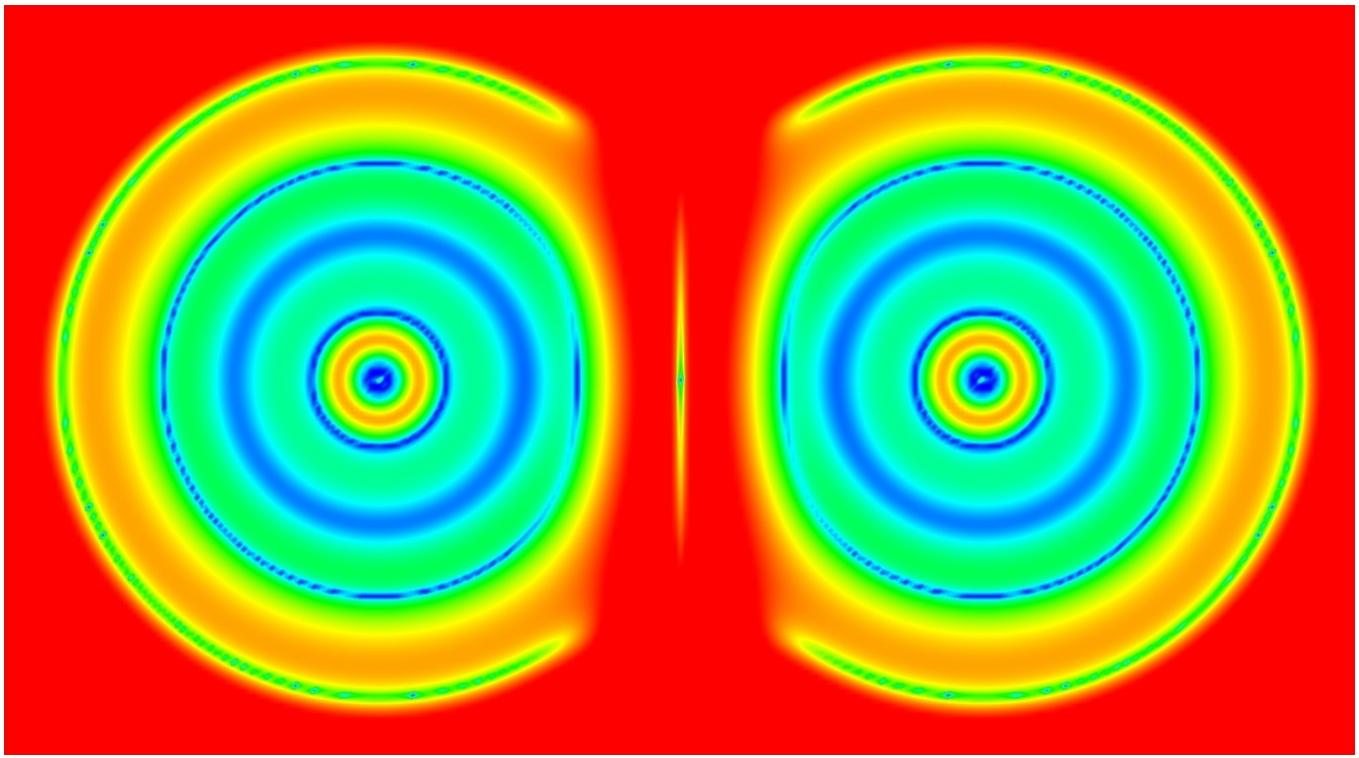
Distance: $5\mathring{A}$

Bond formation: N_2



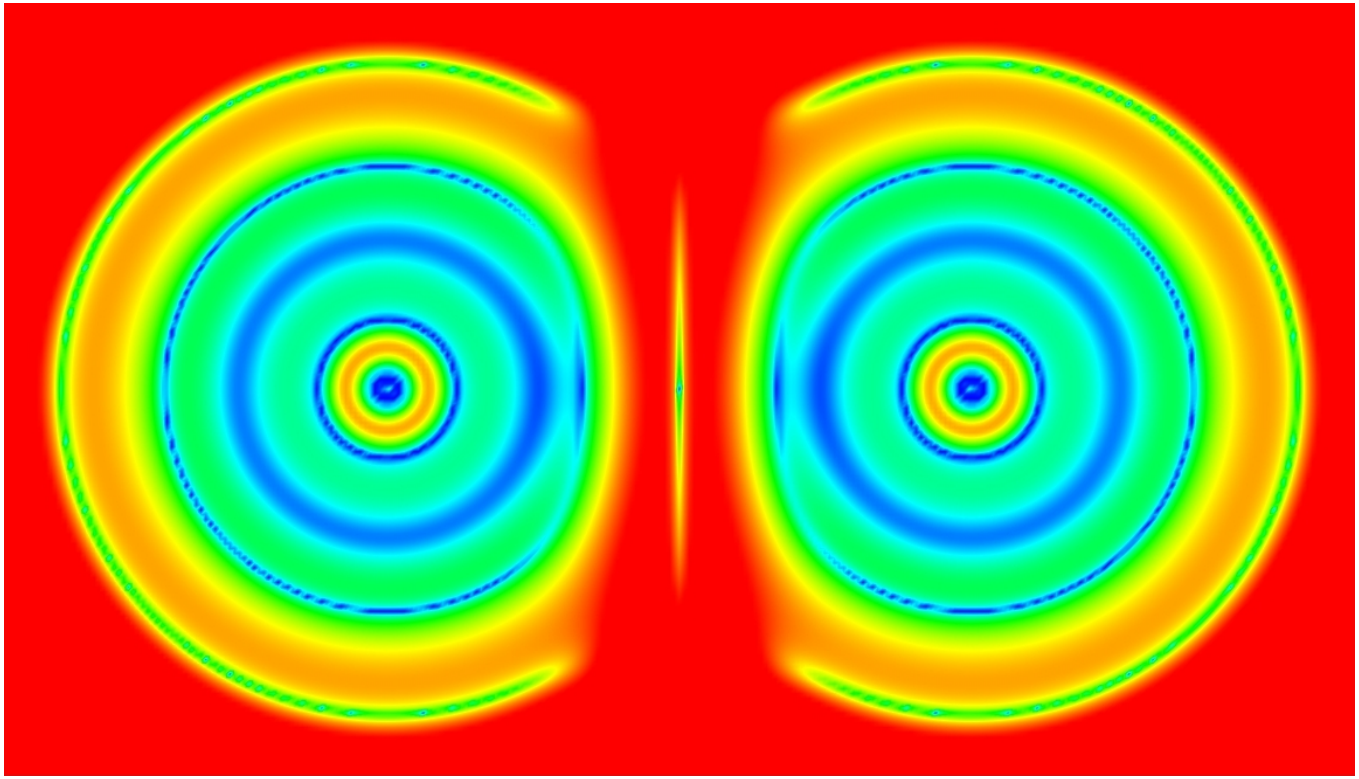
Distance: $4\mathring{A}$

Bond formation: N_2



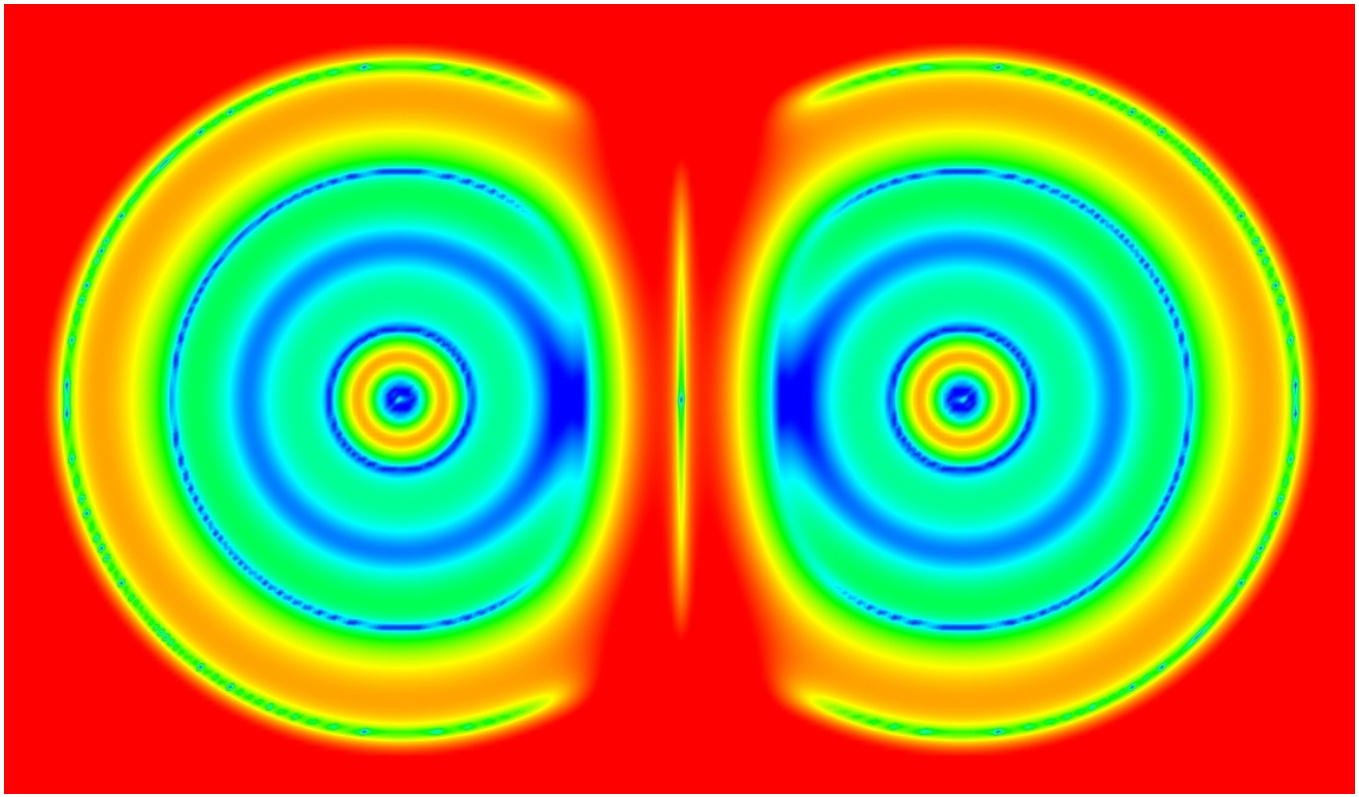
Distance: $3.4\mathring{A}$

Bond formation: N_2



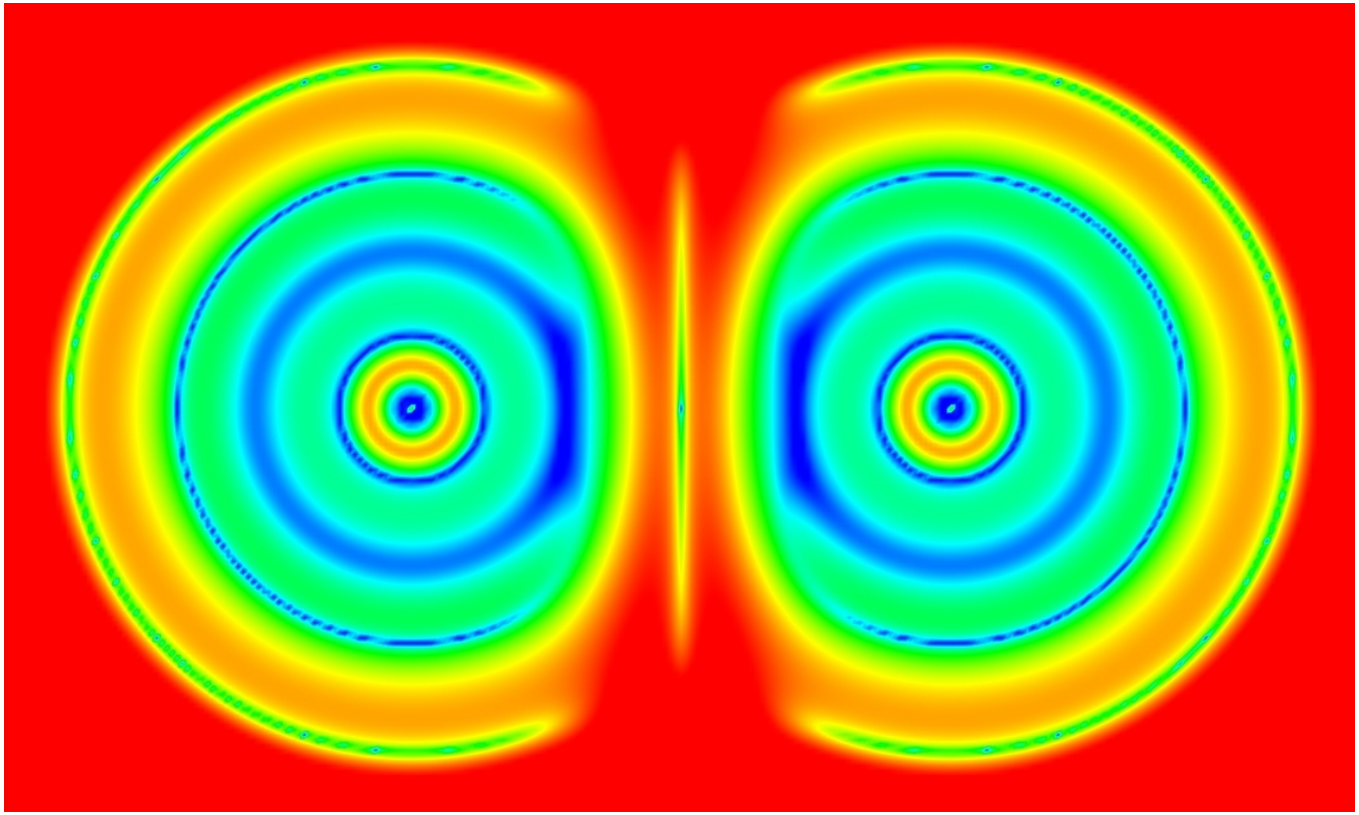
Distance: $3.2\mathring{A}$

Bond formation: N_2



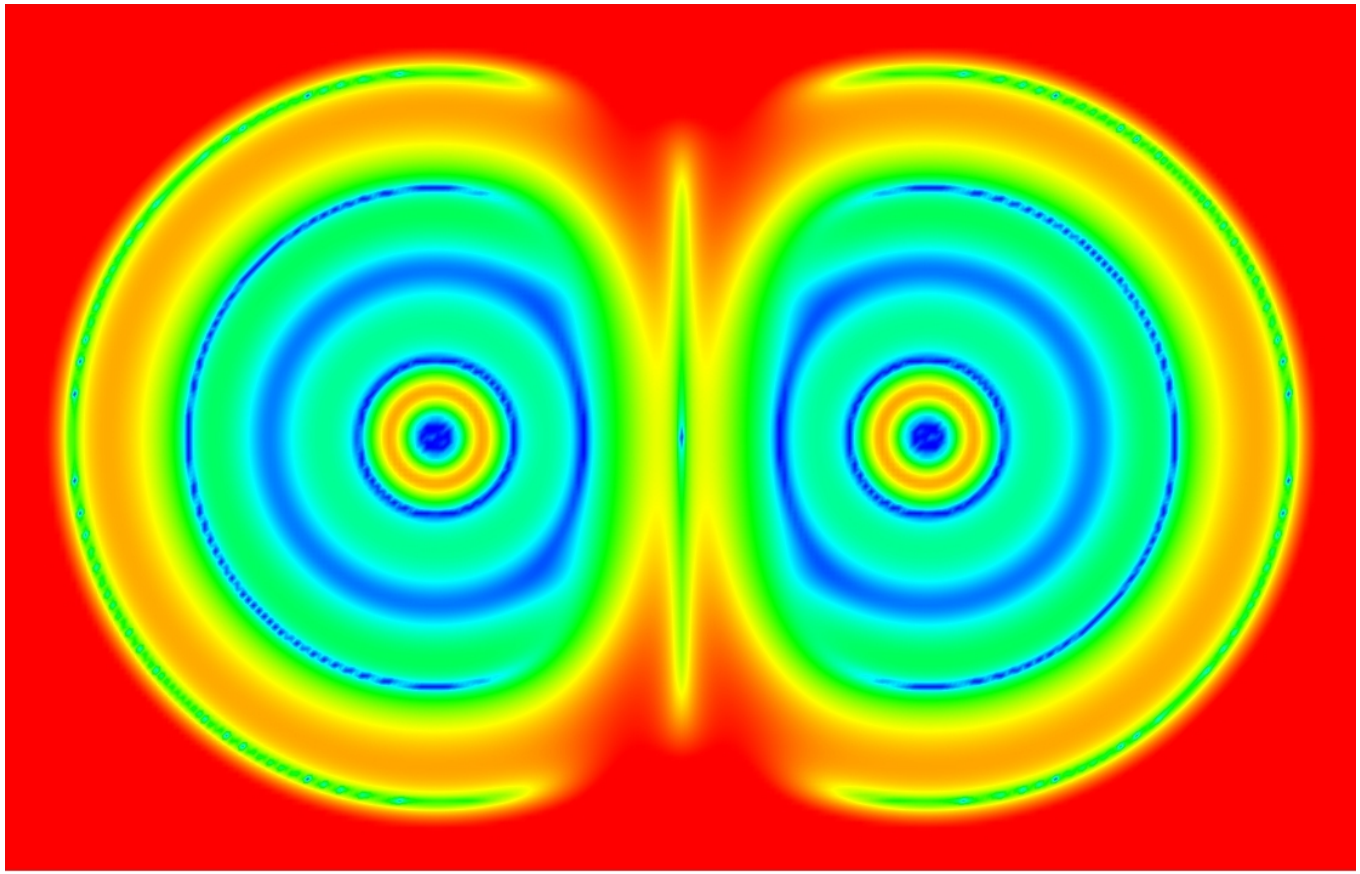
Distance: $3\mathring{A}$

Bond formation: N_2



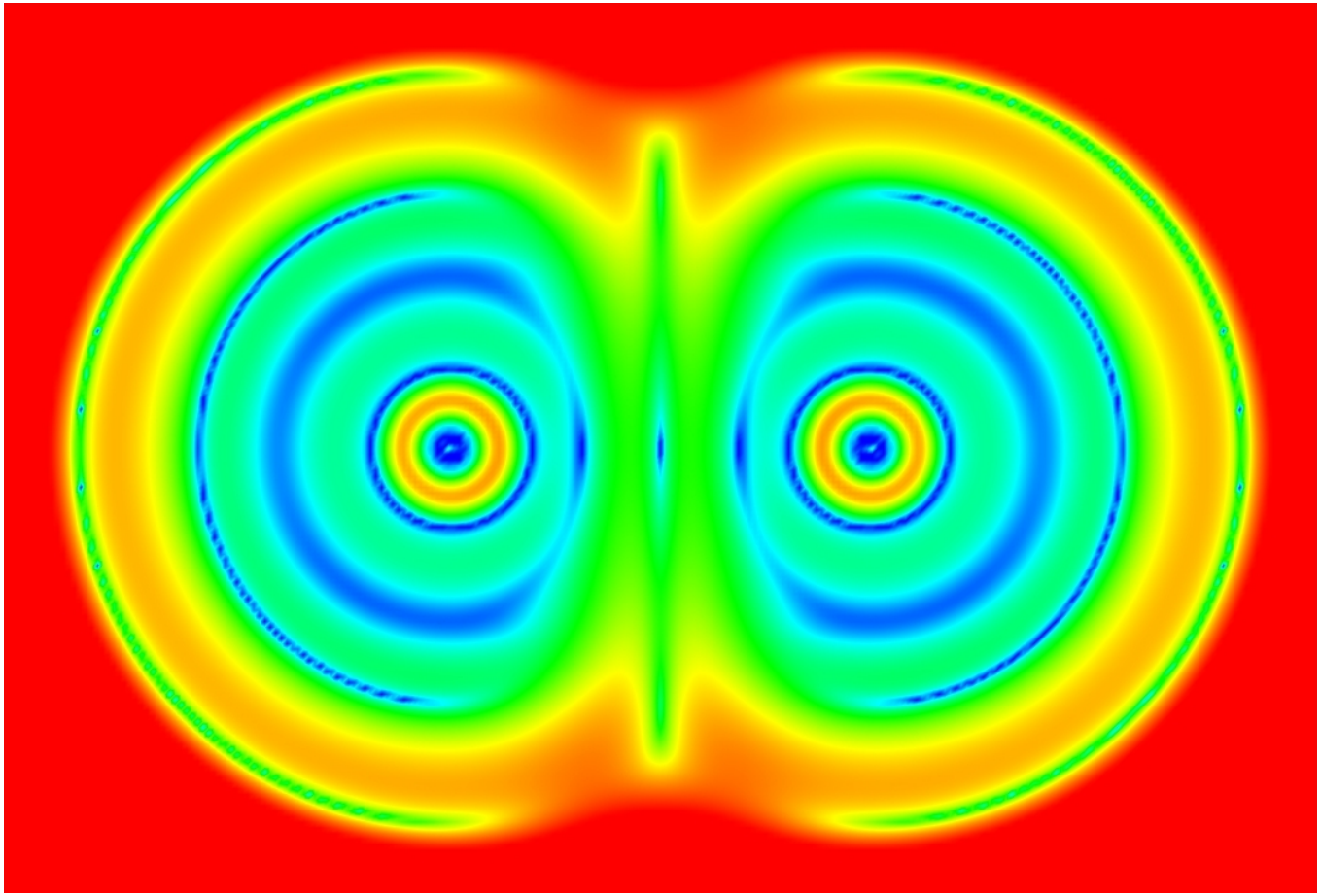
Distance: $2.8\mathring{A}$

Bond formation: N_2



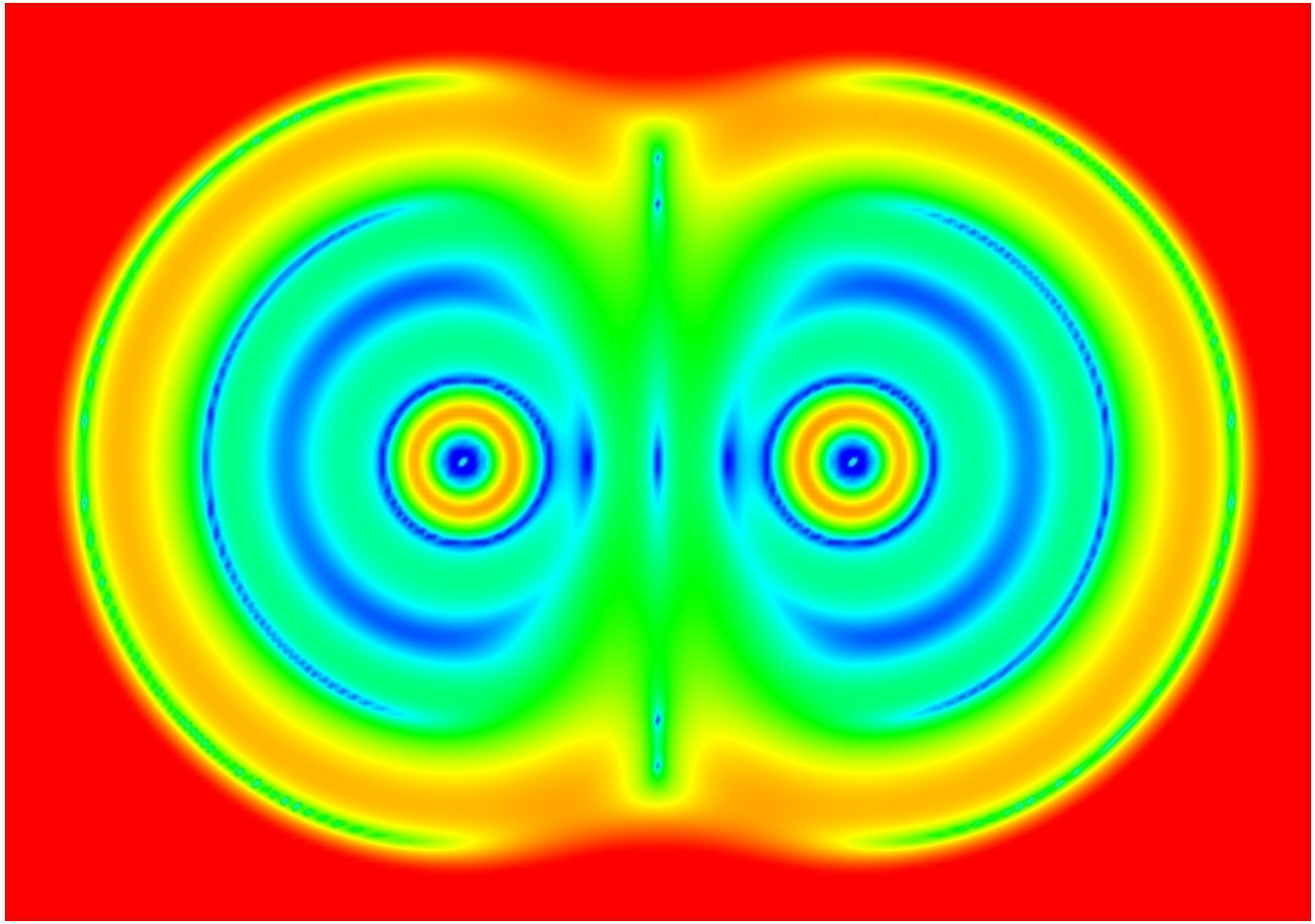
Distance: $2.0\mathring{A}$

Bond formation: N_2



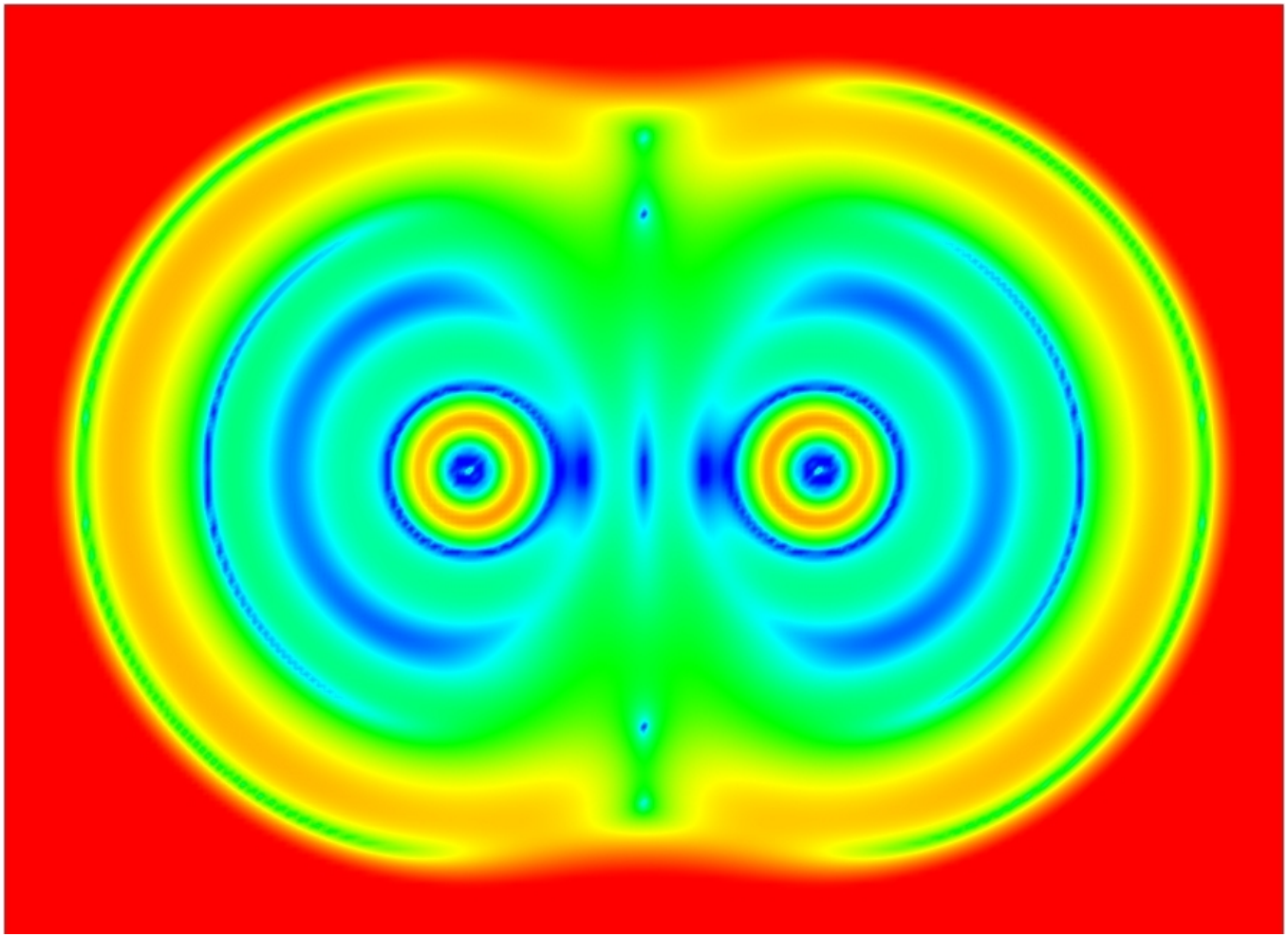
Distance: $2\mathring{A}$

Bond formation: N_2



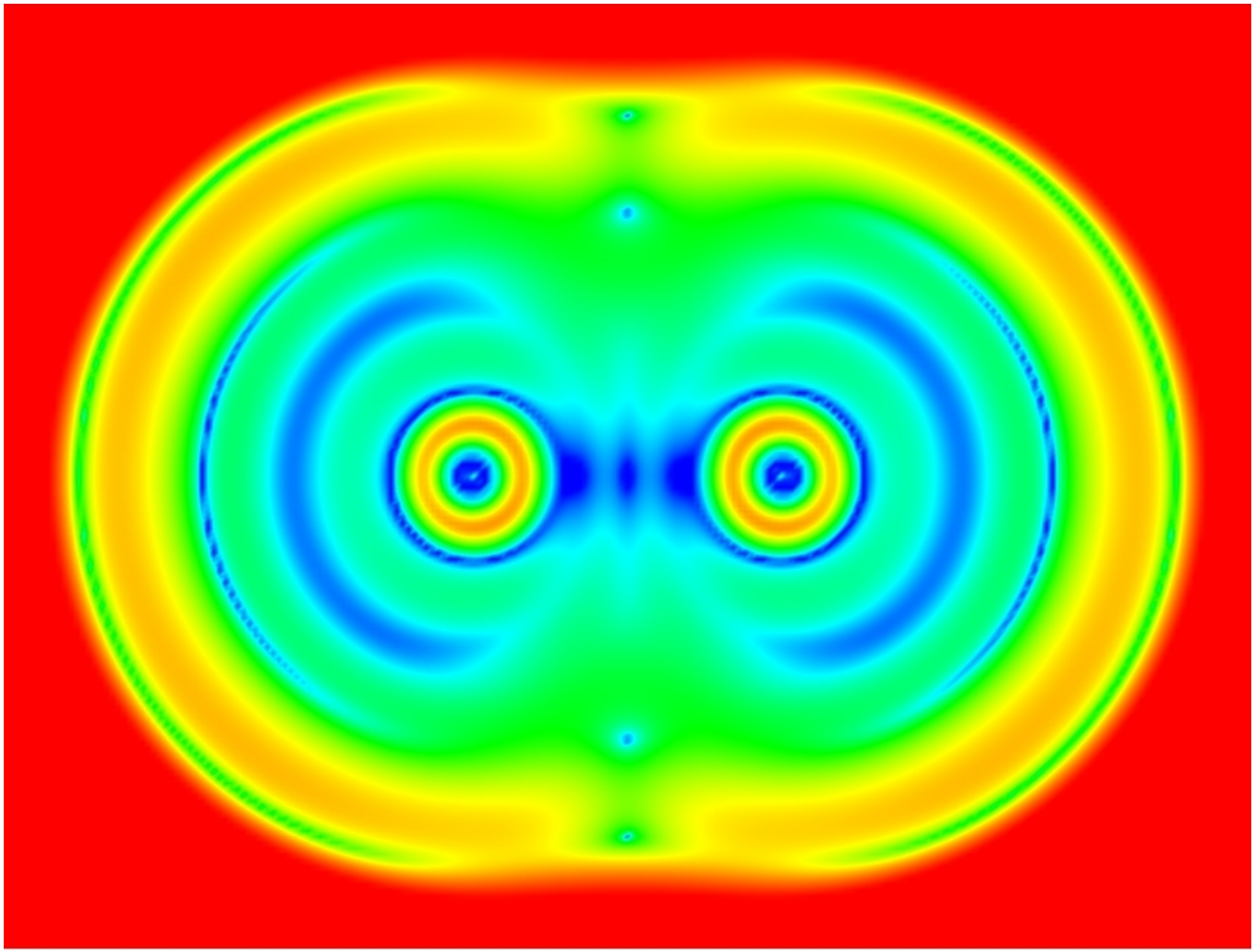
Distance: $1.8\mathring{A}$

Bond formation: N_2



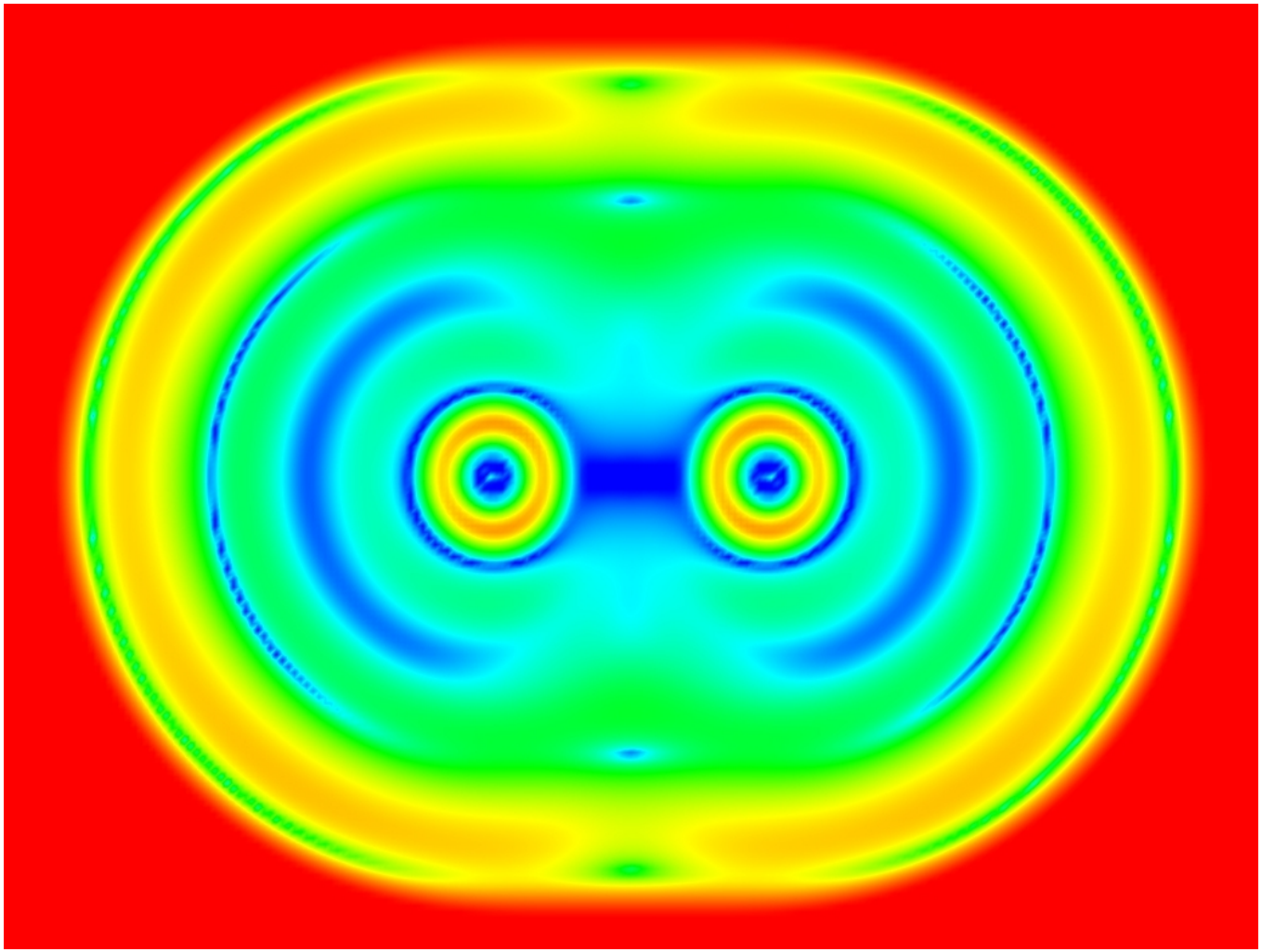
Distance: $1.6\mathring{A}$

Bond formation: N_2



Distance: $1.4\mathring{A}$

Bond formation: N_2



Distance: $1.2\mathring{A}$

Advantages of SEDD

- Reveals elements of electronic structure corresponding to chemical intuition.
- In practice, range of values is system-independent.
- Only density + 1st and 2nd derivatives are needed.
- Easy to implement and cheap to calculate.
- Well defined at any level of theory.
- Directly applicable to experimental densities
- Potentially useful in development of density functionals.