Bonds in motion –
the time-dependent
electron localization function

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Classification of bonds

How can one give a rigorous mathematical meaning to chemical concepts such as

- single, double and triple bonds

- lone pairs

The electron density $n_\sigma(\boldsymbol{r}, t)$ is not useful and the one-particle orbitals that stem from a density functional theory calculation are generally quite delocalised over several atoms, ambiguous and not very intuitive.

Definitions

$$D_\sigma(\boldsymbol{r}, \boldsymbol{r}') := \sum_{\sigma_3,\ldots,\sigma_N} \int \mathrm{d}^3\boldsymbol{r}_3 \cdots \int \mathrm{d}^3\boldsymbol{r}_N \left| \Psi(\boldsymbol{r}\sigma, \boldsymbol{r}'\sigma, \boldsymbol{r}_3\sigma_3, \ldots, \boldsymbol{r}_N\sigma_N, t) \right|^2$$

is the diagonal of the two-body density matrix and gives the probability of finding an electron at $\boldsymbol{r}$ and another with the same spin at $\boldsymbol{r}'$.

$$P_\sigma(\boldsymbol{r}, \boldsymbol{r}') := \frac{D_\sigma(\boldsymbol{r}, \boldsymbol{r}')}{\rho_\sigma(\boldsymbol{r})}$$

is the conditional probability of finding an electron with spin σ at $\boldsymbol{r}$, knowing with certainty that there is an electron with the same spin at $\boldsymbol{r}'$.

Coordinate transformation

Since we are only interested in the probability near the reference point $\boldsymbol{r}$, we make a spherical average, setting $\boldsymbol{r}' := \boldsymbol{r} + \boldsymbol{s}$

$$p_\sigma(\boldsymbol{r}, s) = \frac{1}{4\pi} \int_0^\pi \mathrm{d}\theta \, \sin\theta \int_0^{2\pi} \mathrm{d}\phi \, P_\sigma\big(\boldsymbol{r}, \boldsymbol{r} + (s, \theta, \phi)\big)$$

and Taylor expand $p_\sigma(\boldsymbol{r}, s)$

$$p_\sigma(\boldsymbol{r}, s) = \underbrace{p_\sigma(\boldsymbol{r}, 0)}_{0} + \underbrace{\frac{\mathrm{d}p_\sigma(\boldsymbol{r}, s)}{\mathrm{d}s}}_{0} + \frac{1}{3}C_\sigma(\boldsymbol{r}) \, \boldsymbol{s}^2.$$

The meaning of $C_\sigma(\boldsymbol{r})$

$C_\sigma(\boldsymbol{r})$ is a measure of electron localization. It gives the probability of finding an electron with the same spin in vicinity of the reference electron.

- If $C_\sigma(\boldsymbol{r})$ is small then this reference electron must be localized.

- $C_\sigma(\boldsymbol{r}) \geq 0$ (since it $p_\sigma(\boldsymbol{r}, s)$ is a probability) and not bounded from above.

Definition of the ELF

The electron localization function is defined as
[Becke, Edgecombe, *JCP* **92**, 5397 (1990)]

$$\mathrm{ELF} = \frac{1}{1 + \left(C_\sigma(\boldsymbol{r})/C_\sigma^{\mathrm{uni}}(\boldsymbol{r})\right)^2},$$

where $C_\sigma^{\mathrm{uni}}(\boldsymbol{r}) = \frac{3}{5}(6\pi)^{2/3} n_\sigma^{5/3}(\boldsymbol{r})$ is the kinetic energy density of the uniform electron gas. With this definition, the ELF is dimensionless and $0 \leq \mathrm{ELF} \leq 1$.

high localization $\Leftrightarrow C_\sigma(\boldsymbol{r}) \approx 0 \Leftrightarrow \mathrm{ELF} \approx 1$

completely delocalized $\Leftrightarrow C_\sigma(\boldsymbol{r}) \approx C_\sigma^{\mathrm{uni}}(\boldsymbol{r}) \Leftrightarrow \mathrm{ELF} \approx 1/2$

Derivation of the ELF

When the wave function is a slater determinant one obtains

- in the static case

$$C_\sigma(\boldsymbol{r}) = \sum_{i=1}^{N_\sigma} \left|\nabla\varphi_{i\sigma}(\boldsymbol{r})\right|^2 - \frac{1}{4}\frac{\left(\nabla n_\sigma(\boldsymbol{r})\right)^2}{n_\sigma(\boldsymbol{r})}$$

- in the time-dependent case

$$C_\sigma(\boldsymbol{r},t) = \sum_{i=1}^{N_\sigma} \left|\nabla\varphi_{i\sigma}(\boldsymbol{r},t)\right|^2 - \frac{1}{4}\frac{\left(\nabla n_\sigma(\boldsymbol{r},t)\right)^2}{n_\sigma(\boldsymbol{r},t)} - \frac{\left(\boldsymbol{j}_\sigma(\boldsymbol{r},t)\right)^2}{n_\sigma(\boldsymbol{r},t)}$$

ELF Examples (static case)
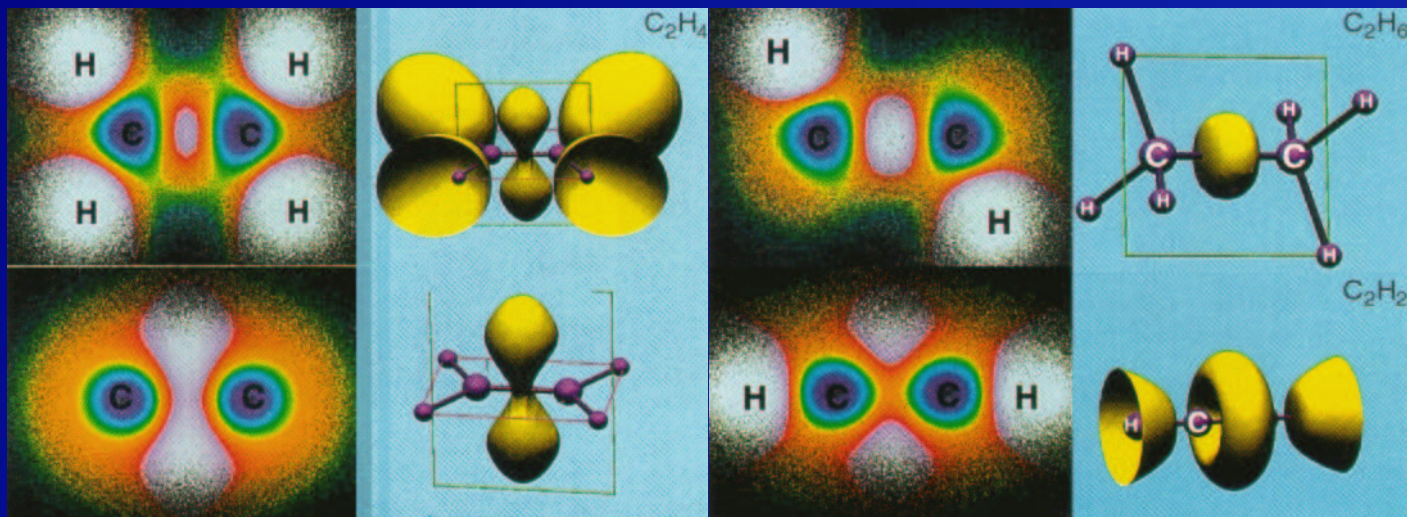
[A. Savin, R. Nesper, S. Wengert and T. F. Fässler,
Angew. Chemie Int. Ed. **36**, 1808 (1997)]

ELF Examples (static case)

Ethyne (acetylene) in a strong laser field
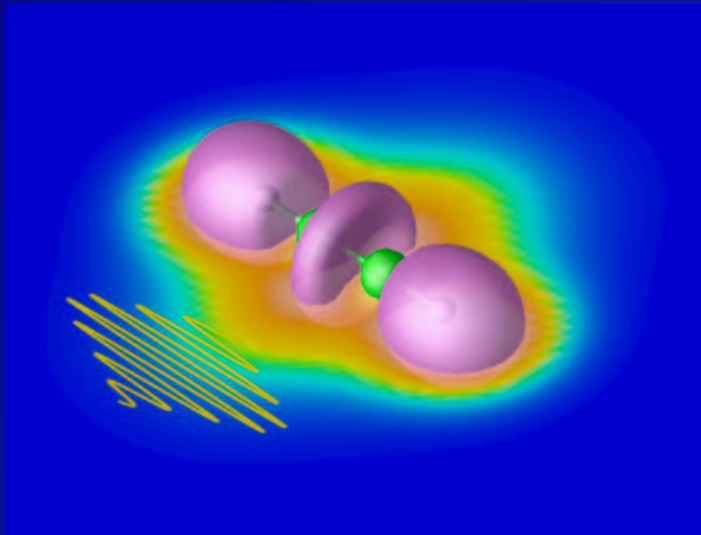
Scattering of a high energetic proton on ethene (ethylene)
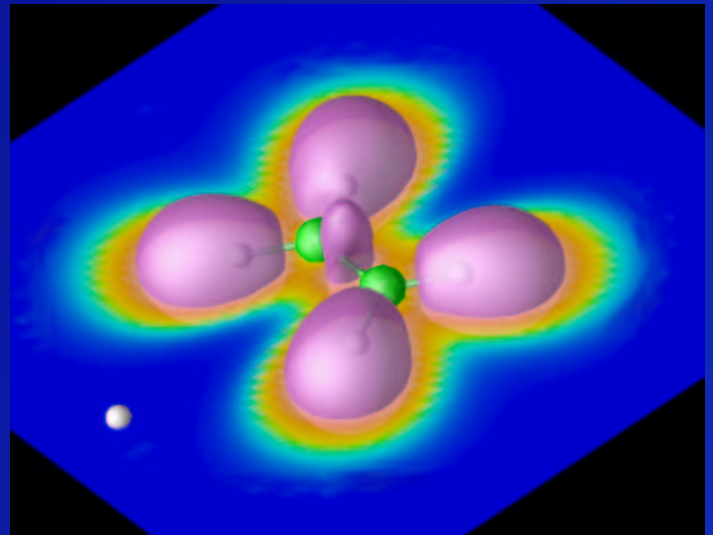
TD-ELF Examples

Ethyne (actylene) in a strong laser field
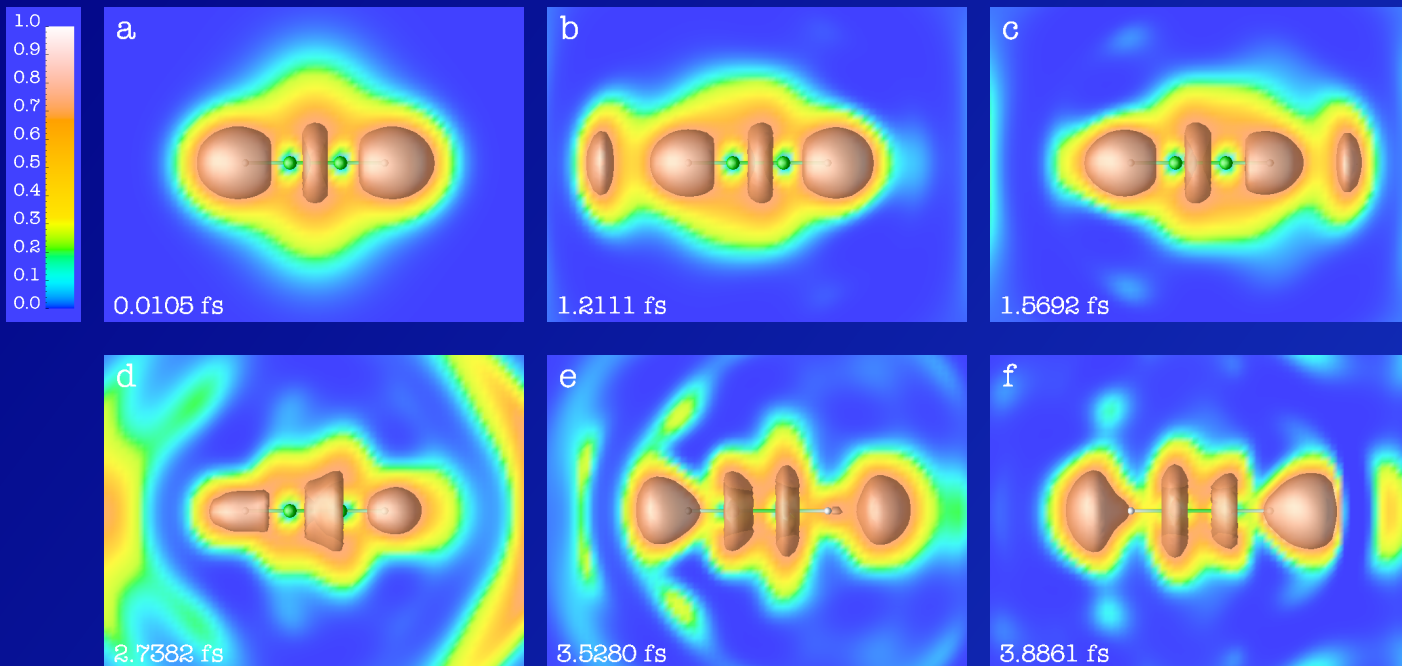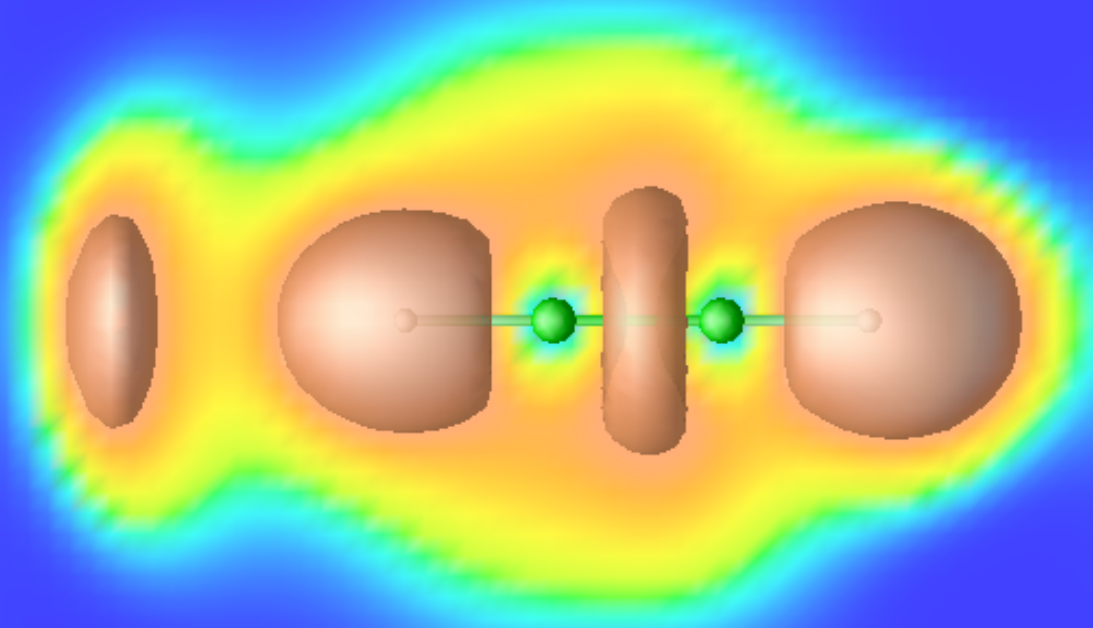
TD-ELF Examples

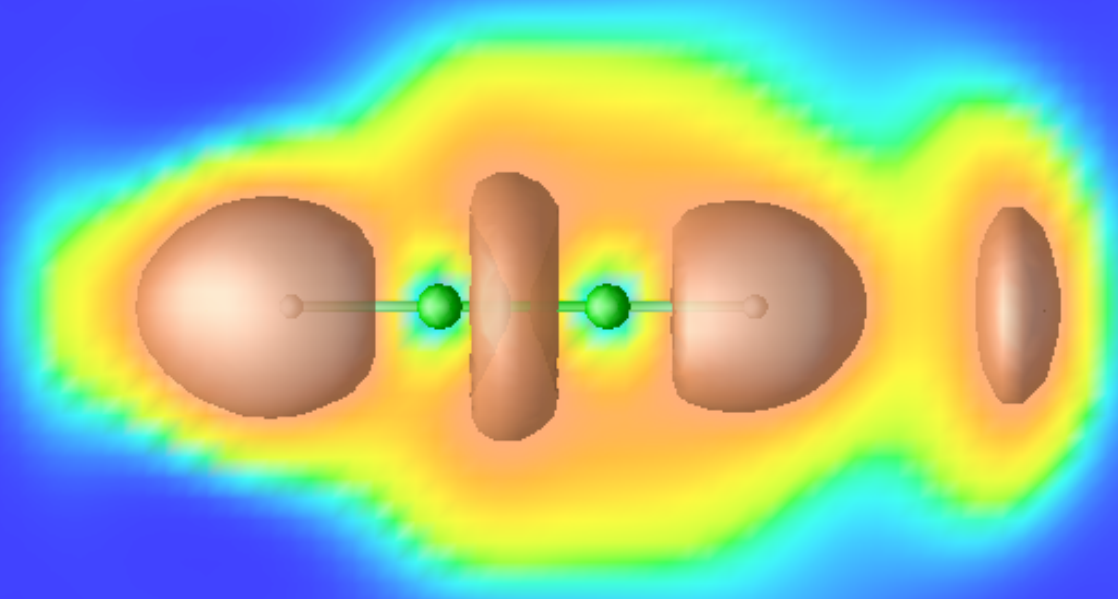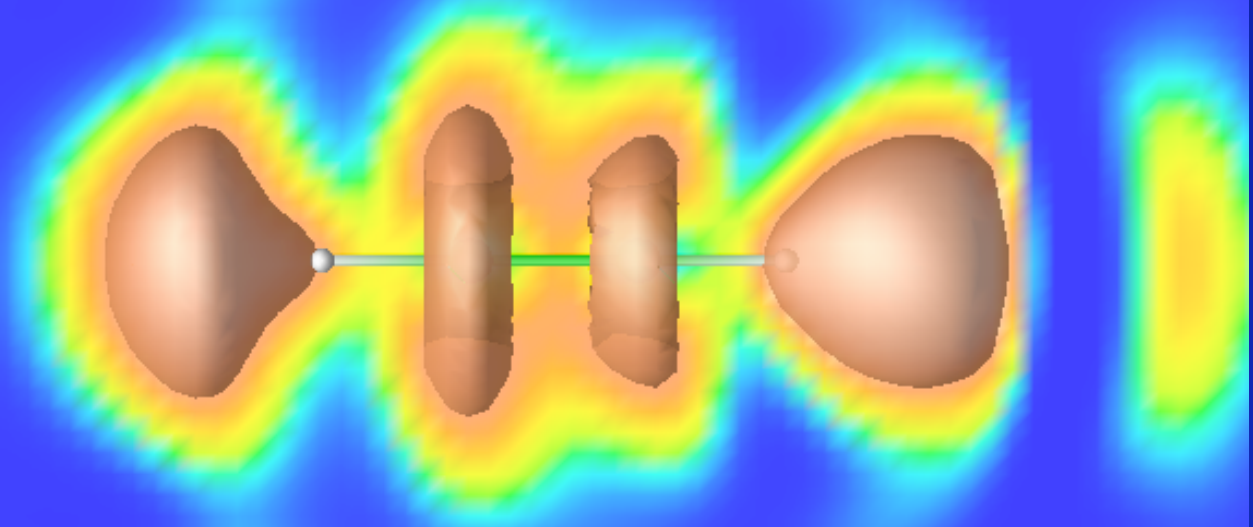Scattering of a high energetic proton on ethene (ethylene)
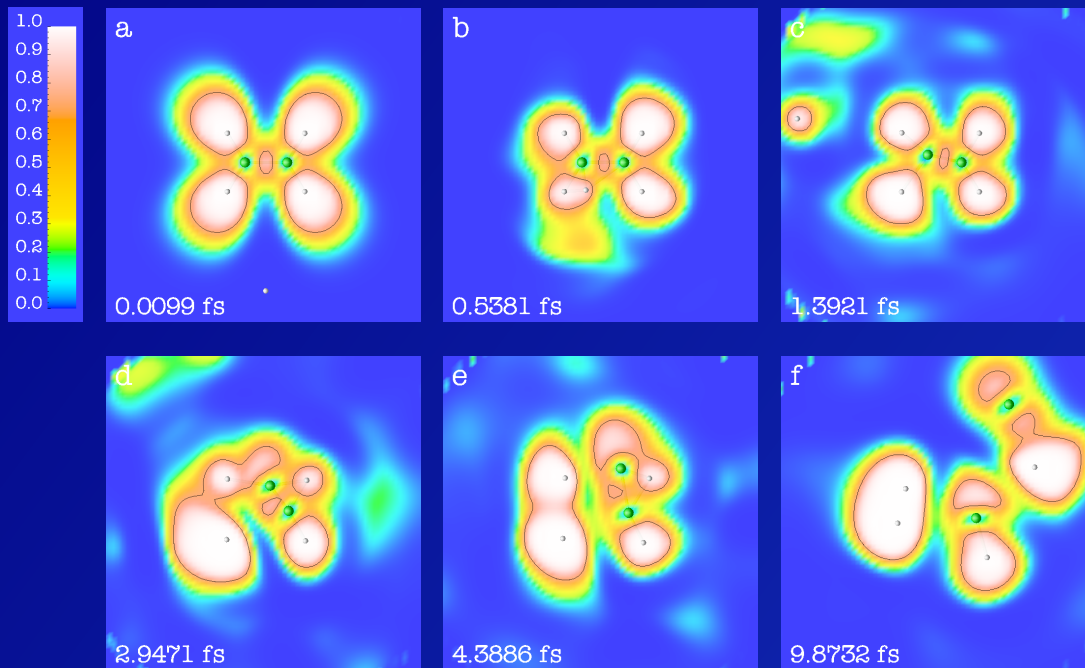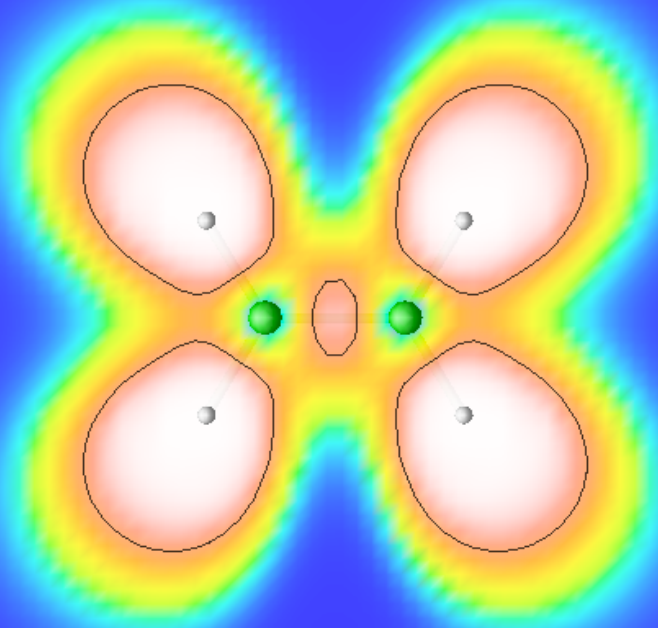
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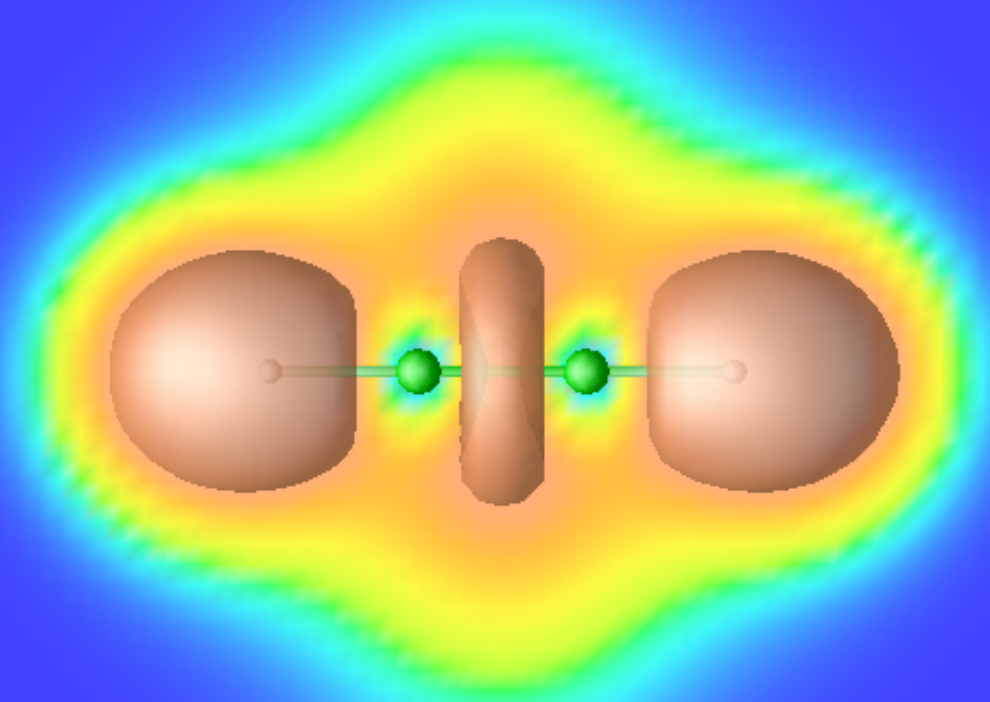
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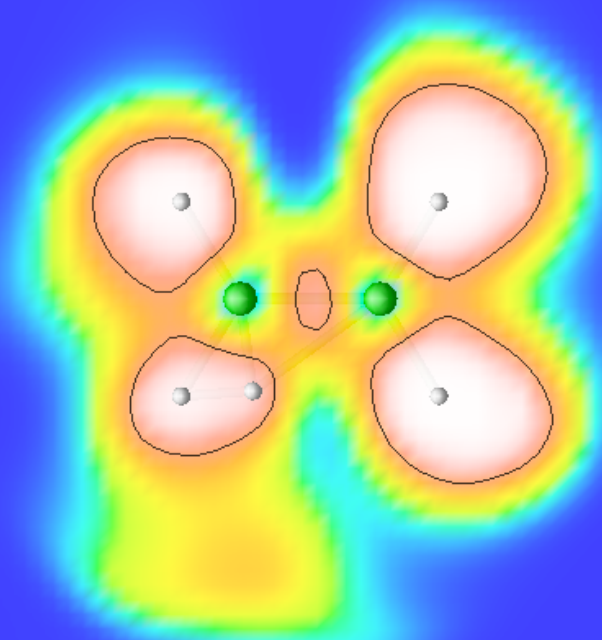
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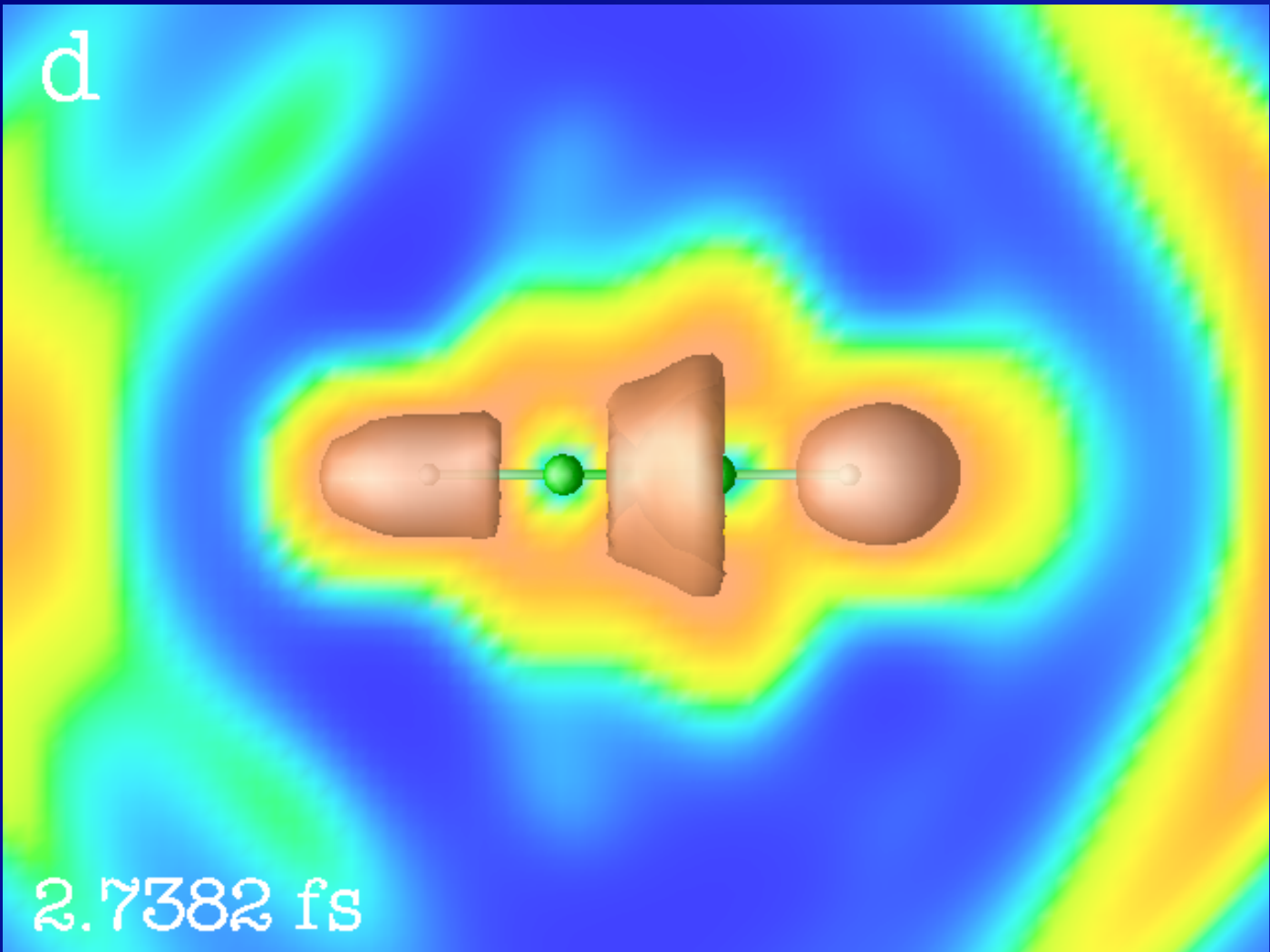
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