A new type of trial wave function for electronic structure calculations with QMC... and also some EPLF.

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Outline

• A new type of trial wavefunction : the multi-Jastrow wavefunction with T.Bouabça (Toulouse) and B. Braîda (Paris)

- PhD work of Thomas Bouabça (Phd Thesis, Univ. of Toulouse, May 2009)

-T. Bouabça, Benoit Braida, and M. Caffarel "Multi-Jastrow trial wavefunctions for electronic structure calculations with quantum Monte Carlo" (submitted to JCP)

• Visualizing the electronic pairing in molecules : the EPLF and analytic EPLF with A. Scemama (Toulouse)

Users : J.P. Piquemal (Paris), R. Chaudret (Paris), Alejandro Ramírez-Solís (Cuernavaca, Mexico), F. Alaray (Toulouse), and J.L. Heully (Toulouse).

Trial wavefunctions

- **Jastrow-Slater form**

The usual form....

- **Geminals**

Casula, Sorella and coll.

Jastrow-Antisymmetrized Geminal Power (JAGP, see Mariapieta's talk)

- **Pfaffian pairing wavefunctions** (generalization of geminals)

Mitas and coll.

- **Use of backflow transformations**

Long history. Recently, for molecules : Mike, Pablo, Richard and many people here....

- **Pfaffian + Backflow** (Mitas et al.)

etc.

Slater-Jastrow

$$\Psi_T = e^{J(\mathbf{r}_1, \ldots, \mathbf{r}_N)} \sum_{k=1}^{N_{det}} c_k Det_k(\{\Phi_i^{\uparrow}\}) Det_k(\{\Phi_i^{\downarrow}\})$$

with (typically)

$$J(\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{i<j} v_{e-e}(r_{ij}) + \sum_{\alpha} v_{e-n}(r_{i\alpha})$$

$$+ \sum_{i<j} \sum_{\alpha} v_{e-e-n}(r_{ij}, r_{i\alpha}, r_{j\alpha})$$

The multi-Jastrow form

$$\Psi_T = \sum_{k=1}^{N_{det}} c_k$$

$$\times \begin{vmatrix} e^{J_{k_1^\uparrow}(\mathbf{r}_1|\mathbf{r}_i \neq \mathbf{r}_1)} \phi_{k_1^\uparrow}(\mathbf{r}_1) & \ldots & e^{J_{k_1^\uparrow}(\mathbf{r}_{N_\uparrow}|\mathbf{r}_i \neq \mathbf{r}_{N_\uparrow})} \phi_{k_1^\uparrow}(\mathbf{r}_{N_\uparrow}) \\ \vdots & \vdots & \vdots \\ e^{J_{k_{N_\uparrow}^\uparrow}(\mathbf{r}_1|\mathbf{r}_i \neq \mathbf{r}_1)} \phi_{k_{N_\uparrow}^\uparrow}(\mathbf{r}_1) & \ldots & e^{J_{k_{N_\uparrow}^\uparrow}(\mathbf{r}_{N_\uparrow}|\mathbf{r}_i \neq \mathbf{r}_{N_\uparrow})} \phi_{k_{N_\uparrow}^\uparrow}(\mathbf{r}_{N_\uparrow}) \end{vmatrix}$$

$$\times \begin{vmatrix} e^{J_{k_1^\downarrow}(\mathbf{r}_{N_\uparrow+1}|\mathbf{r}_i \neq \mathbf{r}_{N_\uparrow+1})} \phi_{k_1^\downarrow}(\mathbf{r}_{N_\uparrow+1}) & \ldots & e^{J_{k_1^\downarrow}(\mathbf{r}_N|\mathbf{r}_i \neq \mathbf{r}_N)} \phi_{k_1^\downarrow}(\mathbf{r}_N) \\ \vdots & \vdots & \vdots \\ e^{J_{k_{N_\downarrow}^\downarrow}(\mathbf{r}_{N_\uparrow+1}|\mathbf{r}_i \neq \mathbf{r}_{N_\uparrow+1})} \phi_{k_{N_\downarrow}^\downarrow}(\mathbf{r}_{N_\uparrow+1}) & \ldots & e^{J_{k_{N_\downarrow}^\downarrow}(\mathbf{r}_N|\mathbf{r}_i \neq \mathbf{r}_N)} \phi_{k_{N_\downarrow}^\downarrow}(\mathbf{r}_N) \end{vmatrix}.$$

The multiJastrow form

Compact notation for molecular Jastrow k :

$$J_k(\mathbf{r}_j|\mathbf{r}_i \neq \mathbf{r_j}) \equiv J_k(\mathbf{r}_j|\mathbf{r}_1, \ldots, \mathbf{r}_i \neq \mathbf{r}_j, \ldots, \mathbf{r}_N)$$

Definitions :

• j : primary electron occupying the molecular orbital associated with J_k

• other electrons ($i \neq j$) : external electrons.

Fundamental constraint :

We impose to each J_k to be symmetric with respect to the exchange of two external electrons.

The multiJastrow form

Two important ideas motivating this form :

I. To be able of describing the electron-electron (dynamic) correlation *locally* and not in a global way as usual

For example :

- J_{1s} for the 1s core atomic orbitals
- J_{3d} for the 3d orbitals of transition metal systems
- J(lone pairs)
- J(aromatic cycle-π orbitals)

etc.

II. To be able to optimize once for all local Jastrows corresponding to well-defined chemical situations and rely on transferability (data bank of pre-optimized Jastrows)

Form of the molecular Jastrow

$$J_k(\mathbf{r}_i|\mathbf{r}_j \neq \mathbf{r_i}) =$$

$$\frac{1}{2}\sum_{j\neq i}\sum_{\alpha}[s_k(\tilde{r}_{ij}) - p_{k\alpha}(\tilde{r}_{i\alpha}) - p_{k\alpha}(\tilde{r}_{j\alpha}) + g_{k\alpha}^{(1)}\tilde{r}_{i\alpha}^2\tilde{r}_{j\alpha}^2 + g_{k\alpha}^{(2)}(\tilde{r}_{i\alpha}^2 + \tilde{r}_{j\alpha}^2)\tilde{r}_{ij}^2]$$

with $\tilde{r}_{ij}^{(k)} \equiv \frac{r_{ij}}{1+b_k r_{ij}}$ $\tilde{r}_{i\alpha}^{(k)} \equiv \frac{r_{i\alpha}}{1+b_{\alpha k} r_{i\alpha}}$

$$s_k(r) = (e_k^{(1)}r + e_k^{(2)}r^2 + e_k^{(3)}r^3 + e_k^{(4)}r^4)$$

$$p_{k\alpha}(r) = (f_{k\alpha}^{(1)}r + f_{k\alpha}^{(2)}r^2 + f_{k\alpha}^{(3)}r^3 + f_{k\alpha}^{(4)}r^4)$$

Computation of derivatives

We need Ψ_T, $\nabla\Psi_T$, and $\nabla^2\Psi_T$. When optimizing (linear method) : $\partial_{c_p}\Psi_T$, and $\nabla^2\frac{\partial\Psi_T}{\partial c_p}$

Computation of derivatives tedious but feasible.

<u>Ideas :</u>

• As usual, except that the derivatives are to be done along all columns or all lines of the Slater matrix.

• Determinants are not systematically computed but obtained by successive modifications of previous ones .
Use of the Sherman-Morison formula

$$(A + u \otimes v)^{-1} = A^{-1} - \frac{z \otimes w}{1 + \lambda}$$

where $\lambda \equiv (v, A^{-1}u)$, $z \equiv A^{-1}u$,   and $w \equiv (A^{-1})^T v$

Computation of derivatives

For example, Laplacian of the trial wave function :

$$\Psi_{ij}^{\sigma} \equiv e^{J_i(\mathbf{r}_j | \mathbf{r}_k \neq \mathbf{r}_j)} \phi_i(\mathbf{r}_j)$$

$$(\delta M_k^{\sigma})_j \equiv -\Psi_{jk}^{\sigma} + \partial_{i,l}^2 \Psi_{jk}^{\sigma} \quad j = 1, N_{\sigma}.$$

$$(P_k^{\sigma})_n = \sum_{j=1}^{N_{\sigma}} [\Psi^{\sigma}]_{nj}^{-1} (\delta M_k^{\sigma})_j$$

$$(P_m^{\sigma})_n = \sum_{j=1}^{N_{\sigma}} [\Psi^{\sigma}]_{nj}^{-1} (\delta M_m^{\sigma})_j$$

$$\partial_{i,l}^2 \Psi^{\sigma} = \sum_{k=1}^{N_{\sigma}} \sum_{m=1}^{N_{\sigma}} \Psi^{\sigma} \{ [1 + (P_k^{\sigma})_k)(1 + (P_m^{\sigma})_m] - (P_m^{\sigma})_k (P_k^{\sigma})_m \}$$

Number of determinants to evaluate at each elementary step (for each walker).

	Slater-Jast.	multi-Jast.
VMC/DMC		
Ψ_T	2	2
$\nabla \Psi_T$	$3N_e$	$3N_e^2$
$\nabla^2 \Psi_T$	$3N_e$	$3N_e[N_e + \frac{N_\uparrow(N_\uparrow - 1)}{2} + \frac{N_\downarrow(N_\downarrow - 1)}{2}]$
Optimization		
$\frac{\partial \Psi_T}{\partial c_p}$	0	N_{line}
$\nabla^2 \frac{\partial \Psi_T}{\partial c_p}$	0	$3N_e[\frac{N_\uparrow(N_\uparrow - 1)}{2} + N_\uparrow]N_{line}(\uparrow)$ $+3N_e[\frac{N_\downarrow(N_\downarrow - 1)}{2} + N_\downarrow]N_{line}(\downarrow)$

$N_{line}(\sigma = \uparrow, \downarrow)$ = total number of lines in Slater matrix σ where a parameter appears. $N_{line} = N_{line}(\uparrow) + N_{line}(\downarrow)$

Timing VMC. O and Cu atoms

	Slat-Jast	1-mJast	2-mJast	3-mJast	5-mJast
O atom					
Jastrow	29.5	30.2			105.2
Matrix elts	18.6	19.2			19.8
S^{-1}	3.9	4.1			4.3
Dets/# of dets	1.6/48	90.5/696			92.4/696
Total	53.6	144.0			221.7
Cu atom					
Jastrow	429.5	262.2	472.7	677.0	
Matrix elts	335.0	337.5	337.5	337.6	
S^{-1}	77.1	75.0	75.1	75.9	
Dets/# of dets	20.2/174	2120.5/22098	2121.2/22098	2123.1/22098	
Total	861.8	2795.2	3006.5	3213.6	

Timing Optimization. O and Cu atoms

	Slat-Jast. 1	Slat-Jast. 19	(1,1,1)	(12,1,1)	(2,1,2)
Oxygen atom					
Jastrow	59.1	92.0	43.5	126.0	43.9
Matrix elements	19.1	19.4	19.3	19.7	19.1
Inverse of Slater matrices	3.6	3.7	4.1	4.7	4.4
Dets	1.6	1.7	111.6	113.8	112.3
Dets optimization	-	-	106.9	1077.3	210.0
Total	83.4	116.8	285.4	1341.5	389.7
Copper atom					
Jastrow	1011.4	1323.2	411.5	3552.9	
Matrix elements	336.5	338.1	339.8	340.5	
Inverse of Slater matrices	80.1	79.0	75.3	92.6	
Dets	20.4	21.5	2130.4	2134.2	
Dets optimization	-	-	2919.6	34507.3	
Total	1448.4	1761.8	5876.6	40627.5	

Optimization

Use of linear optimization method of Umrigar et al (2007)

Ref. C. J. Umrigar, J. Toulouse, C. Filippi, S. Sorella, and R. G. Hennig, Phys. Rev. Lett. **98**, 110201 (2007)

VMC/DMC Oxygen atom

Method	Energy (a.u.)	σ^2(Energy)	Correlation energy
Hartree-Fock[?]	-74.8094	-	0%
"Exact" non-relativistic[?]	-75.0673	-	100%
VMC :			
HF (no Jastrow of any type)	-74.808(2)	15.9(3)	$0.\% \pm 0.8\%$
HF + optimized common Jastrow	-75.025(1)	1.178(7)	$83.6\% \pm 0.4\%$
HF + optimized molecular Jastrows	-75.0275(4)	1.133(8)	$84.6\% \pm 0.2\%$
FN-DMC :			
Hartree-Fock nodes	-75.052(1)		$94.1\% \pm 0.4\%$
Molecular Jastrow nodes	-75.052(1)		$94.1\% \pm 0.4\%$

VMC/DMC Copper atom

Method	Energy (a.u.)	σ^2(Energy)	Correlation energy
Hartree-Fock[?]	-1638.9637	-	0%
"Exact" non-relativistic[?]	-1640.5677	-	100%
VMC :			
HF (no Jastrow of any type)	-1638.970(6)	423(7)	$0.\% \pm 0.8\%$
HF + optimized common Jastrow	-1639.672(5)	587(14)	$44.2\% \pm 0.3\%$
HF + optimized molecular Jastrows	-1640.1725(74)	131(3)	$75.4\% \pm 0.5\%$
FN-DMC :			
Hartree-Fock nodes	-1640.401(9)		$89.6\% \pm 0.6\%$
Molecular Jastrow nodes	-1640.407(8)		$90.0\% \pm 0.5\%$

HF Molecule

Using the multi-Jastrow wavefunction the atomic e-e and valence e-e correlation can be separated.

Atomic part : No Jastrow for the fluor 1s electrons

Valence part : A common *valence* Jastrow for the valence molecular orbitals

Spectroscopic constants of HF

Method	R_e (a.u.)	ω_e (cm^{-1})	ΔE (kcal/mol)
DMC[2-det CASSCF (DZ basis) nodes]	1.7042	4508.	131.9(3)
DMC[2-det CASSCF (TZ basis) nodes]	1.7186	4378.	137.7(3)
DMC[2-det CASSCF (QZ basis) nodes]	1.7368	3915.	138.0(4)
DMC[2-det CASSCF (5Z basis) nodes]	1.7257	3782.	138.2(4)
DMC[2-det CASSCF (DZ basis)+ val. Jast. nodes]	1.7209	3927.	135.3(3)
DMC[2-det CASSCF (TZ basis)+ val. Jast. nodes]	1.7146	4706.	139.4(4)
DMC[2-det CASSCF (QZ basis)+ val. Jast. nodes]	1.7248	4304.	140.3(4)
DMC[2-det CASSCF (5Z basis)+ val. Jast. nodes]	1.7174	4160	140.5(4)
Exact	1.7326	4137	141.5

Electronic Pair Localizat. Funct., EPLF

Ref. A. Scemama, P. Chaquin, M. Caffarel JCP **121**, 1725 (2004)

$$d_{\sigma\sigma}(\vec{r}) \equiv \sum_{i=1}^{N} \langle\langle \delta(\vec{r} - \vec{r_i}) \min_{j;\ \sigma_j=\sigma_i} |\vec{r_i} - \vec{r_j}| \rangle\rangle$$

$$d_{\sigma\bar{\sigma}}(\vec{r}) \equiv \sum_{i=1}^{N} \langle\langle \delta(\vec{r} - \vec{r_i}) \min_{j;\ \sigma_j\neq\sigma_i} |\vec{r_i} - \vec{r_j}| \rangle\rangle \qquad (1)$$

$$\mathrm{EPLF}(\vec{r}) = \frac{d_{\sigma\sigma}(\vec{r}) - d_{\sigma\bar{\sigma}}(\vec{r})}{d_{\sigma\sigma}(\vec{r}) + d_{\sigma\bar{\sigma}}(\vec{r})} \qquad (2)$$

Visualization of electronic distributions

● In regions of space where electrons are unpaired the average distances between spin-like and spin-unlike electrons are similar, $d_{\sigma\bar{\sigma}} \approx d_{\sigma\sigma}$, and EPLF goes to zero.

● When spin-unlike electrons are paired we have $d_{\sigma\bar{\sigma}} \ll d_{\sigma\sigma}$ and EPLF goes to 1.

● when spin-like electrons are paired, $d_{\sigma\bar{\sigma}} \gg d_{\sigma\sigma}$ and, thus, EPLF goes to -1.

Polyacethylene + Li
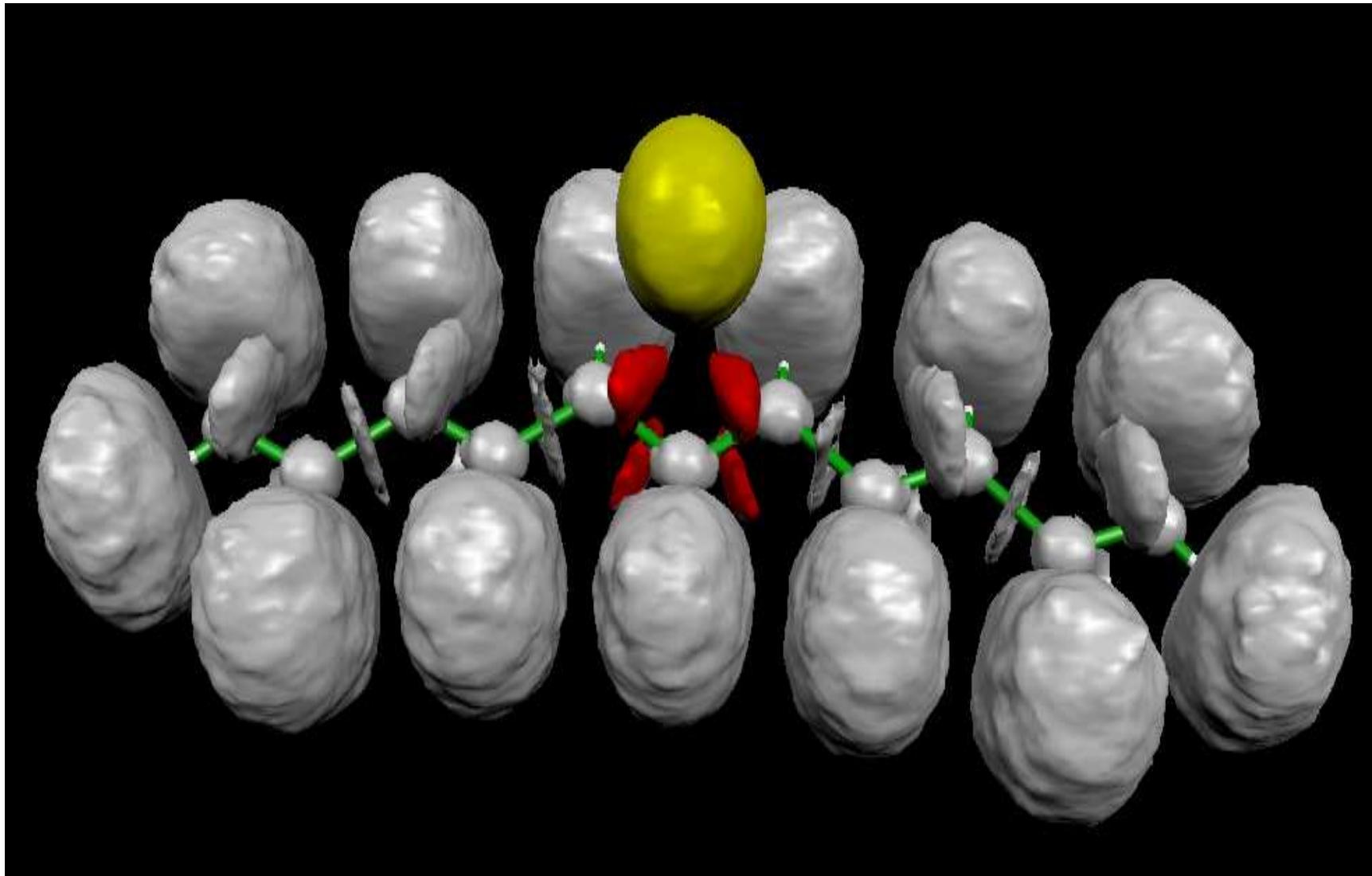
Hemocyanine
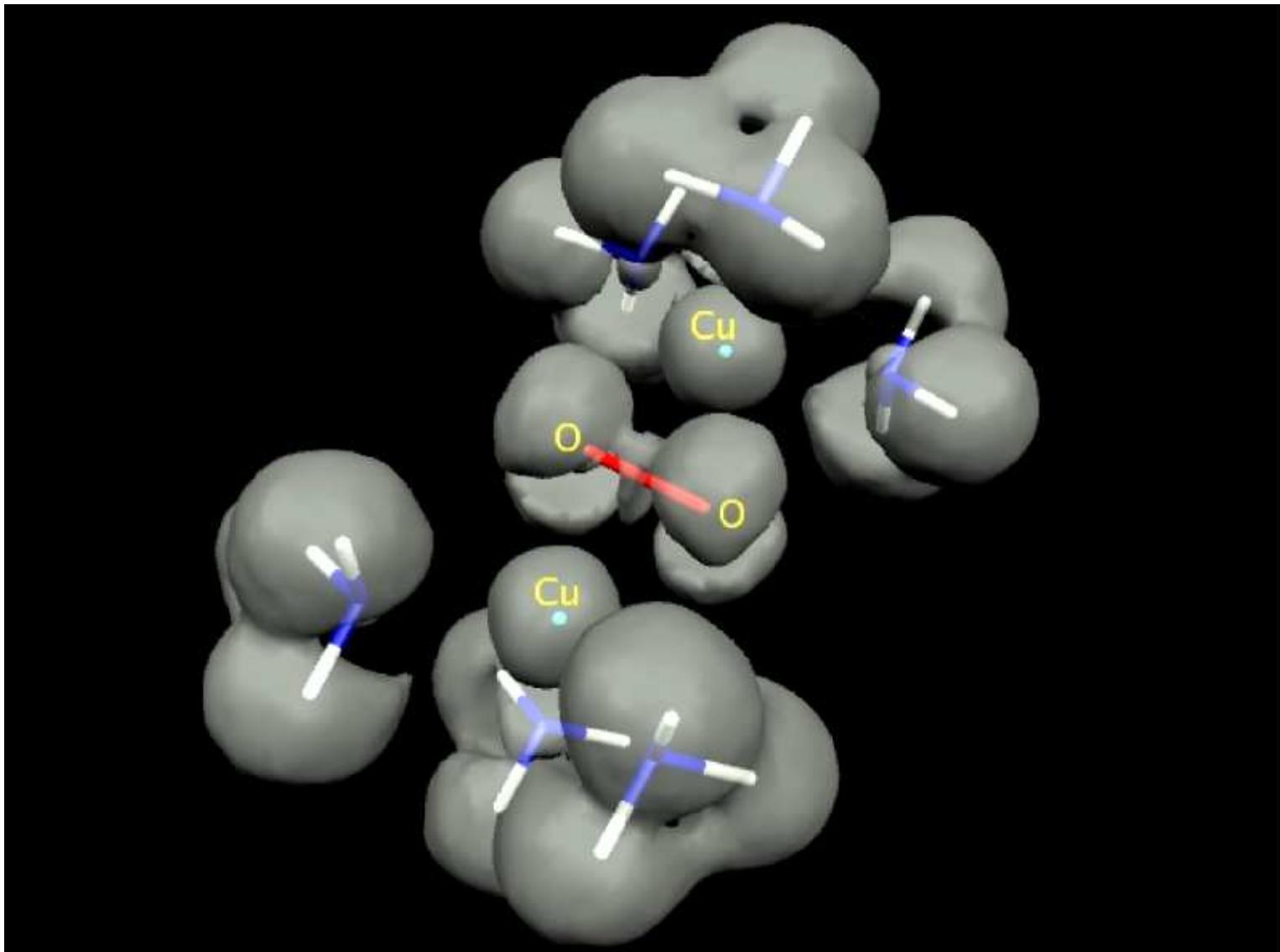
Chemical reactivity : O$_4$

O$_4$ 1

2

TS   3

4

5

6

7

2O$_2$ 8
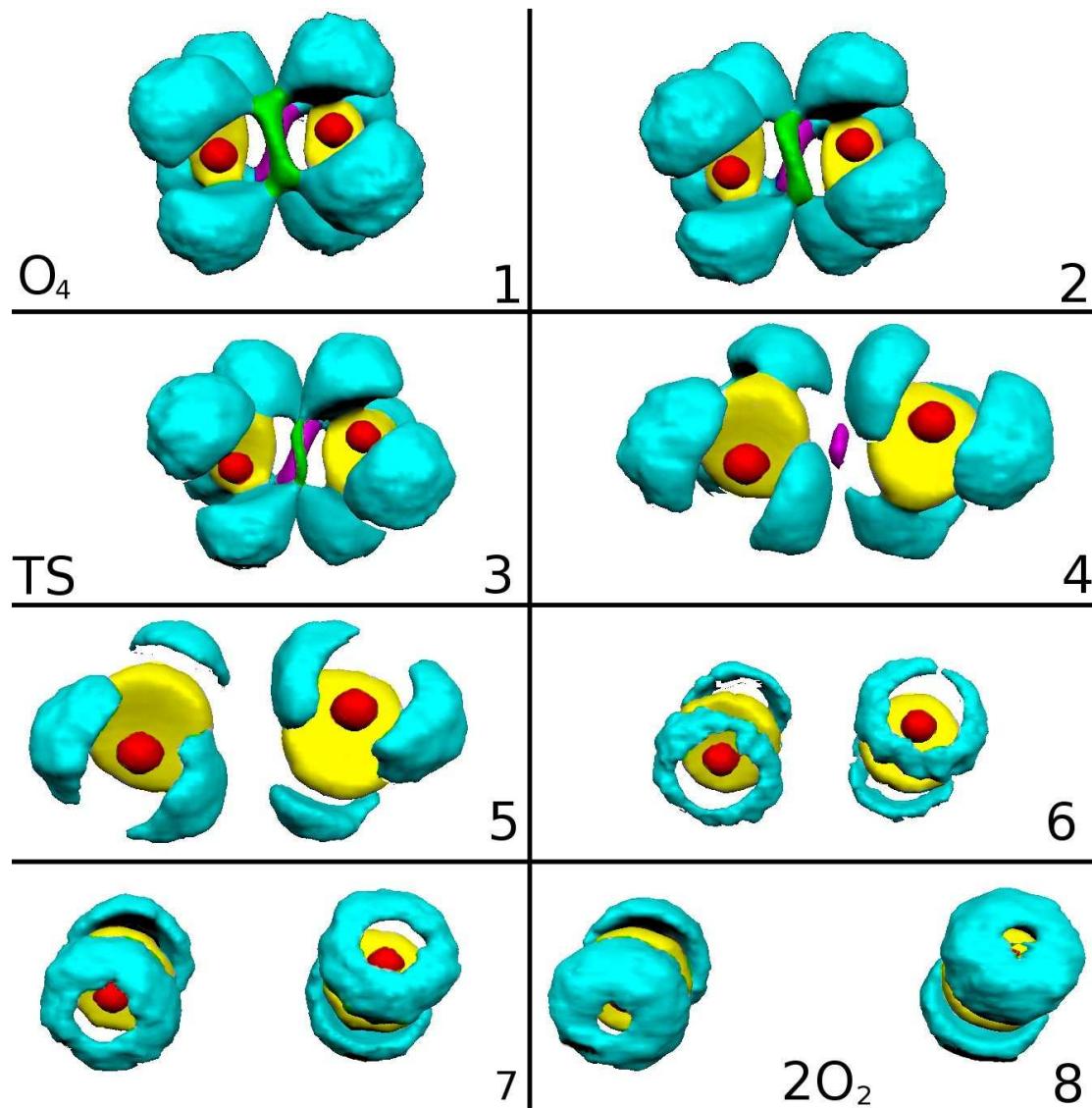
Modified EPLF

Exact representation :

$$min|\vec{r}_i - \vec{r}_j| = \sqrt{\lim_{\gamma \to \infty} -\frac{1}{\gamma} \ln[\sum_{j \neq i}^{N} e^{-\gamma|\vec{r}_i - \vec{r}_j|^2}]}$$

New definition :

$$d_{\sigma\sigma}(\vec{r}) \sim \lim_{\gamma \to \infty} \sqrt{-\frac{1}{\gamma} \ln < \sum_{i=1}^{N} \delta(\vec{r} - \vec{r}_i) \sum_{j \neq i; \sigma_i = \sigma_j}^{N} e^{-\gamma|\vec{r}_i - \vec{r}_j|^2} >}$$

and a similar definition for $d_{\sigma\bar{\sigma}}(\vec{r})$

Ref. F. Alary, J.L. Heully, B. Garreau de Bonneval, K.I. Chane-Ching, A. Scemama, and M. Caffarel *Structural and optical properties of a neutral nickel bisdithiolene complex*" (submitted to TCA)

Modified EPLF

- Different definition of d's because $ln < X > \neq < lnX >$

- However, same chemical content.

- Moreover, new d's can be computed analytically for any multiconfigurational wavefunction.
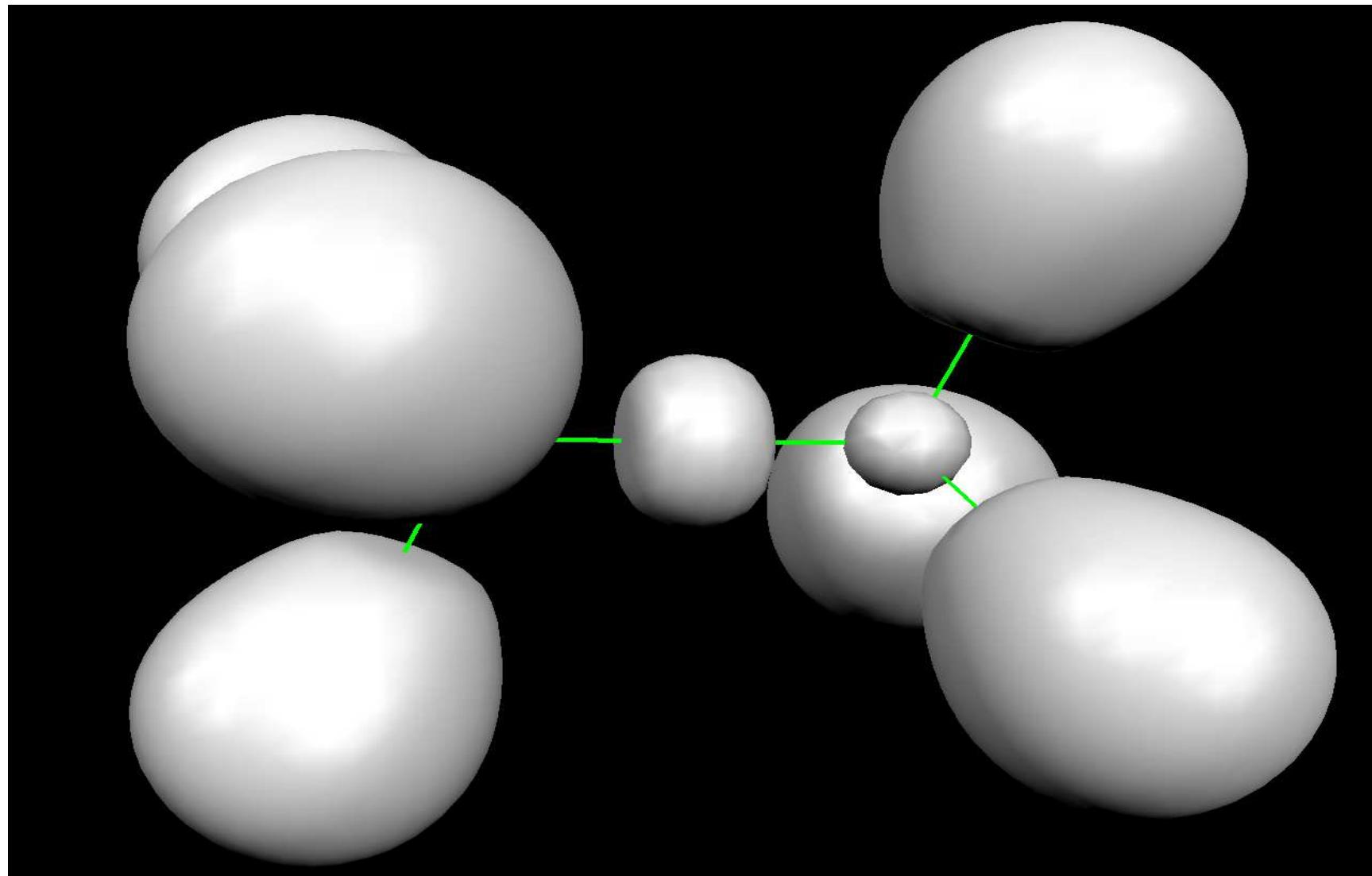
# $\mathbf{C_2H_4}$
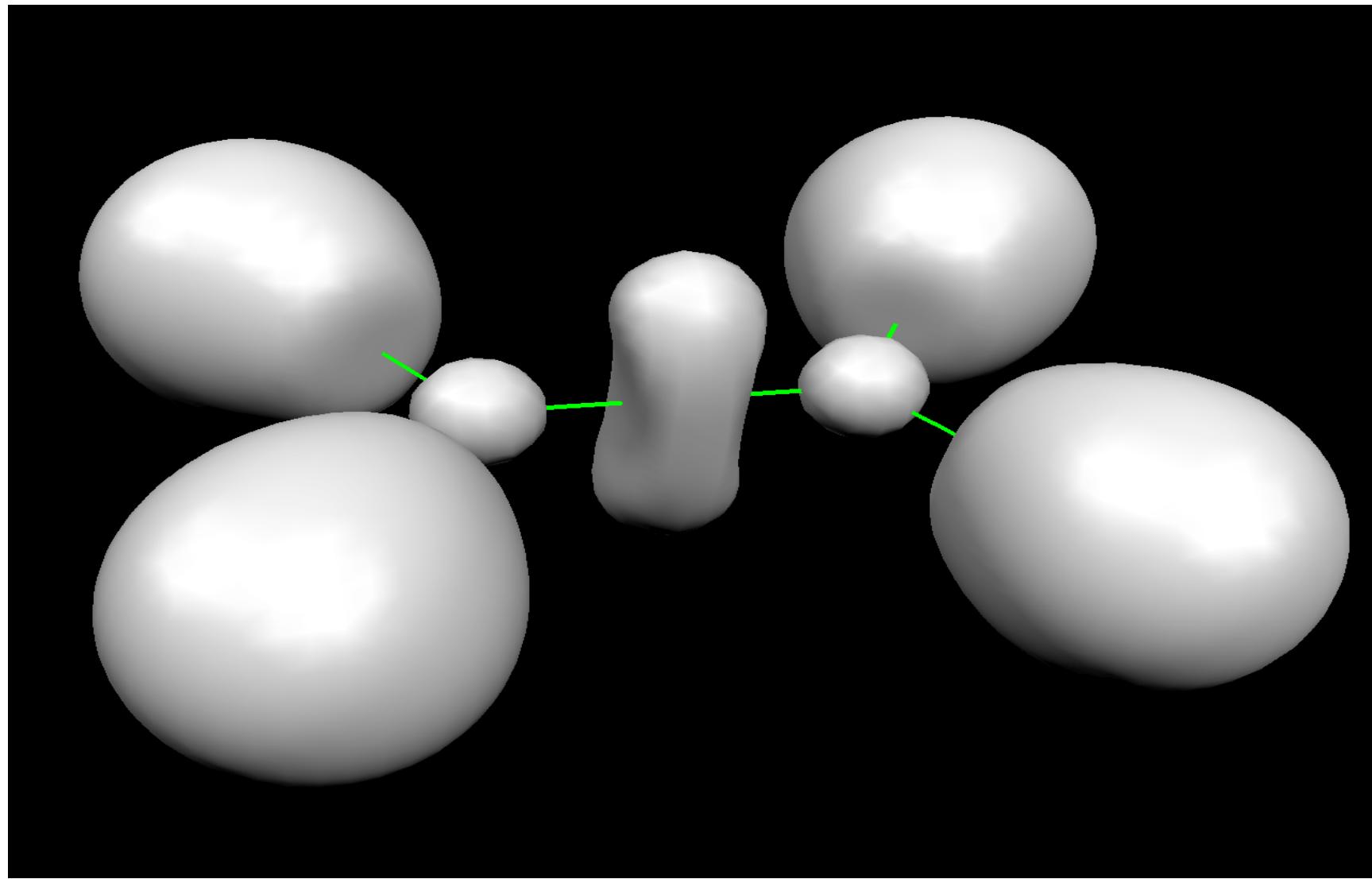
Radical C$_2$H
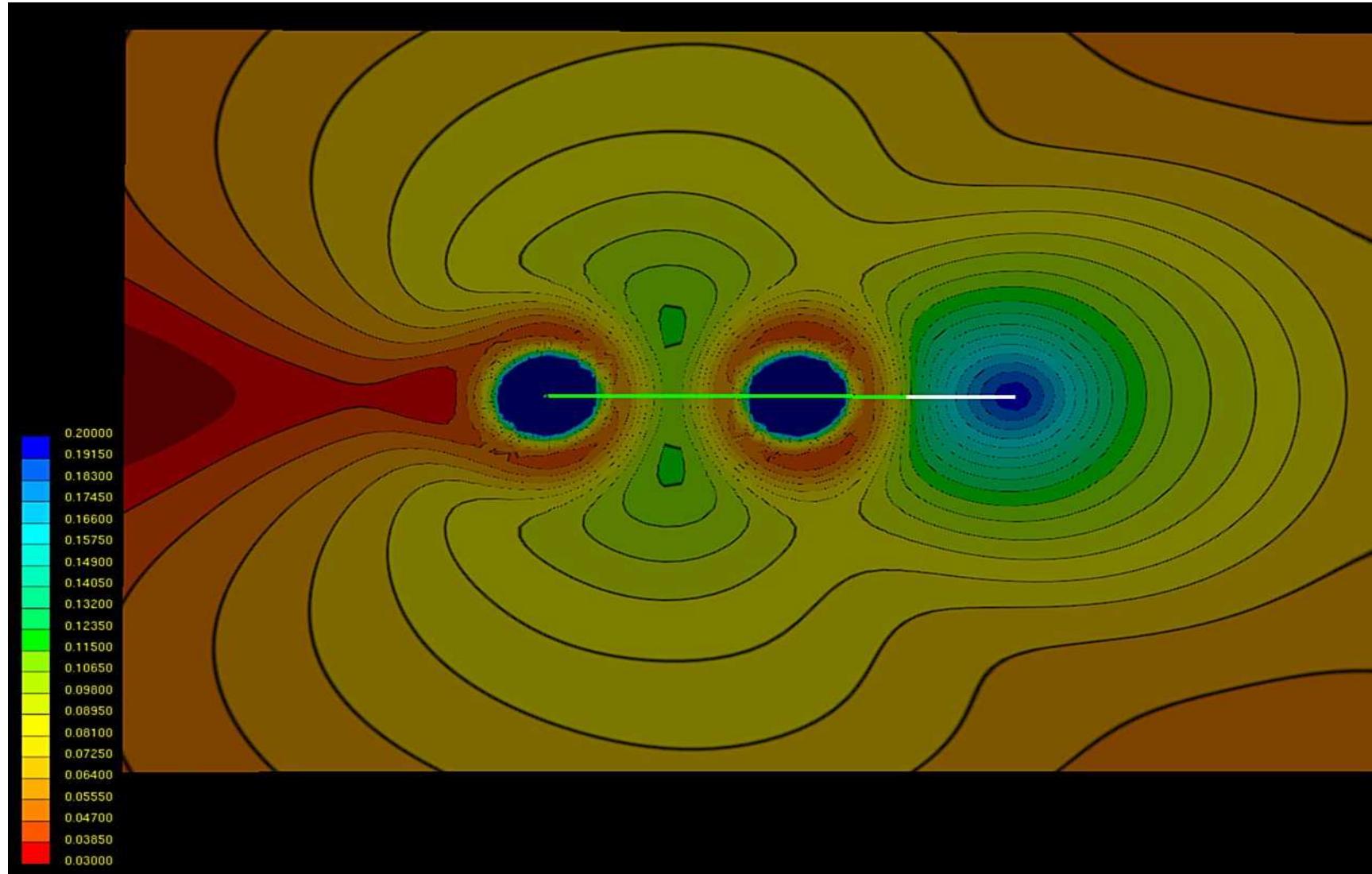
Thiophene
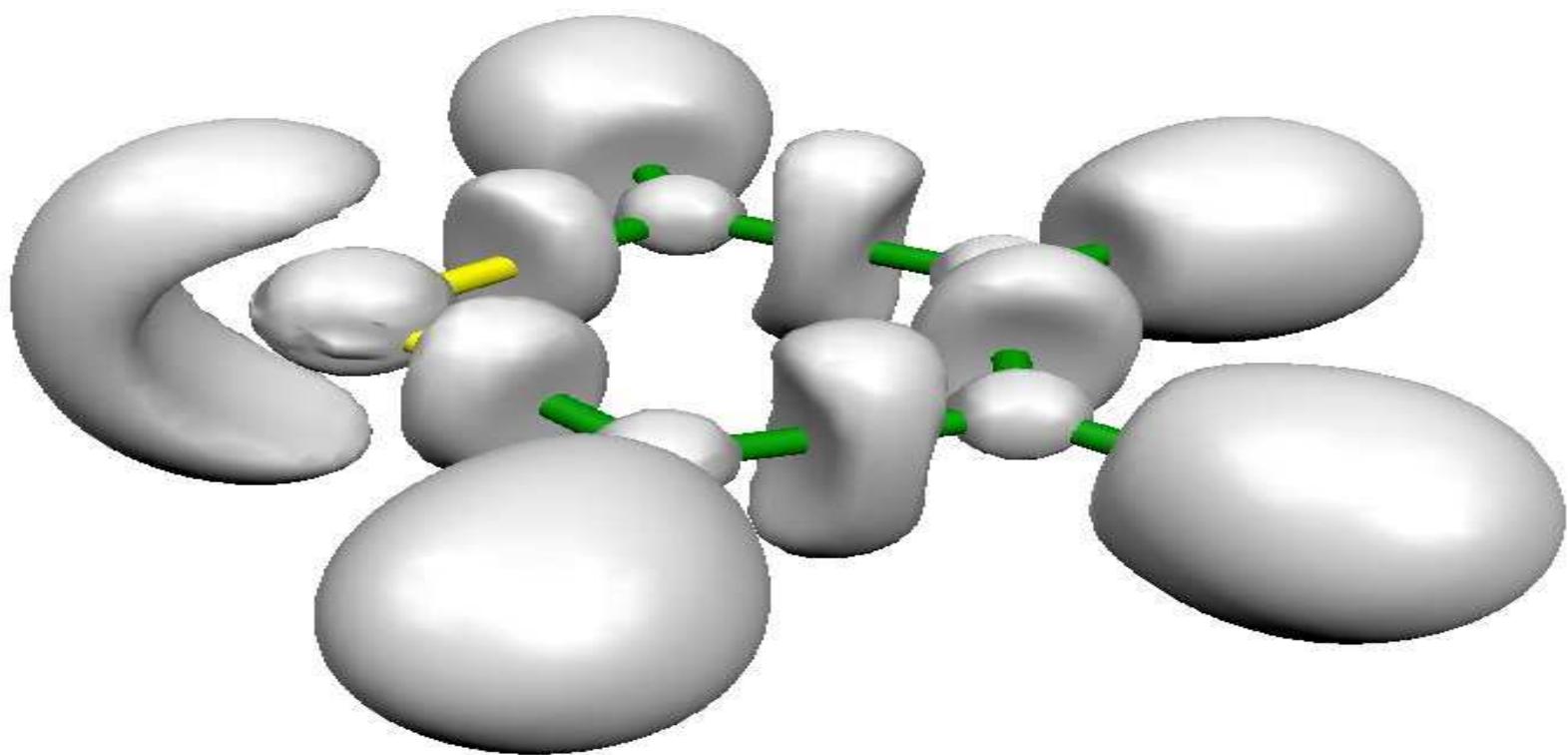
Thiophene + Li
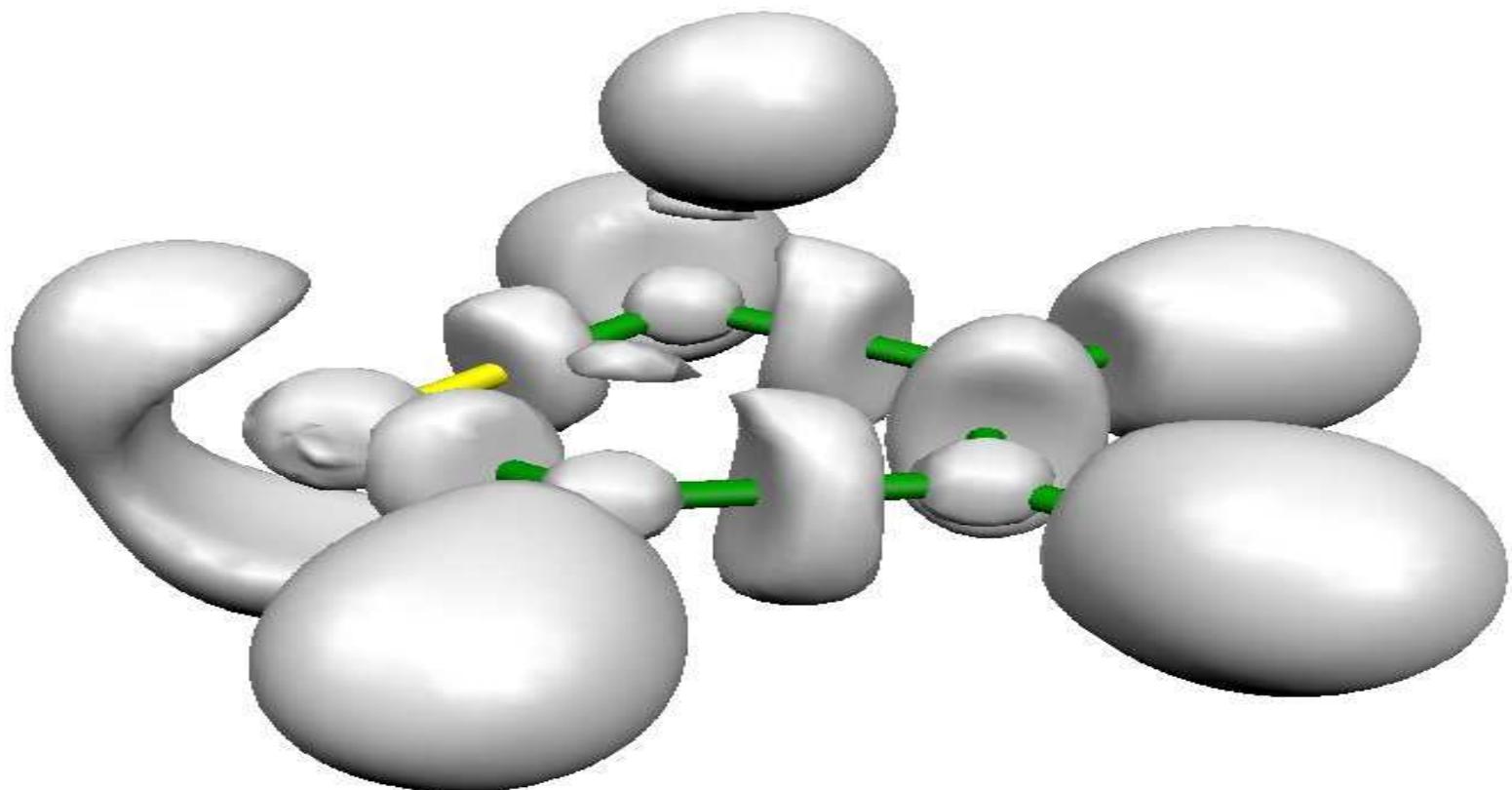
Adenine

Nickel bisdithiolene complex