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Elongation Cutoff Technique at Kohn-Sham level of Theory - Local Exchange-Correlation Approximation,

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Outline

- Elongation Cutoff Technique
    - Kohn-Sham Realization
    - Illustrative Examples
- Generalized Elongation Cutoff Technique
- Conclusions

Elongation Method

1) Initialization

$$M_1 \overset{\text{SCF}}{=} (A_1 \mid B_1)$$

2) Propagation

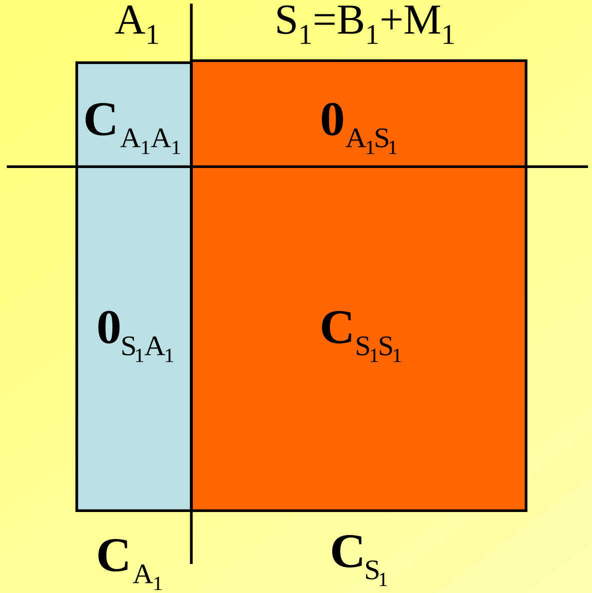
$$\begin{cases} M_2 = (A_1 \mid B_1 + C_1) \equiv (A_1 \mid S_1) \overset{\text{SCF}}{=} (A_1 + A_2 \mid B_2) \equiv (A^2 \mid B_2) \\ M_3 = (A^2 \mid B_2 + C_2) \equiv (A^2 \mid S_2) \overset{\text{SCF}}{=} (A^2 + A_3 \mid B_3) \equiv (A^3 \mid B_3) \\ \quad \vdots \\ M_{n-1} = (A^{n-2} \mid S_{n-2}) \overset{\text{SCF}}{=} (A^{n-2} + A_{n-1} \mid B_{n-1}) \equiv (A^{n-1} \mid B_{n-1}) \end{cases}$$

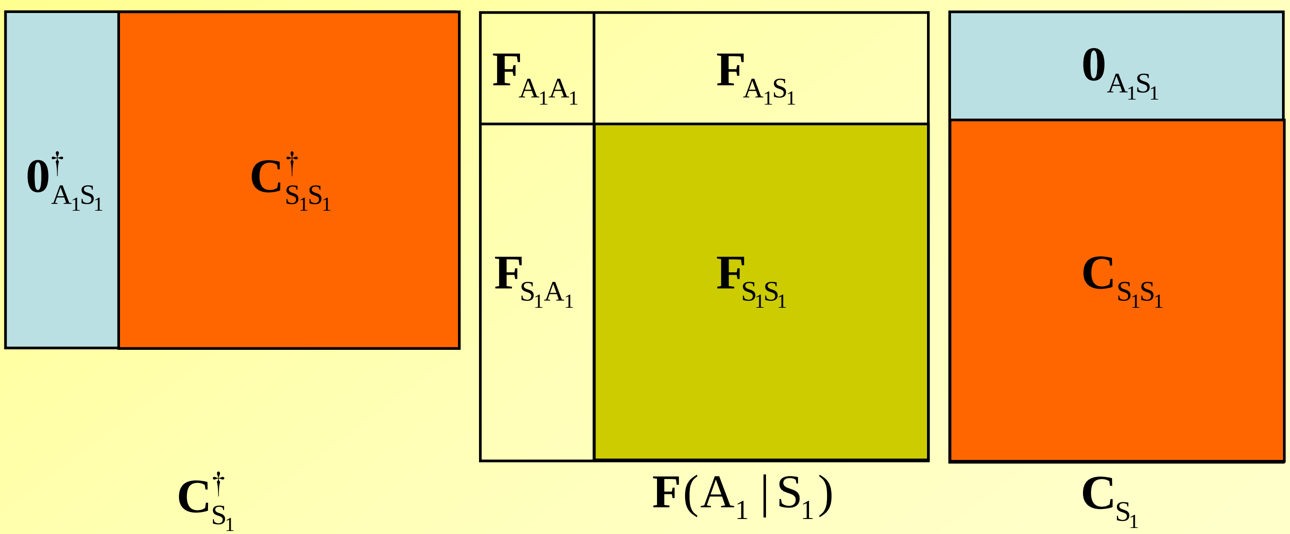
3) Termination

$$M_n = (A^{n-1} \mid B_{n-1} + C_{n-1}) \equiv (A^{n-1} \mid S_{n-1})$$

(HF and KS at restricted, restrited open-shell, unrestricted level of theory for ‘conventional’ and ‘direct’ mode of computation)

Elongation Cut-off Technique





Elongation Cut-off Technique

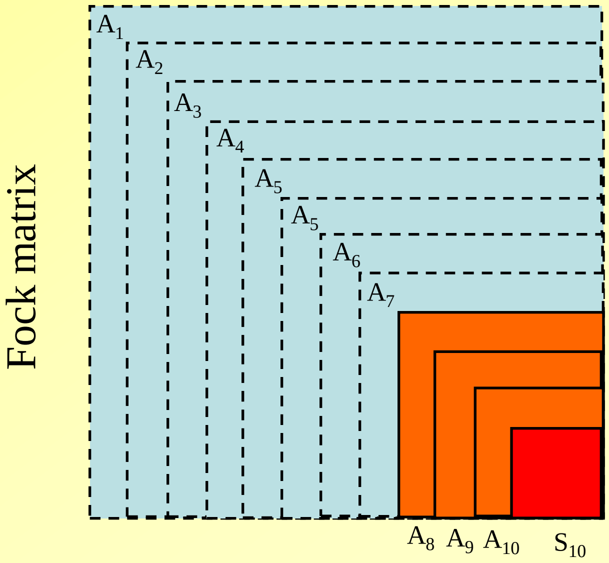
$$M_1 \overset{\text{SCF}}{=} (A_1 \mid B_1)$$

$$M_2 = (A_1 \mid B_1 + C_1) \equiv (A_1 \mid S_1) \overset{\text{SCF}}{=} (A_1 + A_2 \mid B_2) \equiv (A^2 \mid B_2)$$

$$\begin{cases} M'_3 = (A_2 \mid B_2 + C_2) \overset{\text{SCF}}{\equiv} (A_2 \mid S_2) \overset{\text{loc}}{=} (A_2 + A_3 \mid B_3) \\ M'_4 = (A_3 \mid B_3 + C_3) \overset{\text{SCF}}{\equiv} (A_3 \mid S_3) \overset{\text{loc}}{=} (A_3 + A_4 \mid B_4) \\ \quad \vdots \\ M'_{n-1} = (A_{n-2} \mid B_{n-2} + C_{n-2}) \overset{\text{SCF}}{\equiv} (A_{n-2} \mid S_{n-2}) \overset{\text{loc}}{=} (A_{n-2} + A_{n-1} \mid B_{n-1}) \end{cases}$$

$$M'_n = (A_{n-1} \mid B_{n-1} + C_{n-1}) \overset{\text{SCF}}{\equiv} (A_{n-1} \mid S_{n-1})$$

$$M_n \overset{\text{Energy}}{=} (A^{n-1} \mid S_{n-1})$$



Kohn-Sham Scheme

$$\hat{f}^{KS}\varphi_i = \varepsilon_i\varphi_i \qquad \hat{f}^{KS} = -\frac{1}{2}\Delta_1 - \sum_{\alpha}^{M}\frac{Z_\alpha}{r_{1\alpha}} + \sum_{j}^{N}\int\frac{\left|\varphi_j(\vec{r}_2)\right|^2}{r_{12}}d\vec{r}_2 + V^{XC}(\vec{r}_1)$$

$$\varphi_i = \sum_{\mu} C_{\mu i}\chi_\mu \qquad \boldsymbol{F}^{KS}\boldsymbol{C} = \boldsymbol{SC\varepsilon}$$

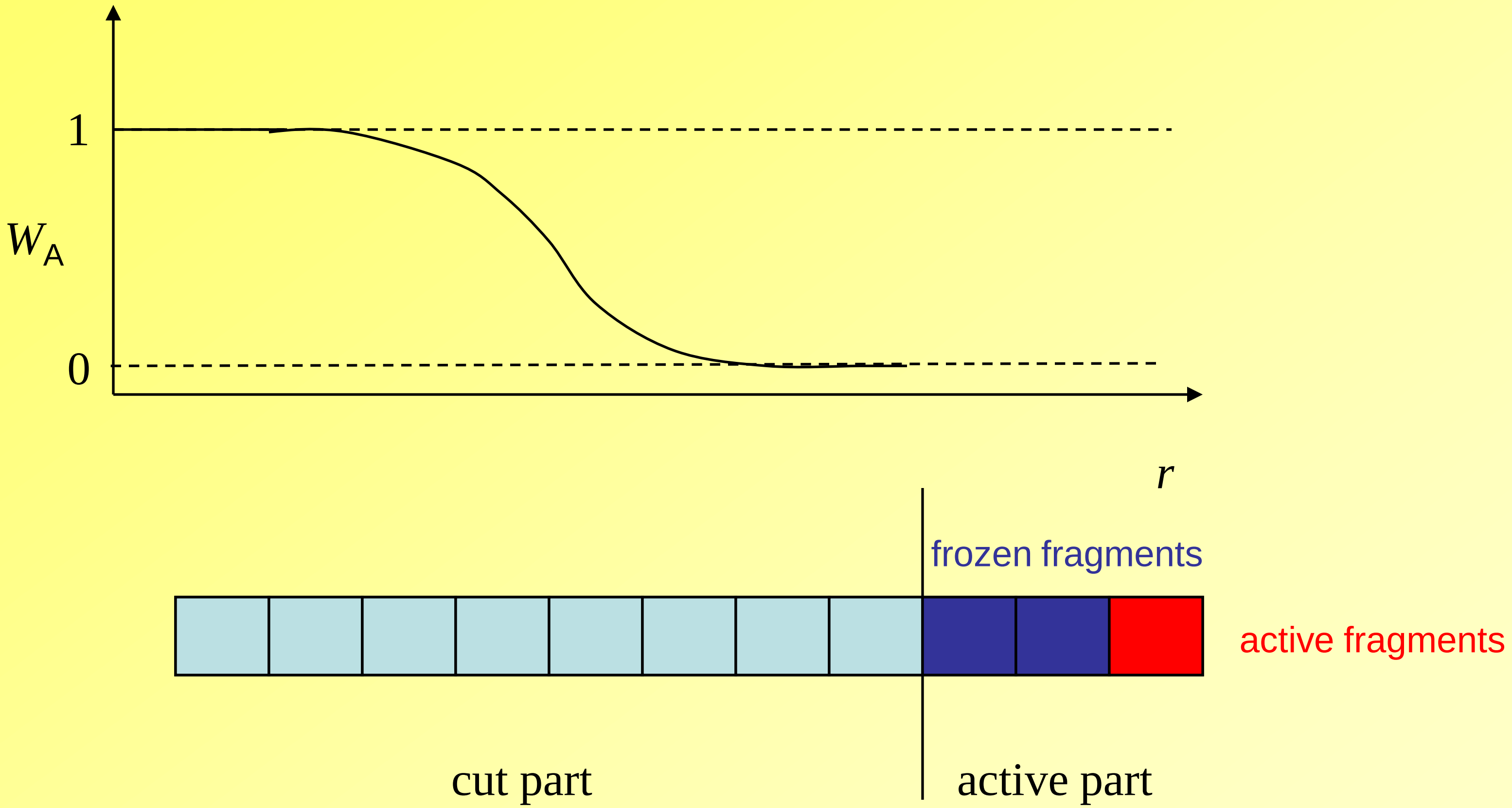
$$V_{\mu\nu}^{XC} = \int \chi_\mu(\vec{r}_1)V^{XC}(\vec{r}_1)\chi_\nu(\vec{r}_1)d\vec{r}_1 \qquad \equiv \int F(\vec{r})d\vec{r} = I$$

$$V_{\mu\nu}^{XC} = \sum_{p}^{P}\chi_\mu(\vec{r}_p)V^{XC}(\vec{r}_p)\chi_\nu(\vec{r}_p)W_p$$

$$I = \sum_{\alpha} I_\alpha = \sum_{\alpha}\int F_\alpha(\vec{r})d\vec{r}$$

$$F(\vec{r}) = \sum_{\alpha} F_\alpha(\vec{r}) \qquad F_\alpha(\vec{r}) = F(\vec{r})W_\alpha(\vec{r}) \qquad \sum_{\alpha=1}^{M} W_\alpha(\vec{r}) = 1$$

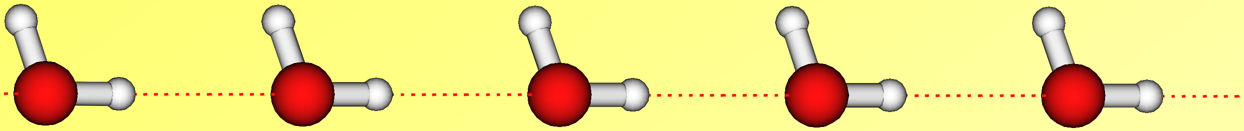
Elongation cutoff technique at Kohn-Sham level of theory

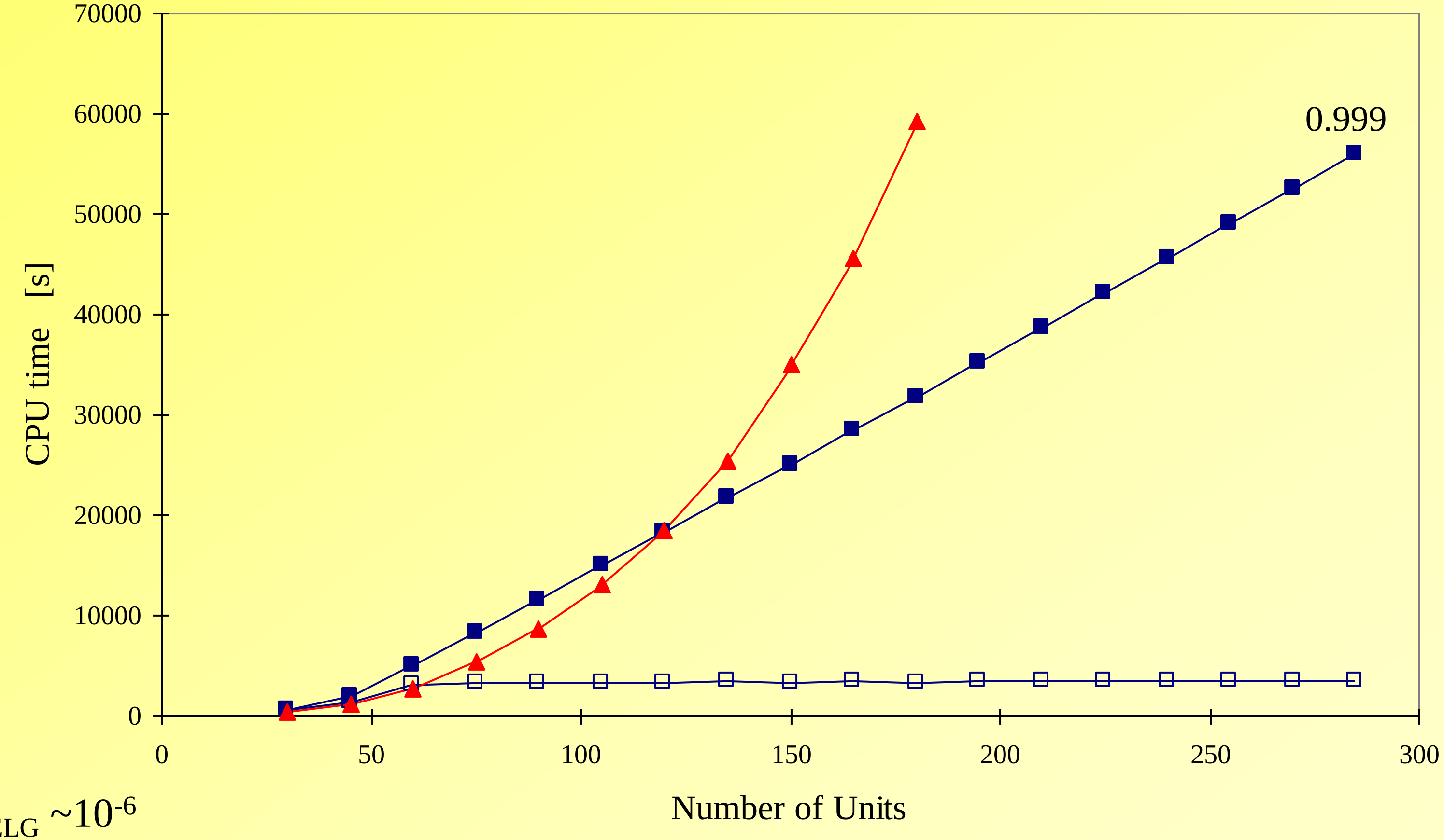


local exchange-correlation approximation

ELG/C BLYP/6-31G

8 CPU
GAMESS
direct calculations
QFMM



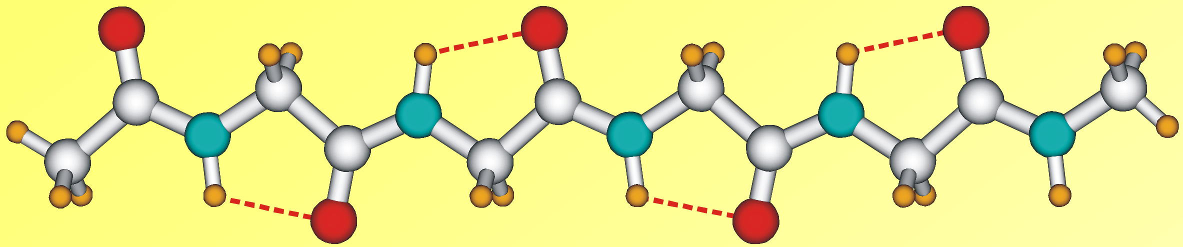


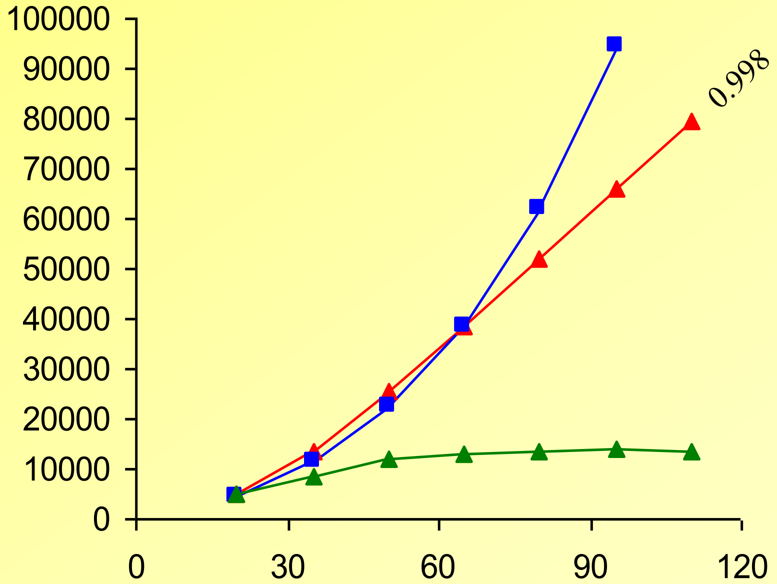
$\Delta E_{ELG} \sim 10^{-6}$

$\Delta E_{XC} \sim 10^{-8}$

ELG/C BLYP/6-31G

20/15

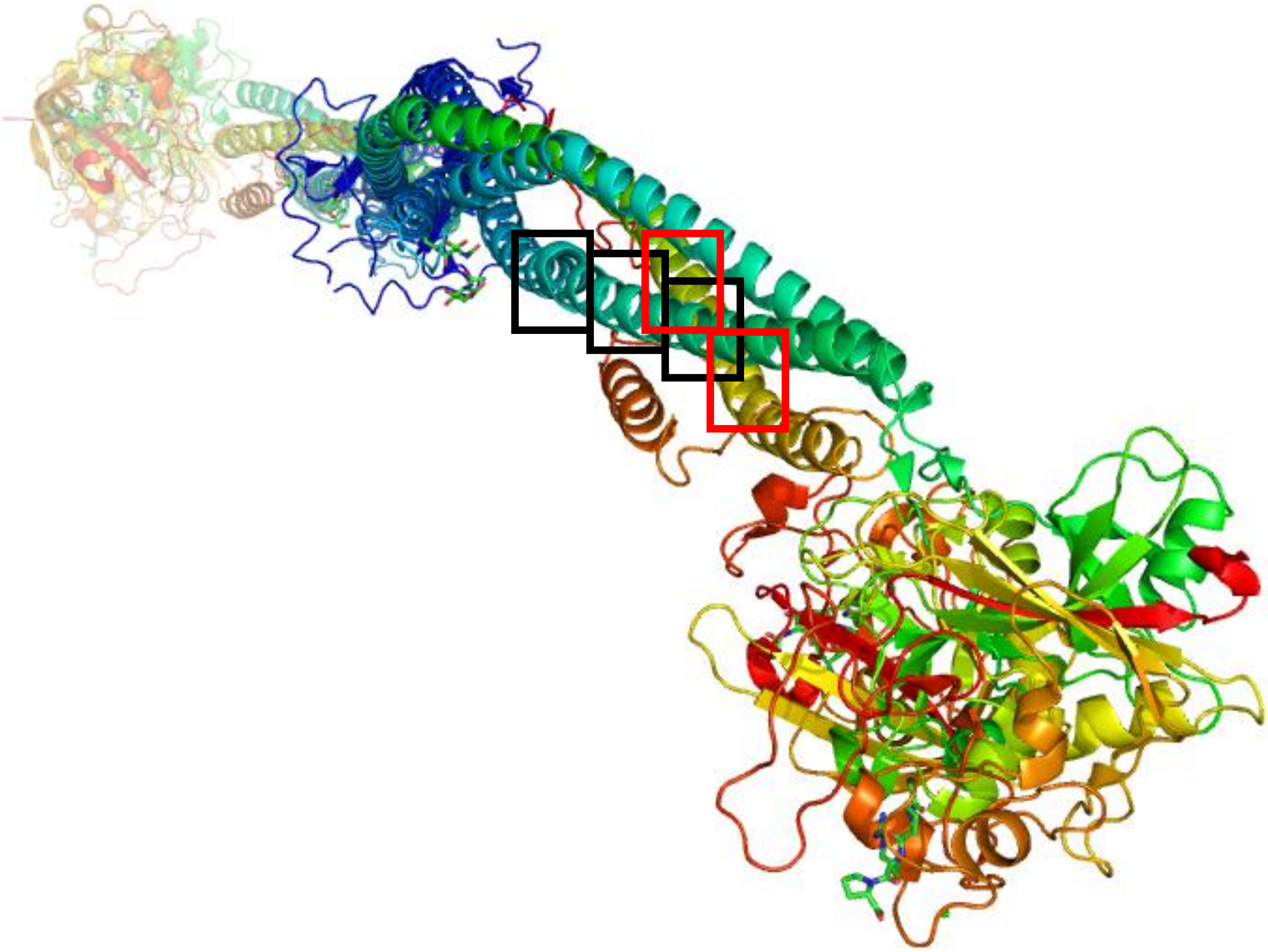




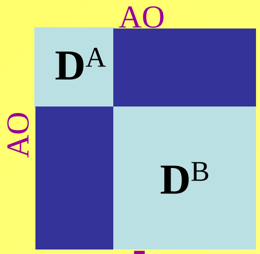
ΔE_{ELG} ~10^{-6}

ΔE_{XC} ~10^{-8}

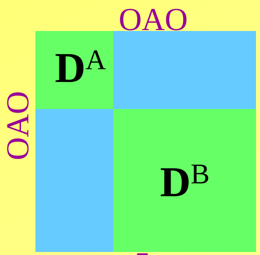
Generalized Elongation Method



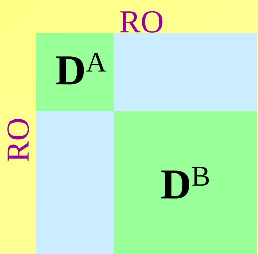
Regional Localized Molecular Orbitals



$$\mathbf{D}^{AO} = \mathbf{C}\mathbf{d}\mathbf{C}^{\dagger}$$
$$\mathbf{D}^{AO}\mathbf{S}^{AO}\mathbf{D}^{AO} = 2\mathbf{D}^{AO}$$

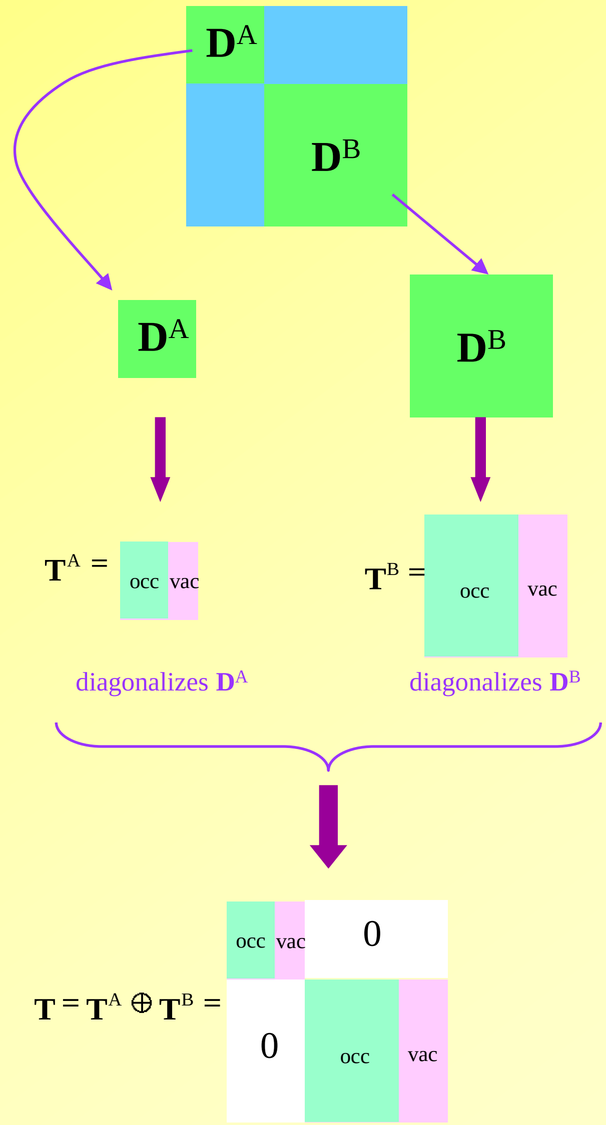


$$\mathbf{D}^{OAO} = \mathbf{S}^{\frac{1}{2}}\mathbf{D}^{AO}\mathbf{S}^{\frac{1}{2}}$$
$$\mathbf{D}^{OAO}\mathbf{D}^{OAO} = 2\mathbf{D}^{OAO}$$



$$\mathbf{D}^{RO} = \mathbf{T}^{\dagger}\mathbf{D}^{OAO}\mathbf{T}$$
$$\mathbf{D}^{RO}\mathbf{D}^{RO} = 2\mathbf{D}^{RO}$$

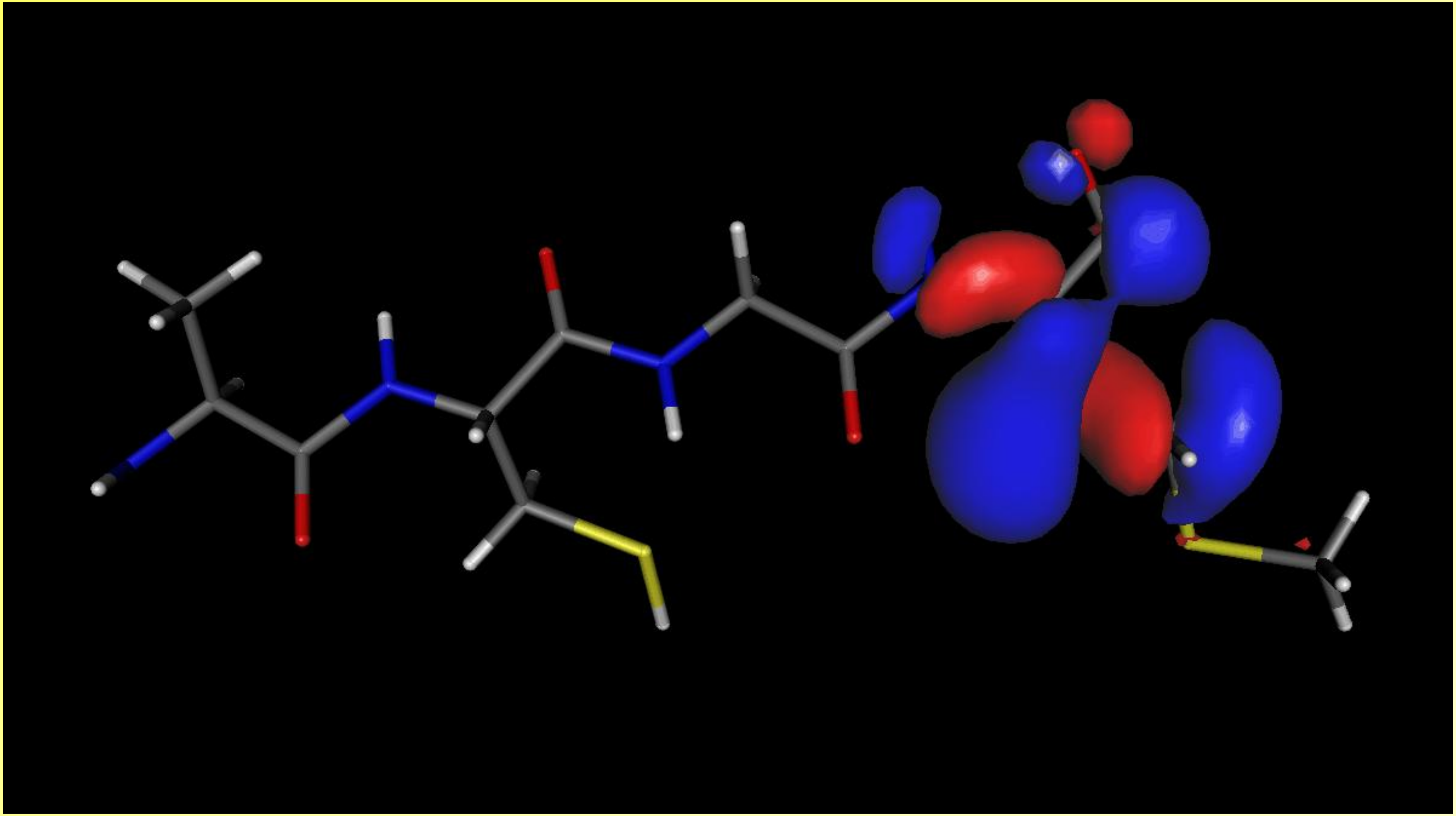
$$\mathbf{D}^{RLMO} = \mathbf{U}^{\dagger}\mathbf{D}^{RO}\mathbf{U} \equiv \mathbf{d}$$



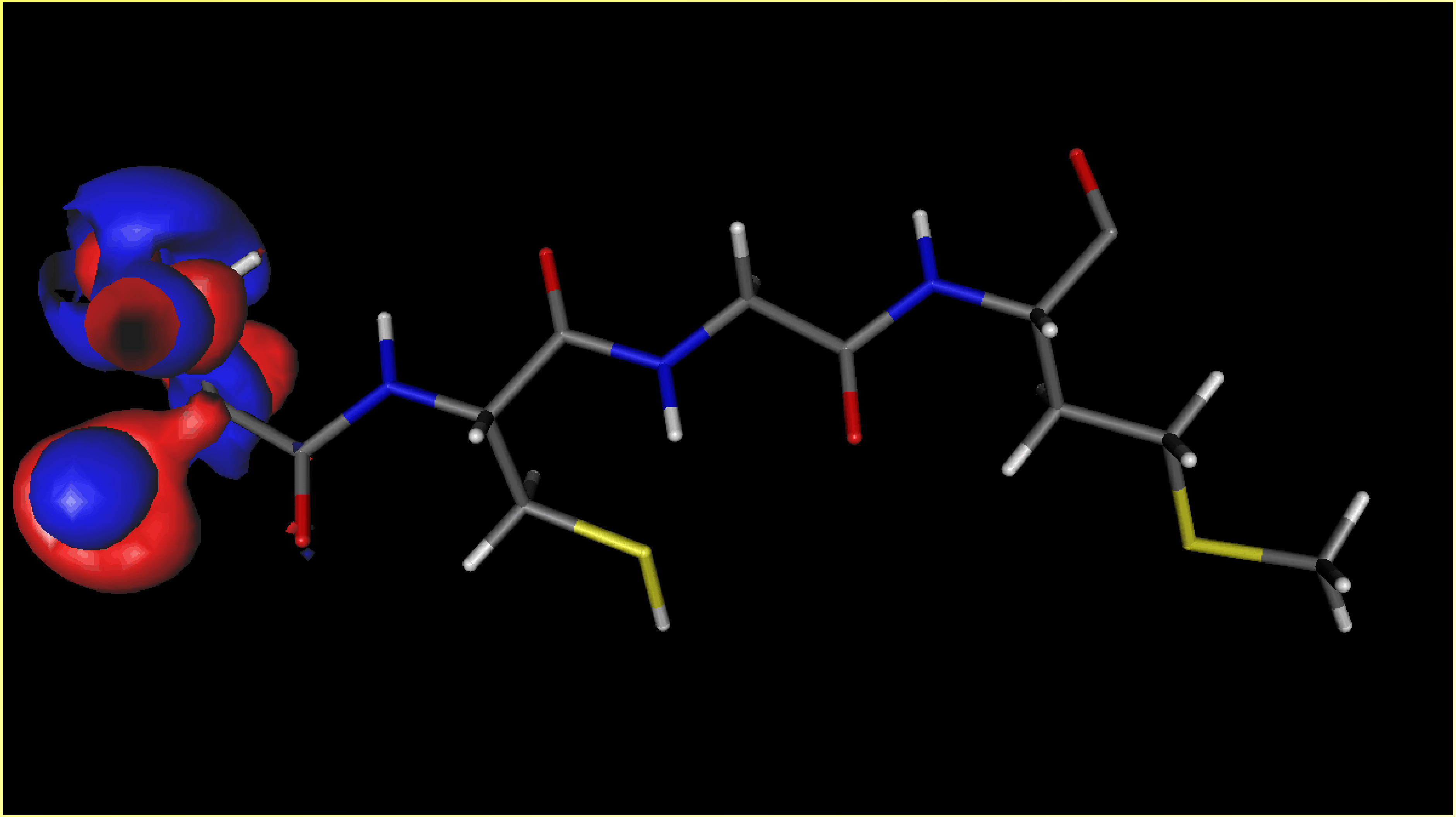
$$\mathbf{C}^{RLMO} = \mathbf{S}^{-\frac{1}{2}}\mathbf{T}\mathbf{U}$$

F. L. Gu, Y. Aoki, J. Korchowiec, A. Imammura, and B. Kirtman, J. Chem. Phys. **121** (2004) 10385

Occupied MO



Virtual MO



Conclusions:

- **Local exchange-correlation approximation doesn't introduce significant error**
- **Step CPU time in ELG/C calculations at KS level of theory is very small in comparison to the reference KS calculations**
- **Total CPU time in ELG/C at KS level of theory is almost linear**
- **ELG/C can lead to huge memory savings**

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„***Rozwój metod skalujących się liniowo z wielkością układu molekularnego"***