Topological approaches to intermolecular interactions

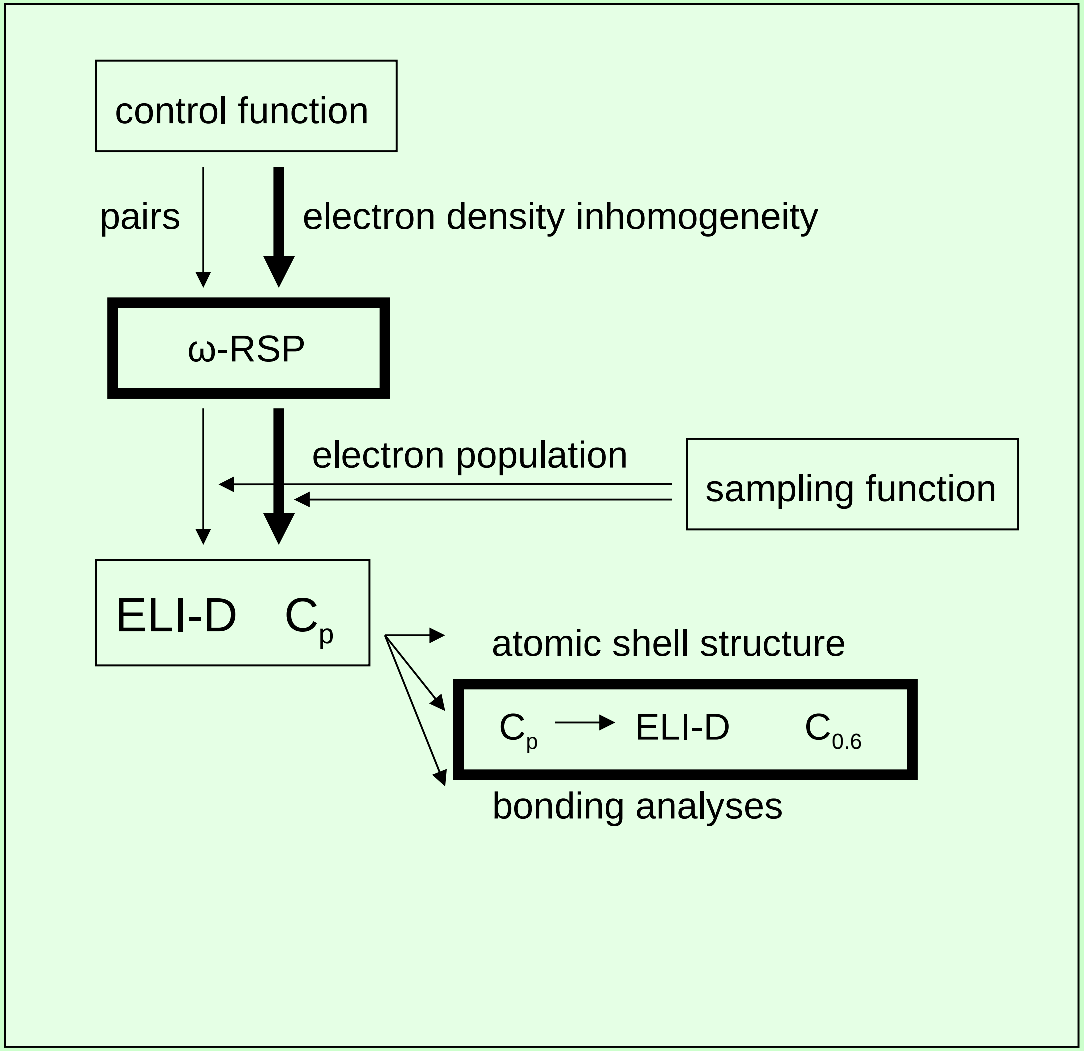
Paris 26 – 28 June

Indicators based on electron density inhomogeneity

Kati Finzel

Max Planck Institute for Chemical Physics of Solids

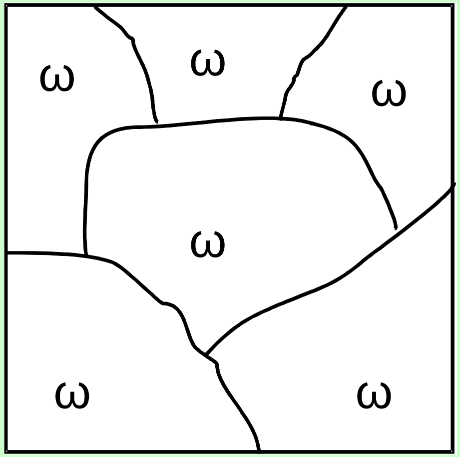
Introduction



ω-restricted partitioning

ω-restricted space partitioning

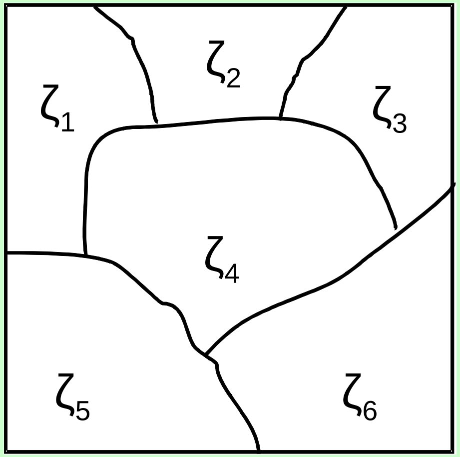
control function f_c $\omega = \int_{\mu_i} f_c\, dV$



compact,
mutually exclusive,
space filling regions

evaluation of the sampling function

$\zeta_i = \int_{\mu_i} f_s\, dV$ **sampling function f_s**



{ζ$_i$}

rescaling

functional

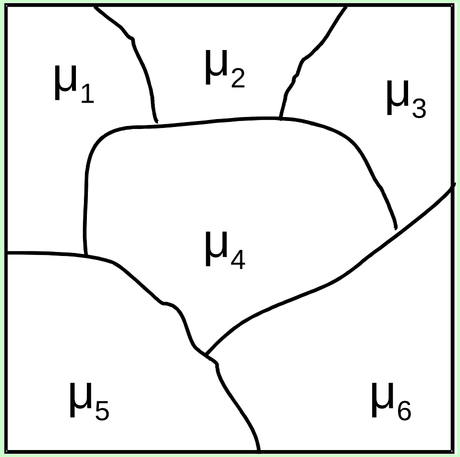
A.M. Pendas, M. Kohout, M.A. Blanco and *E. Francisco, Beyond Standard Charge Density Topological Analyses, in Modern Charge Density Analyses, by C. Gatti and P. Macchi, Springer, 2012*

Derivation of the functional C_p

ω-restricted space partitioning

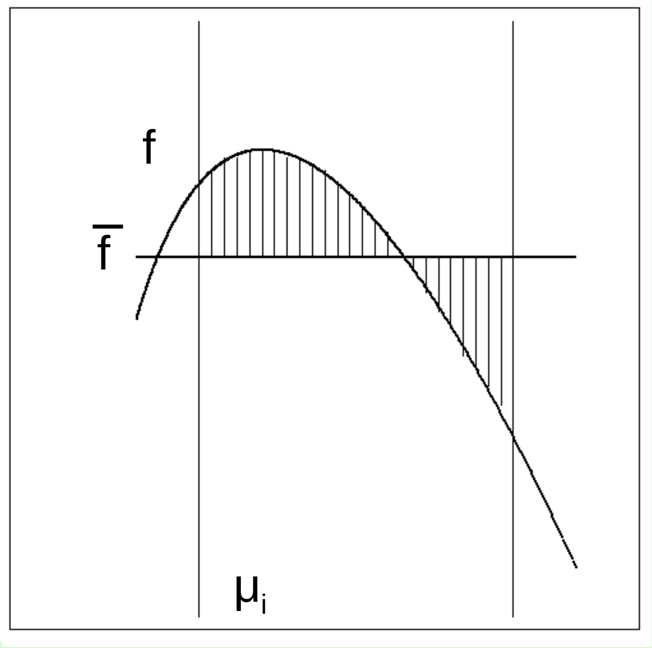
electron density inhomogeneity I_p

$$I_p(i)=\sqrt[p]{\int_{\mu_i}|\rho-\bar{\rho}_i|^p\,dV}$$



$$d(f,g)=\sqrt[p]{\int_{\mu_i}|f-g|^p\,dV}$$

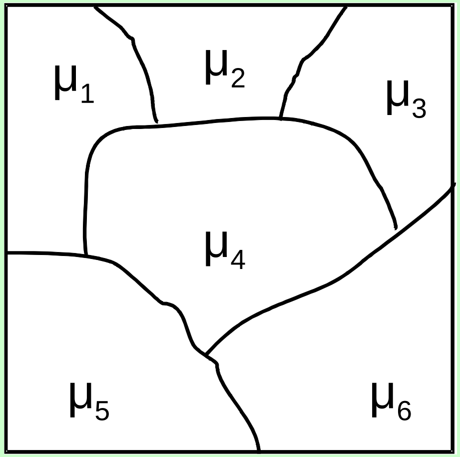
$$d(f,\bar{f})=\sqrt[p]{\int_{\mu_i}|f-\bar{f}|^p\,dV}$$



Derivation of the functional C_p

ω-restricted space partitioning

electron density inhomogeneity I_p



$$I_p(i) = \sqrt[p]{\int_{\mu_i} |\rho - \bar{\rho}_i|^p \, dV}$$

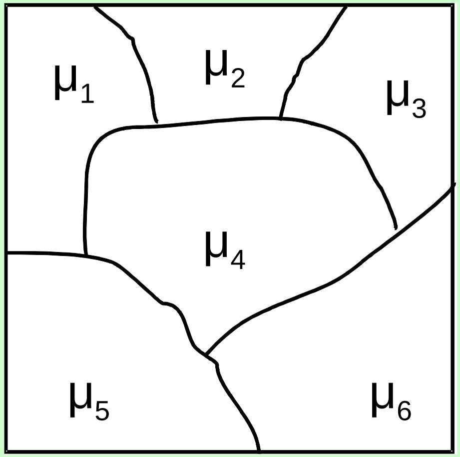
$$I_p(i) \approx \frac{1}{2(p+1)^{1/p}} \, |\nabla \rho(a_i)| \, V_i^{\frac{p+3}{3p}}$$

$$V_i \approx \omega_p^{\frac{3p}{p+3}} \left[\frac{2^p (p+1)}{|\nabla \rho(a_i)|^p} \right]^{\frac{3}{p+3}}$$

Derivation of the functional C_p

ω-restricted space partitioning

electron density inhomogeneity I_p



$$I_p(i)=\sqrt[p]{\int_{\mu_i} |\rho-\bar{\rho}_i|^p \, dV}$$

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Derivation of the functional C_p

$$V_i \approx \omega_p^{\frac{3p}{p+3}} \left[\frac{2^p (p+1)}{|\nabla \rho(a_i)|^p} \right]^{\frac{3}{p+3}}$$

$$q_i = \int_{\mu_i} \rho \, dV \approx \rho(a_i) \, V_i$$

$$q_i \approx \omega_p^{\frac{3p}{p+3}} \left[\frac{2^p (p+1)}{|\nabla \rho(a_i)|^p} \right]^{\frac{3}{p+3}} \rho(a_i)$$

$$C_p(a_i) = \frac{q_i}{\omega_p^{\frac{3p}{p+3}}} \approx \left[\frac{2^p (p+1)}{|\nabla \rho(a_i)|^p} \right]^{\frac{3}{p+3}} \rho(a_i)$$

$$\tilde{C}_p(r) = \left[\frac{2^p (p+1)}{|\nabla \rho(r)|^p} \right]^{\frac{3}{p+3}} \rho(r)$$

$\{q_i\}$

↓ rescaling

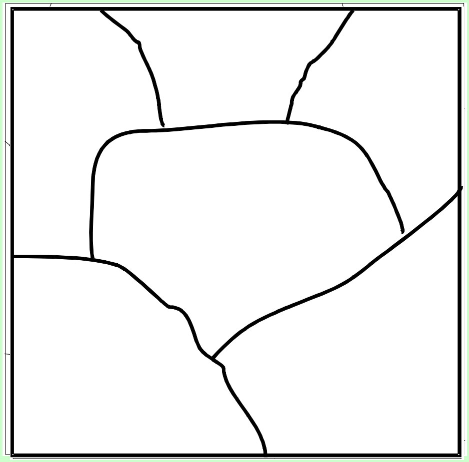
C_p

Limit after rescaling

evaluation of the sampling function

electron population

$\omega_p \longrightarrow \{q_1, \ldots, q_6\}$



$\omega'_p \longrightarrow \{q_1, \ldots, q_{15}\}$

Derivation of the functional C_p

$$V_i \approx \omega_p^{\frac{3p}{p+3}} \left[\frac{2^p(p+1)}{|\nabla\rho(a_i)|^p}\right]^{\frac{3}{p+3}}$$

$$q_i = \int_{\mu_i} \rho \, dV \approx \rho(a_i)\, V_i$$

$$q_i \approx \omega_p^{\frac{3p}{p+3}} \left[\frac{2^p(p+1)}{|\nabla\rho(a_i)|^p}\right]^{\frac{3}{p+3}} \rho(a_i)$$

$$C_p(a_i) = \frac{q_i}{\omega_p^{\frac{3p}{p+3}}} \approx \left[\frac{2^p(p+1)}{|\nabla\rho(a_i)|^p}\right]^{\frac{3}{p+3}} \rho(a_i)$$

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$\{q_i\}$

↓ rescaling

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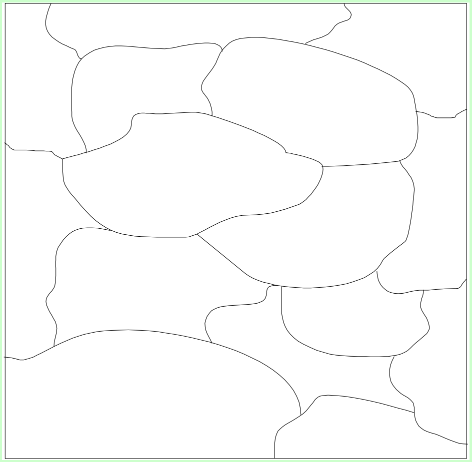


$\omega'_p \longrightarrow \{q_1, \ldots, q_{15}\}$

Derivation of the functional C_p

$$V_i \approx \omega_p^{\frac{3p}{p+3}} \left[\frac{2^p (p+1)}{|\nabla \rho(a_i)|^p} \right]^{\frac{3}{p+3}}$$

$$q_i = \int_{\mu_i} \rho \, dV \approx \rho(a_i) \, V_i$$

$$q_i \approx \omega_p^{\frac{3p}{p+3}} \left[\frac{2^p (p+1)}{|\nabla \rho(a_i)|^p} \right]^{\frac{3}{p+3}} \rho(a_i)$$

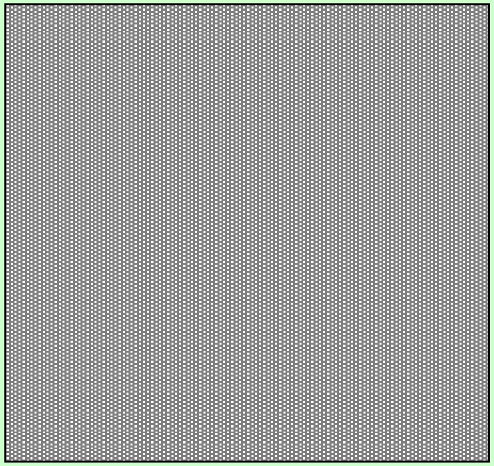
$$C_p(a_i) = \frac{q_i}{\omega_p^{\frac{3p}{p+3}}} \approx \left[\frac{2^p (p+1)}{|\nabla \rho(a_i)|^p} \right]^{\frac{3}{p+3}} \rho(a_i)$$

$$\tilde{C}_p(r) = \left[\frac{2^p (p+1)}{|\nabla \rho(r)|^p} \right]^{\frac{3}{p+3}} \rho(r)$$

evaluation of the sampling function

electron population

$\omega_p \longrightarrow \{q_1, \ldots, q_6\}$



$\omega'_p \longrightarrow \{q_1, \ldots, q_{15}\}$

$\{q_i\}$

↓ rescaling

C_p

Limit after rescaling

Derivation of the functional C_p

$$I_p(i) = \sqrt[p]{\int_{\mu_i} |\rho - \bar{\rho}_i|^p \, dV}$$

↓

ω-RSP

↓

$$q_i = \int_{\mu_i} \rho \; dV$$

↓

rescaling

↓

$$\tilde{C}_p(r) = \left[\frac{2^p (p+1)}{|\nabla \rho(r)|^p} \right]^{\frac{3}{p+3}} \rho(r)$$

$$\tilde{C}_1(r) = 4^{3/4} \frac{1}{|\nabla \rho(r)|^{3/4}} \rho(r)$$

$$\tilde{C}_1^{4/3}(r) = 4 \frac{1}{|\nabla \rho(r)|} \rho(r)^{4/3}$$

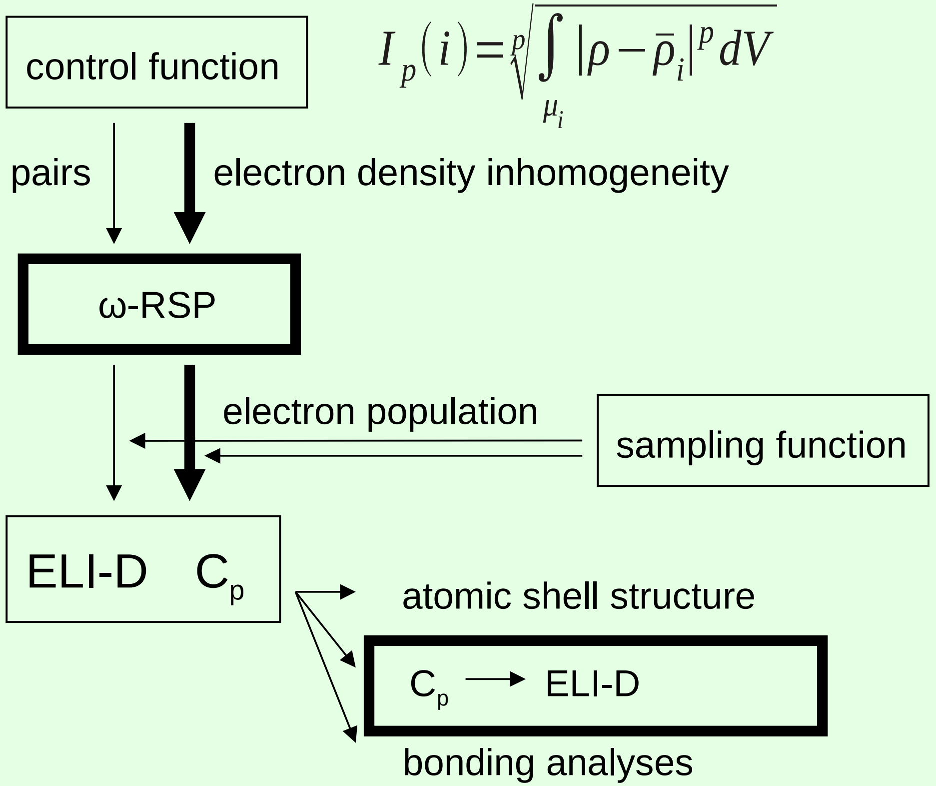
↓

Proportional to the inverse
of the NCI indicator

$$s(r) = \frac{1}{2k_F} \frac{|\nabla \rho(r)|}{\rho(r)^{4/3}}$$

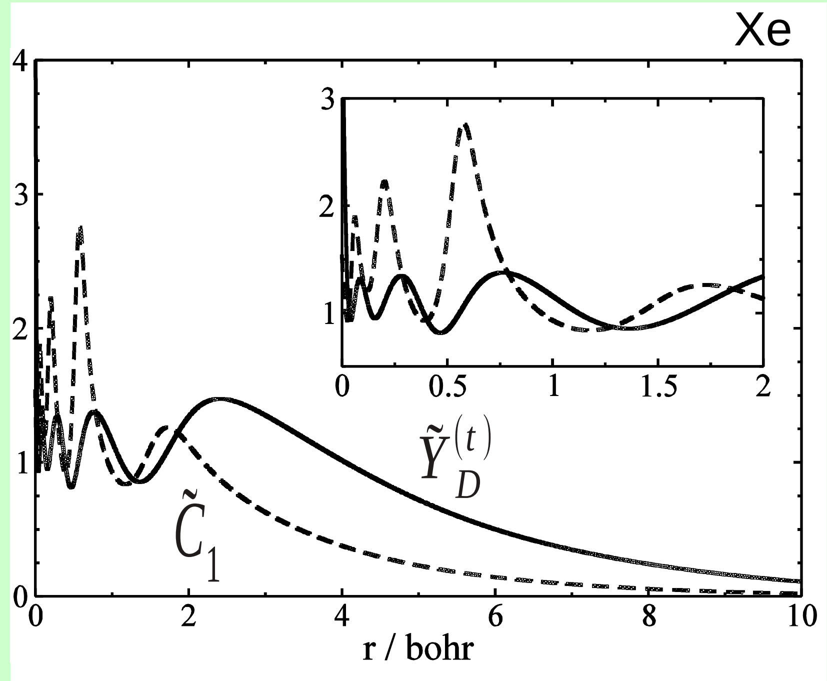
The functional C_p

$$I_p(i)=\sqrt[p]{\int_{\mu_i} |\rho-\bar{\rho}_i|^p\, dV}$$



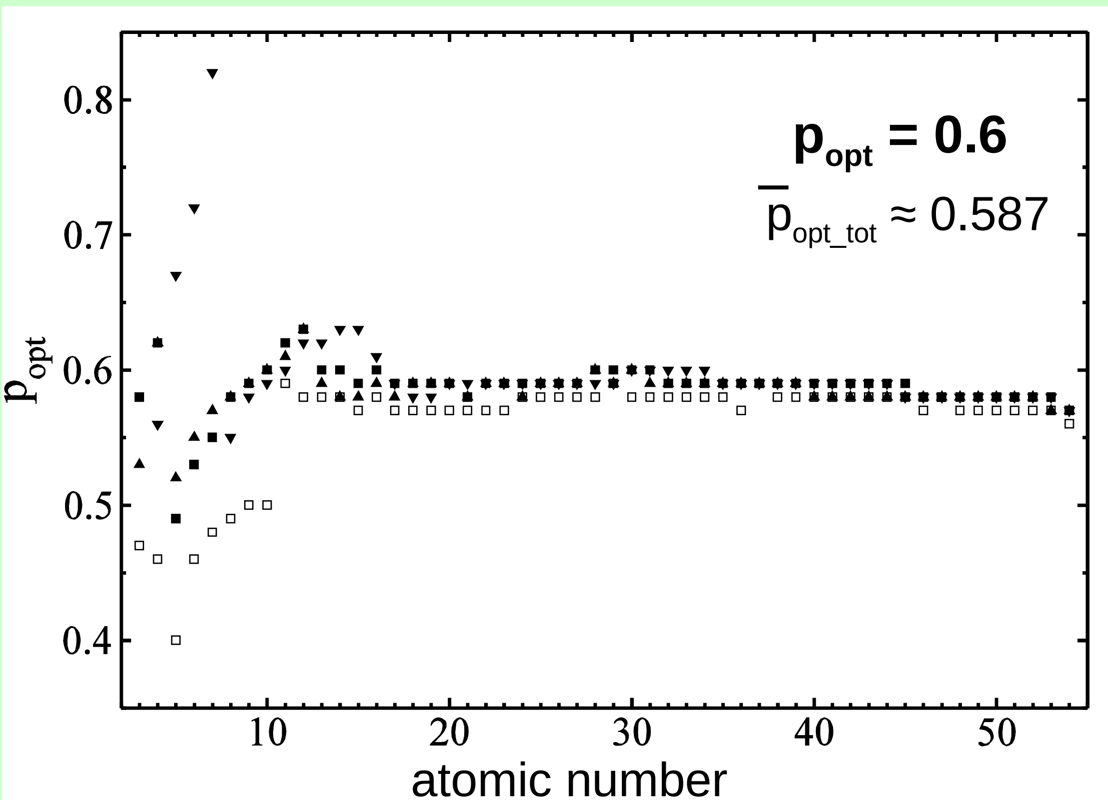
$$\frac{\nabla \tilde{V}_D(r)}{\tilde{V}_D(r)}=\frac{\nabla \tilde{V}_{I_p}(r)}{\tilde{V}_{I_p}(r)}$$

$$\tilde{Y}_D(r)=\tilde{V}_D(r)\,\rho(r) \qquad \tilde{C}_p(r)=\tilde{V}_{I_p}(r)\,\rho(r)$$



Adjustment of C_p to ELI-D

	separate spin channels				total density	
indicator	C_p^{α}	$\rightarrow Y_D^{\alpha}$	C_p^{β}	$\rightarrow Y_D^{\beta}$	C_p	$\rightarrow Y_{D^{(t)}}$
control property	$I_p(\rho^{\alpha})$	$D^{\alpha\alpha}$	$I_p(\rho^{\beta})$	$D^{\beta\beta}$	$I_p(\rho)$	$D^{(t)}$
sampling property	q^{α}	q^{α}	q^{β}	q^{β}	q	q



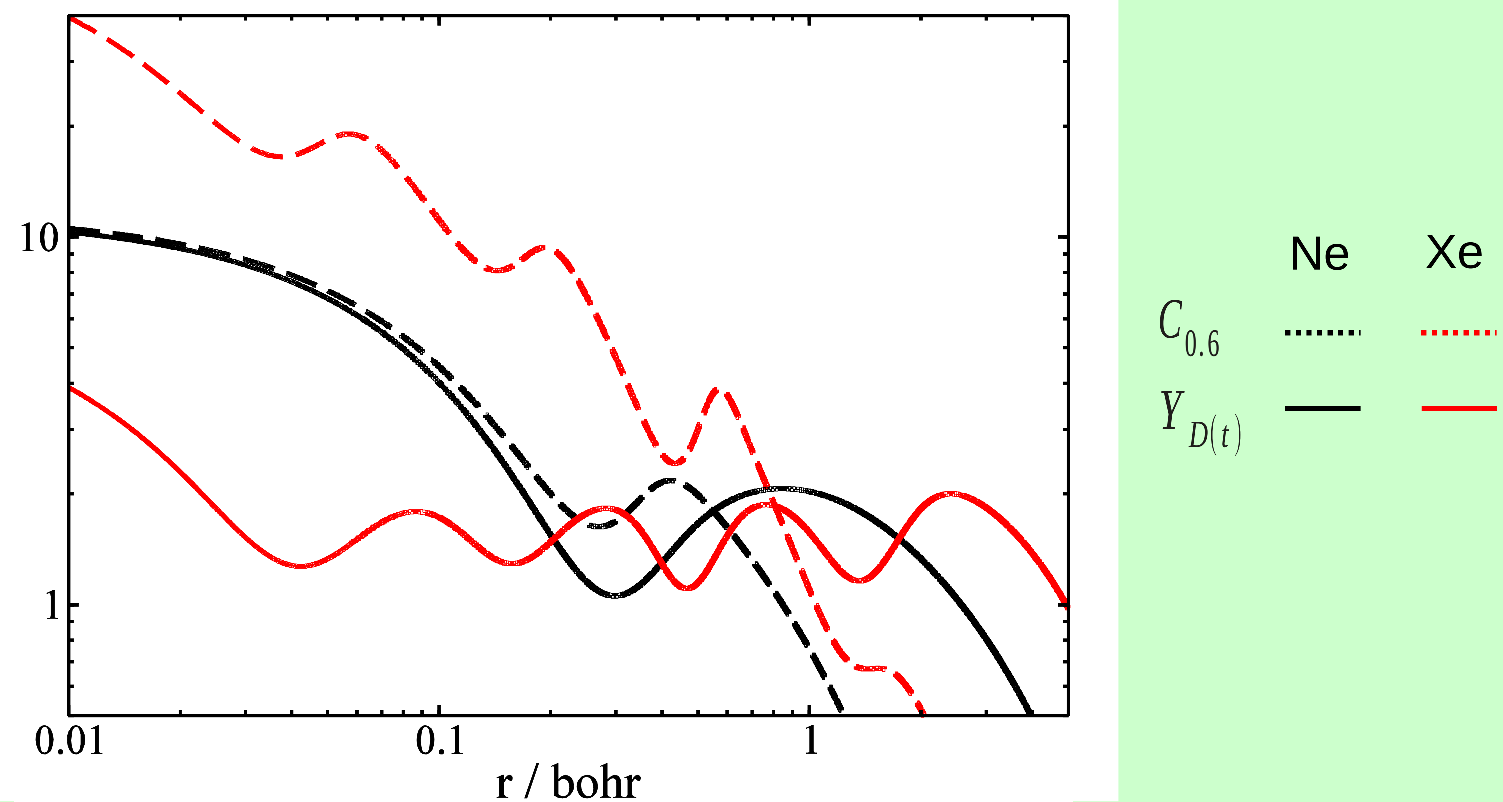
■ total density
▲ majority density
▼ minority density

● optimization for the "whole" atom
○ optimization for the core part

HF wave function from E. Clementi and C. Roetti, At. Nucl. Data Tables, 1974.

Adjustment of C_p to ELI-D

	separate spin channels				total density	
indicator	C_p^{α} →	Y_D^{α}	C_p^{β} →	Y_D^{β}	C_p →	$Y_{D(t)}$
control property	$I_p(\rho^{\alpha})$	$D_{\alpha\alpha}$	$I_p(\rho^{\beta})$	$D_{\beta\beta}$	$I_p(\rho)$	D_t
sampling property	q^{α}	q^{α}	q^{β}	q^{β}	q	q



Adjustment of C_p to ELI-D

control function

$$I_p(i)=\sqrt[p]{\int_{\mu_i} |\rho-\bar{\rho}_i|^p \, dV}$$

pairs

electron density inhomogeneity

ω-RSP

electron population

sampling function

ELI-D C_p

atomic shell structure

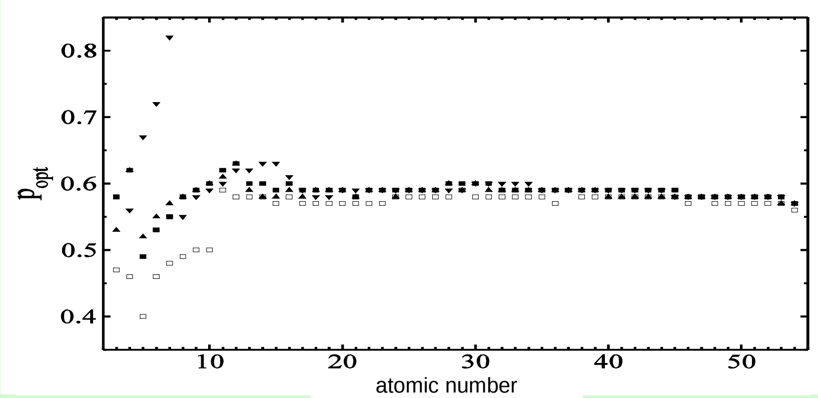
C_p → ELI-D $C_{0.6}$

bonding analyses

$$\tilde{Y}_D(r)=\tilde{V}_D(r)\,\rho(r) \qquad \tilde{C}_p(r)=\tilde{V}_{I_p}(r)\,\rho(r)$$

$$\frac{\nabla \tilde{V}_D(r)}{\tilde{V}_D(r)}=\frac{\nabla \tilde{V}_{I_p}(r)}{\tilde{V}_{I_p}(r)}$$

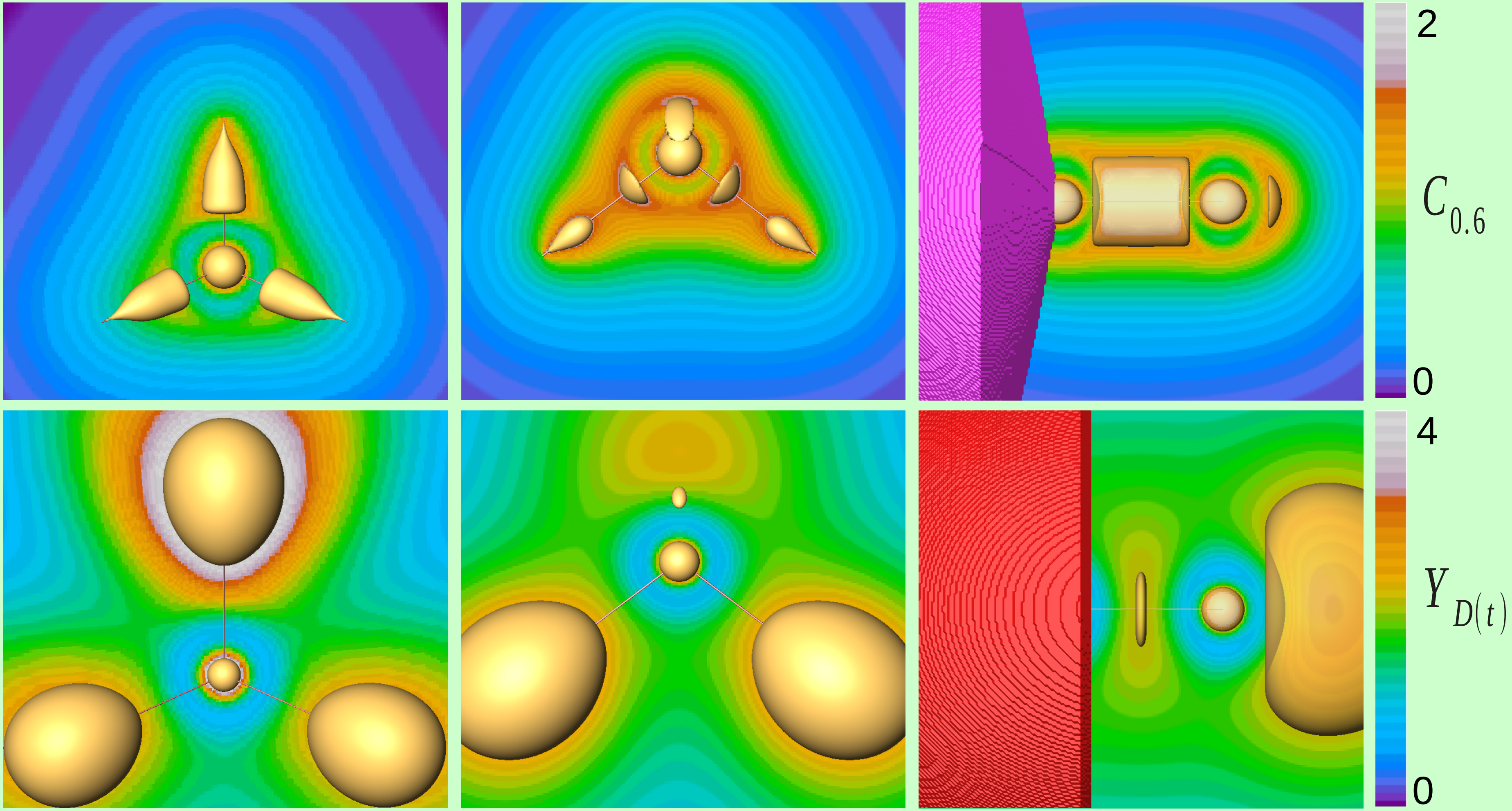
$$p_{opt}=0.6 \rightarrow C_{0.6}$$



Comparison between $C_{0.6}$ and ELI-D for molecules

CH_4, H_2O: ADF/HF/QZ4P

N_2: G09/HF/cc-pVQZ

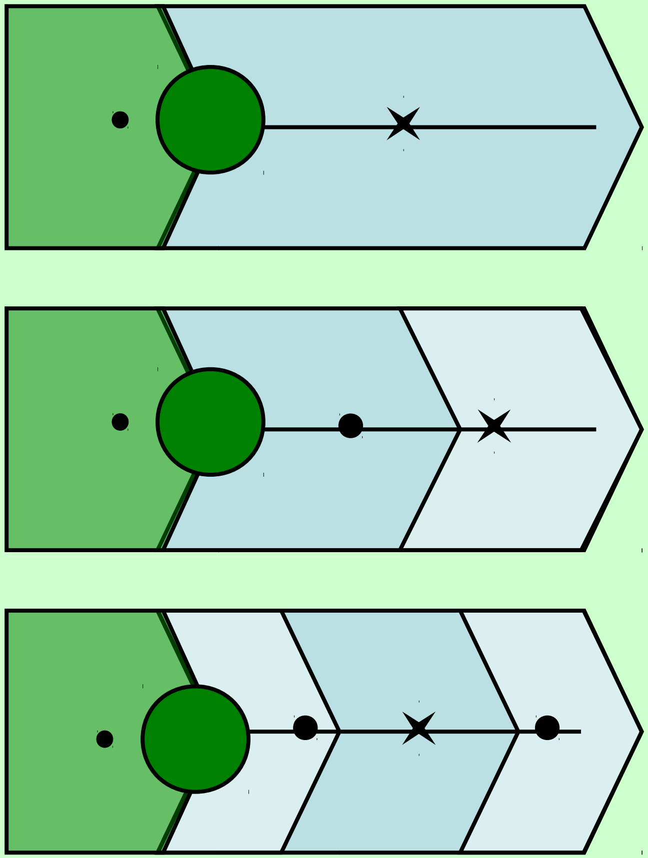


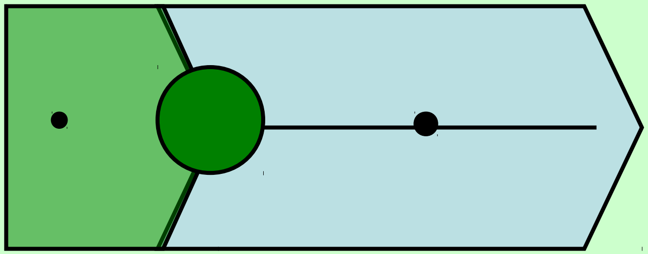
CH_4 **H_2O** **N_2**

Comparison between $C_{0.6}$ and ELI-D for molecules

$$C_{0.6} = \rho \frac{a}{\sqrt{|\nabla \rho|}}$$

ELI-D





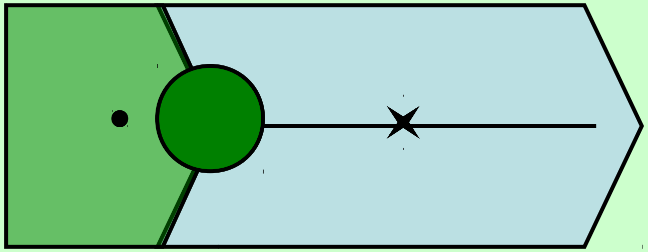
Core regions are alike

Lone pair regions are similar

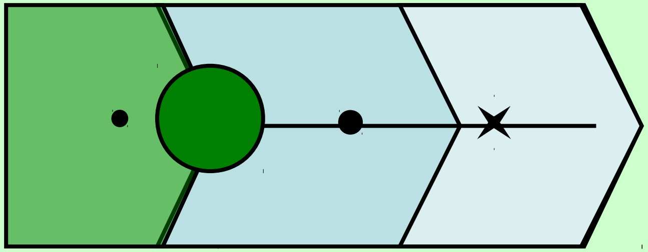
Bonding regions are different

Comparison between $C_{0.6}$ and ELI-D for molecules

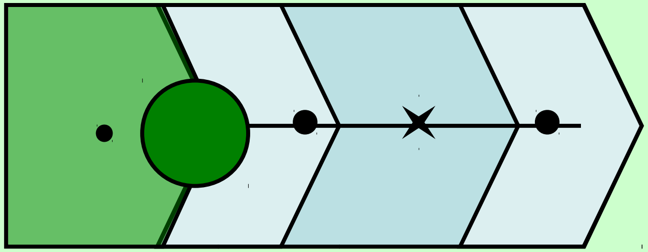
$$C_{0.6} = \rho \frac{a}{\sqrt{|\nabla \rho|}}$$



non polar bonds



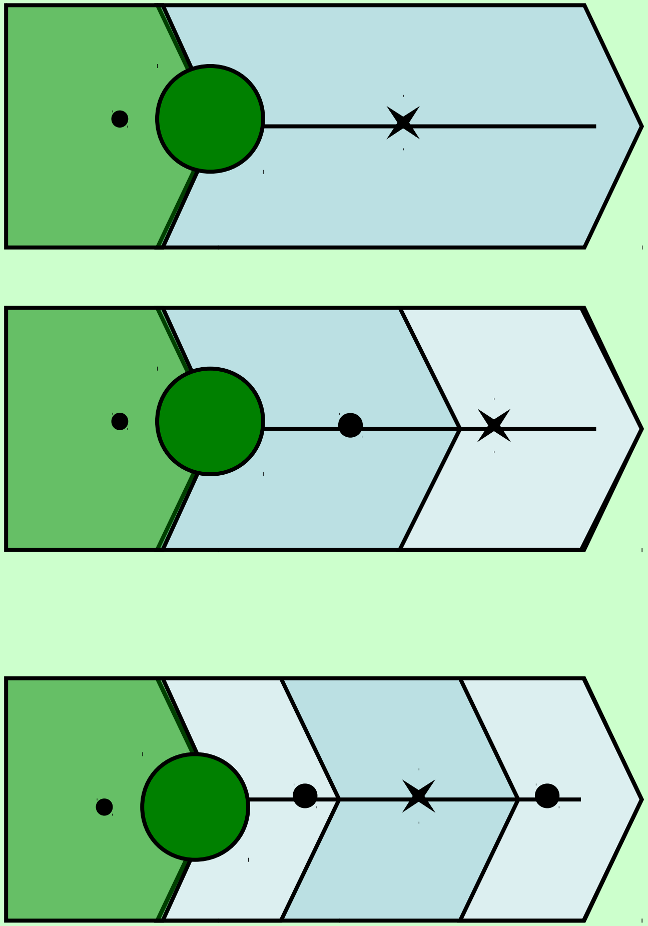
polar bonds



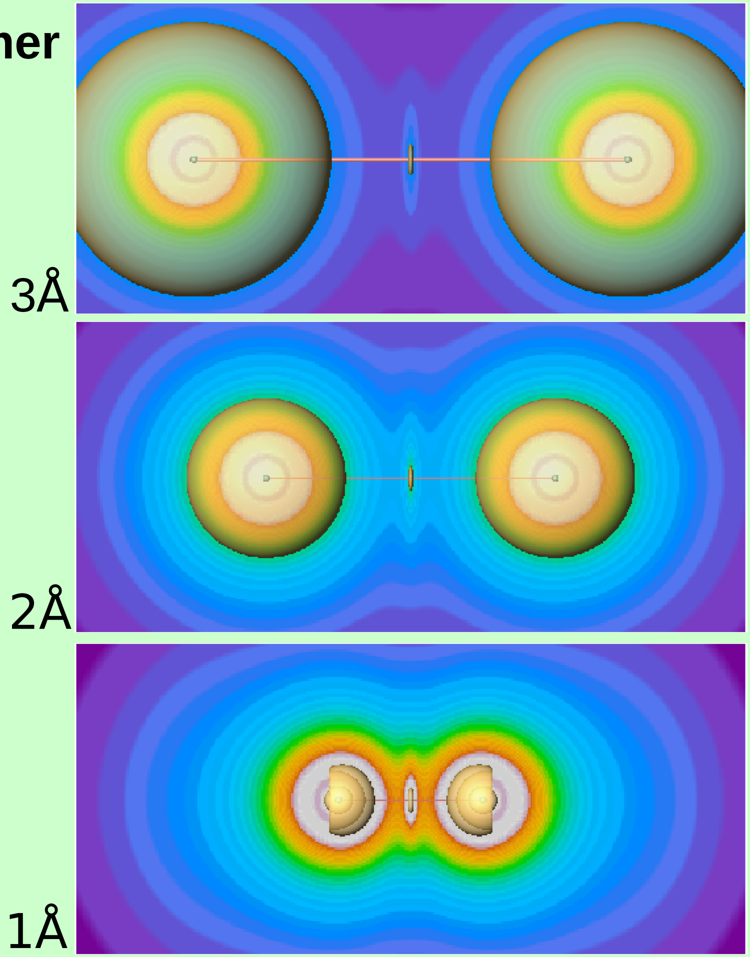
non bonded systems
non covalent interactions

Comparison between $C_{0.6}$ and ELI-D for molecules

$$C_{0.6} = \rho \frac{a}{\sqrt{|\nabla \rho|}}$$

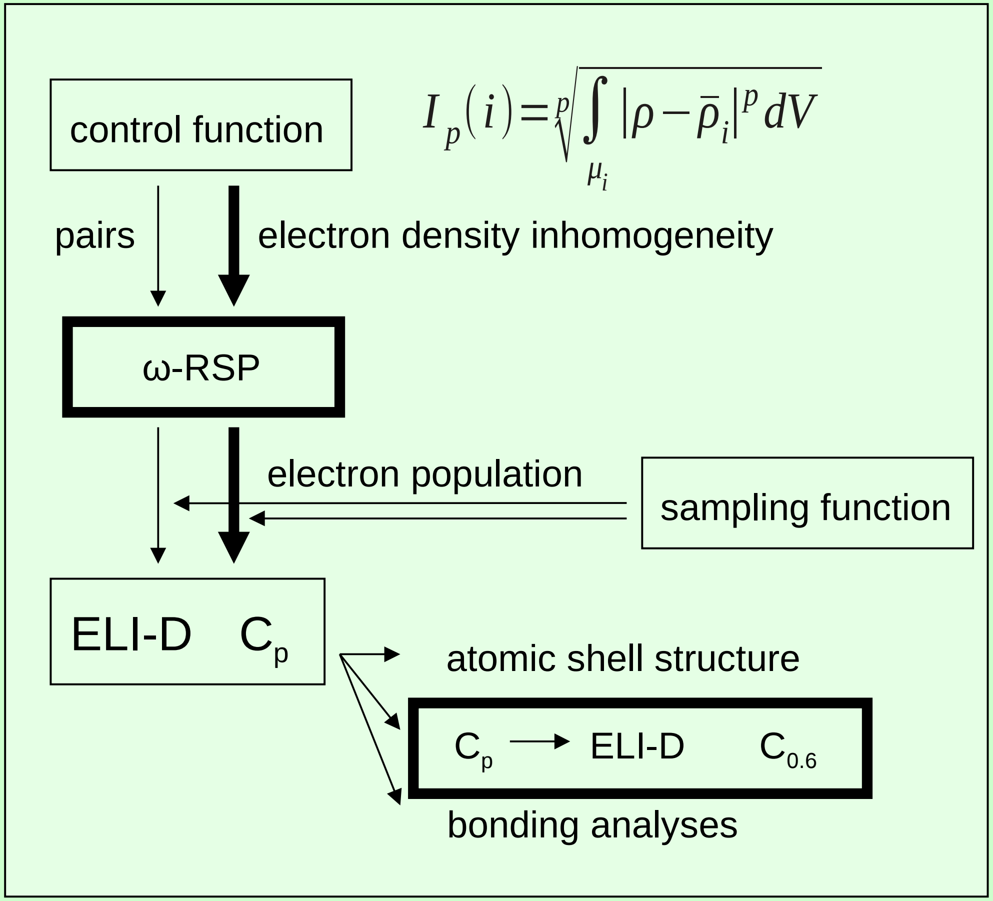


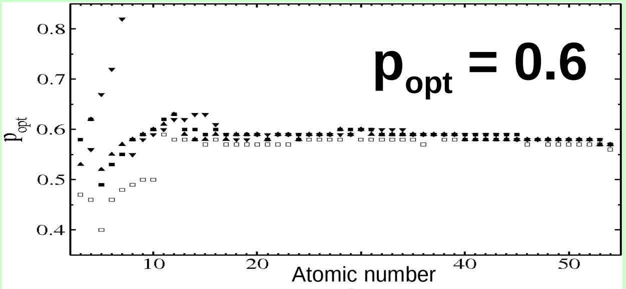
Ne dimer

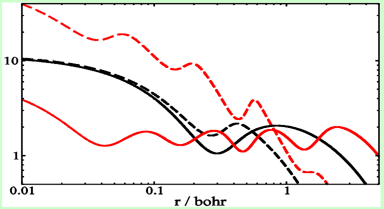


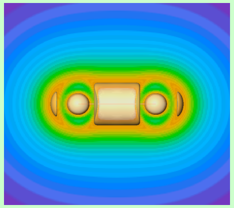
non bonded systems
non covalent interactions

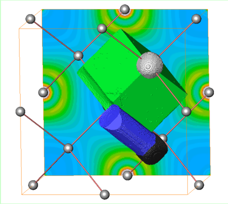
Summary

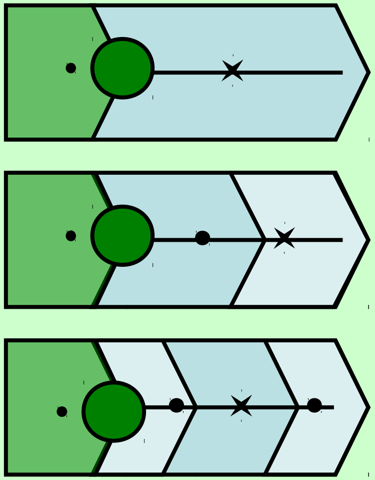












non polar

polar

non bonded

Thesis – google: Kati Finzel

K. Wagner, M. Kohout, Theor. Chem. Acc., 128, 39-46, 2011

K. Finzel, Yu. Grin, M. Kohout, Theor. Chem. Acc., 131, 1-8, 1106, 2012