Babes-Bolyai University
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WEST UNIVERSITY OF TIMIȘOARA

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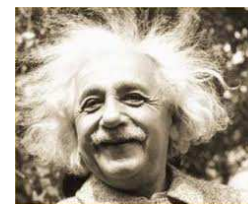**CHEMICAL ORTHOGONAL SPACES OF ATOMS AND MOLECULES**

Habilitation Thesis

E-mails: mvputz@cbg.uvt.ro
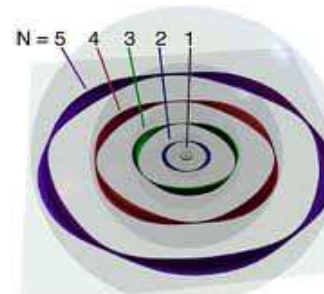mv_putz@yahoo.com;
Web: http://www.mvputz.iqstorm.ro

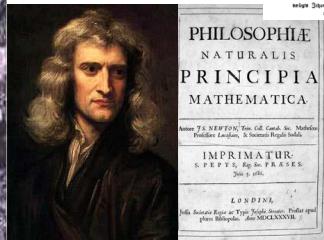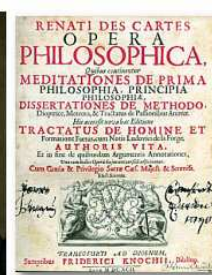# INTRODUCING
CHEMICAL ORTHOGONAL SPACES (COS)

(C)Ham

Melancolia

Ouroboros

N = 5 4 3 2 1

Bohr-de Broglie electron matterwave orbits shells 1-5

$\Delta p \cdot \Delta q \sim h$
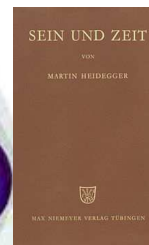
COS1: Orthogonal space of chemical reactivity;
COS2: Orthogonal space of electronic localization function;
COS3: Orthogonal space of bondonic (bosonic) condensation in chemical bond;
COS4: Orthogonal space of enzyme-substrate binding's probability;
COS5: Orthogonal space of chemical structure-biological activity correlations

COS1: Chemical Reactivity
Electronegativity and Chemical Hardness

$$\chi \equiv -\left(\frac{\partial E_N}{\partial N}\right)_{V(r)}$$

$$\cong -\frac{E_{N_0+1} - E_{N_0-1}}{2}$$
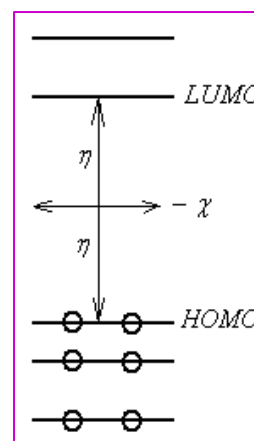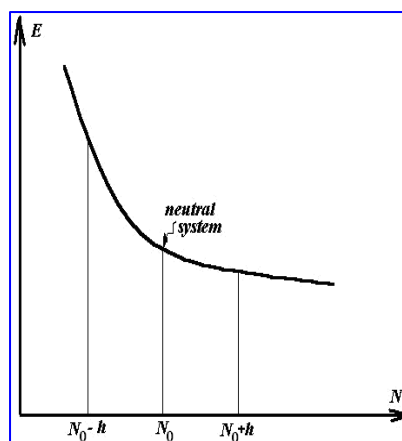
$$= \frac{\left(E_{N_0-1} - E_{N_0}\right) + \left(E_{N_0} - E_{N_{0+1}}\right)}{2}$$

$$= \frac{IP + EA}{2} \cong -\frac{\varepsilon_{LUMO} + \varepsilon_{HOMO}}{2}$$

$$\eta \equiv -\frac{1}{2}\left(\frac{\partial \chi}{\partial N}\right)_{V(r)}$$

$$= \frac{1}{2}\left(\frac{\partial^2 E_N}{\partial N^2}\right)_{V(r)}$$

$$\cong \frac{E_{N_0+1} - 2E_{N_0} + E_{N_0-1}}{2}$$

$$= \frac{IP - EA}{2} \cong \frac{\varepsilon_{LUMO} - \varepsilon_{HOMO}}{2}$$

Parr R.G.; Donnelly R.A.; Levy M.; Palke W.E. (**1978**) Electronegativity: the density functional viewpoint. *J. Chem. Phys. 68*, 3801–3808; **Parr R.G.; Pearson R.G.** (**1983**) Absolute hardness: companion parameter to absolute electronegativity. *J. Am. Chem. Soc. 105*, 7512-7516; **Parr R.G.; Yang W.** (**1989**) *Density Functional Theory of Atoms and Molecules*. Oxford University Press: New York; **Putz M.V.** (**2007**) Can quantum-mechanical description of chemical bond be considered complete? Expert Commentary In: Quantum Chemistry Research Trends, Ed. Kaisas M.P., Nova Science Publishers Inc.: New York (ISBN: 978-160021-620-6), 3-5; **Putz M.V.** (**2007**) Unifying absolute and chemical electronegativity and hardness density functional formulations through the chemical action concept. In: Progress in Quantum Chemistry Research, Ed. Hoffman E.O., Nova Science Publishers Inc.: New York (ISBN: 978-1-60021-621-3), 59-121; **Putz M.V.** (**2008**) *Absolute and Chemical Electronegativity and Hardness*, NOVA Science Publishers Inc.: New York (ISBN: 978-1-60456-937-7), pp. 95; **Putz M.V.** (**2011**) Electronegativity and chemical hardness: different patterns in quantum chemistry. Curr. Phys. Chem. 1(2), 111-139; **Putz M.V.** (**2012**) Chemical reactivity and biological activity criteria from DFT parabolic dependency E=E(N). In: Theoretical and Computational Developments in Modern Density Functional Theory, Ed. Roy A.K., NOVA Science Publishers Inc.: New York (ISBN: 978-1-61942-779-2), Chapter 17.

COS1: Chemical Reactivity

Electronegativity and Chemical Hardness

Chemical Principle	Principle of Bonding
$\delta\chi = 0$	*Electronegativity equality*: "Electronegativity of all constituent atoms in a bond or molecule have the same value" (Sanderson, 1988)
$\delta\int \rho(\mathbf{r})V(\mathbf{r})d\mathbf{r} = 0$	*Chemical action minimum variation*: Global minimum of bonding is attained by optimizing the convolution of the applied potential with the response density (Putz, 2011)
$\Delta\chi < 0$	*Minimum (residual) electronegativity*: "the constancy of the chemical potential is perturbed by the electrons of bonds bringing about a finite difference in regional chemical potential even after chemical equilibrium is attained globally" (Tachibana et al., 1999)
$\delta\eta = 0$	*Hard-and-soft acids and bases*: "hard likes hard and soft likes soft" (Pearson, 1973, 1990, 1997)
$\Delta\eta > 0$	*Maximum (residual) hardness*: "molecules arranges themselves as to be as hard as possible" (Chattaraj et al., 1991, 1995)

Sanderson R.T. (**1988**) Principles of electronegativity Part I. General nature. *J. Chem. Educ. 65*, 112-119; **Putz M.V.** (**2011**): Chemical action concept and principle. *MATCH Commun. Math. Comput. Chem. 66*(1), 35-63; **Tachibana A.; Nakamura K.; Sakata K.; Morisaki T.** (**1999**) Application of the regional density functional theory: the chemical potential inequality in the HeH+ system. *Int. J. Quantum Chem. 74*, 669-679; **Pearson R.G.** (**1973**) *Hard and Soft Acids and Bases*. Dowden, Hutchinson & Ross: Stroudsberg (PA); **Pearson R.G.** (**1990**) Hard and soft acids and bases—the evolution of a chemical concept. *Coord. Chem. Rev.100*, 403–425; Pearson R. G. (**1997**) *Chemical Hardness*. Wiley-VCH: Weinheim; **Chattaraj P.K.; Lee H.; Parr R.G.** (**1991**) Principle of maximum hardness. *J. Am. Chem. Soc. 113*, 1854-1855; **Chattaraj P.K.; Liu G.H.; Parr R.G.** (**1995**) The maximum hardness principle in the Gyftpoulos-Hatsopoulos three-level model for an atomic or molecular species and its positive and negative ions. *Chem. Phys. Lett. 237*, 171-176.

COS1: Chemical Reactivity

Observability of Electronegativity and Chemical Hardness

$$\chi_\lambda = -\frac{\partial \langle E_\lambda \rangle}{\partial \rho_\lambda} = -\frac{\partial \langle E_\lambda \rangle}{\partial \lambda}\frac{\partial \lambda}{\partial \rho_\lambda}$$

$$\eta_\lambda = \frac{1}{2}\frac{\partial^2 \langle E_\lambda \rangle}{\partial \rho_\lambda^2} = \frac{1}{2}\left\{\left[\frac{\partial}{\partial \lambda}\left(\frac{\partial \langle E_\lambda \rangle}{\partial \lambda}\right)\right]\frac{\partial \lambda}{\partial \rho_\lambda} + \frac{\partial \langle E_\lambda \rangle}{\partial \lambda}\left[\frac{\partial}{\partial \lambda}\left(\frac{\partial \lambda}{\partial \rho_\lambda}\right)\right]\right\}\frac{\partial \lambda}{\partial \rho_\lambda}$$

$$\langle E_{\lambda \in \Re}^{I \leftrightarrow A}\rangle := \frac{\langle \psi_\lambda^I | \hat{H} | \psi_\lambda^A \rangle}{\langle \psi_\lambda^I | \psi_\lambda^A \rangle}$$

$$\rho_{\lambda \in \Re}^{I \leftrightarrow A} := \frac{\langle \psi_\lambda^I | \hat{a}^+ \hat{a} | \psi_\lambda^A \rangle}{\langle \psi_\lambda^I | \psi_\lambda^A \rangle}$$

$$|\psi_\lambda^I\rangle = (1 + \lambda \hat{a}\hat{a}^+)\psi_0\rangle = |\psi_0\rangle + \lambda |0\rangle\langle 1|1\rangle\langle 0|\psi_0\rangle = |\psi_0\rangle + \lambda\sqrt{1 - \rho_0}|0\rangle$$

$$|\psi_\lambda^A\rangle = (1 + \lambda \hat{a}^+ \hat{a})\psi_0\rangle = |\psi_0\rangle + \lambda |1\rangle\langle 0|0\rangle\langle 1|\psi_0\rangle = |\psi_0\rangle + \lambda\sqrt{\rho_0}|1\rangle$$

$$\boxed{\hat{a}^+ = |1\rangle\langle 0|} \quad \boxed{\hat{a} = |0\rangle\langle 1|} \quad \boxed{\hat{a}^+|0\rangle = |1\rangle\langle 0|0\rangle = |1\rangle} \quad \boxed{\hat{a}|1\rangle = |0\rangle\langle 1|1\rangle = |0\rangle}$$

$$\boxed{\hat{H}|\psi_0\rangle = E_0 |\psi_0\rangle}$$

$$\hat{1} = |0\rangle\langle 0| + |1\rangle\langle 1| = \hat{a}\hat{a}^+ + \hat{a}^+\hat{a} = \{\hat{a}, \hat{a}^+\}$$

$$1 = \langle \psi_0 | \psi_0 \rangle = \langle \psi_0 | \hat{1} | \psi_0 \rangle = \langle \psi_0 | (\hat{a}\hat{a}^+ + \hat{a}^+\hat{a}) | \psi_0 \rangle = \langle \psi_0 | \hat{a}\hat{a}^+ | \psi_0 \rangle + \langle \psi_0 | \hat{a}^+\hat{a} | \psi_0 \rangle$$

$$= |\langle 0 | \psi_0 \rangle|^2 + |\langle 1 | \psi_0 \rangle|^2 = (1 - \rho_0) + \rho_0 \quad \rho_0 \in [0,1]$$

$$\rho_{\lambda \in \Re}^{I \leftrightarrow A} = \frac{\langle \psi_\lambda^I | \hat{a}^+\hat{a} | \psi_\lambda^A \rangle}{\langle \psi_\lambda^I | \psi_\lambda^A \rangle_{0 << \rho_0 \le 1}}$$

$$= \rho_0 \frac{1 + \lambda}{1 + \lambda \rho_0}$$

$$\boxed{\chi_\lambda = -\frac{E_0}{\rho_0} = -\mu_0 = \begin{cases} \infty & , \rho_0 \to 0\,(E_0 < 0) \\ -E_0 = -\langle \psi_0 | H | \psi_0 \rangle, & \rho_0 \to 1 \end{cases}}$$

$$\langle E_{\lambda \in \Re}^{I \leftrightarrow A}\rangle = \frac{\langle \psi_\lambda^I | \hat{H} | \psi_\lambda^A \rangle}{\langle \psi_\lambda^I | \psi_\lambda^A \rangle_{0 << \rho_0 \le 1}}$$

$$= E_0 \frac{1 + \lambda}{1 + \lambda \rho_0}$$

$$\boxed{\eta_\lambda = 0 \cdot E_0 \frac{1 + \lambda \rho_0}{\rho_0(1 - \rho_0)} = \begin{cases} 0, & \rho_0 \in (0,1) \\ 0 \cdot \infty = ?, & \rho_0 \to 0 \\ 0 \cdot \infty = ?, & \rho_0 \to 1 \end{cases}}$$

Putz M.V. (**2009**) Electronegativity: quantum observable. *Int. J. Quantum Chem.* 109(4), 733-738; **Putz M.V.** (**2010**) Chemical hardness: quantum observable? *Studia Univ. Babeş-Bolyai - Seria Chemia* 55 (2) –Tom I, 47-50.

COS1: Chemical Reactivity

Atomic Periodicity. Density Functional Softness Theory Approach

$$\chi_{FD} \propto \langle \Delta E \rangle_{(N_0-1, N_0+1)}$$

$$\eta_{FD} \propto \langle \Delta \chi \rangle_{(N_0-1, N_0+1)}$$

$$N = \int \rho(\mathbf{r}) d\mathbf{r}$$

$$\chi_A = -\frac{1}{2} \int_{N_0-1}^{N_0+1} dE_N$$

$$\eta_A = -\frac{1}{2} \int_{N_0-1}^{N_0+1} d\chi_D$$

$$E_N = E_N[N, V(\mathbf{r})]$$

$$\chi_D = \chi_D[N, V(\mathbf{r})]$$

$$dE_N = \left(\frac{\partial E_N}{\partial N}\right)_{V(\mathbf{r})} dN + \frac{1}{2}\left(\frac{\partial^2 E_N}{\partial N^2}\right)_{V(\mathbf{r})} dNdN + \int\left(\frac{\delta E_N}{\delta V(\mathbf{r})}\right)_N \delta V(\mathbf{r}) d\mathbf{r}$$

$$d\chi_D = \left(\frac{\partial \chi_D}{\partial N}\right)_{V(\mathbf{r})} dN + \frac{1}{2}\left[\frac{\partial}{\partial N}\left(\frac{\partial \chi_D}{\partial N}\right)_{V(\mathbf{r})}\right]_{V(\mathbf{r})} dNdN + \int\left(\frac{\delta \chi_D}{\delta V(\mathbf{r})}\right)_N \delta V(\mathbf{r}) d\mathbf{r}$$

$$S = -\left(\frac{\partial N}{\partial \chi_D}\right)_{V(\mathbf{r})}$$

$$s(\mathbf{r}) = -\left(\frac{\partial \rho(\mathbf{r})}{\partial \chi_D}\right)_{V(\mathbf{r})}$$

$$\frac{1}{2\eta} \equiv S = \int s(\mathbf{r}) d\mathbf{r}$$

$$d\chi_D^{[DFST]} = -\frac{1}{S} dN - \frac{1}{2}\left[\frac{\partial}{\partial N}\left(\frac{1}{S}\right)\right] dNdN - \int \frac{s(\mathbf{r})}{S} \delta V(\mathbf{r}) d\mathbf{r}$$

$$dE_N^{[DFST]} = -\chi_D^{[DFST]}(N) dN - \frac{1}{2}\left(\frac{\partial \chi_D^{[DFST]}(N)}{\partial N}\right)_{V(r)} dNdN + \int \rho(\mathbf{r}) \delta V(\mathbf{r}) d\mathbf{r}$$

Putz M.V. (**2006**) Systematic formulation for electronegativity and hardness and their atomic scales within density functional softness theory. *Int. J. Quantum Chem.* 106(2), 361-389.

COS1: Chemical Reactivity

Atomic Periodicity. Density Functional Softness Theory Approach

the electronic (density-potential) response function (Garza & Robles, 1993)

Garza J.; Robles J. (**1993**) Density functional theory softness kernel. *Phys. Rev. A* 47, 2680-2685.

$$\chi_A^{[DFST]} = -\frac{1}{2}\int_{N_v-1}^{N_v+1} dE_N^{[DFST]} = \frac{3}{16a}\left\{ \begin{array}{l} 4N_v + 2\sqrt{a}\left[(2b+3N_v-3)\arctan\frac{N_v-1}{\sqrt{a}} - (2b+3N_v+3)\arctan\left(\frac{N_v+1}{\sqrt{a}}\right)\right] \\ + a(2C_A-3)\ln\left[\frac{a+(N_v-1)^2}{a+(N_v+1)^2}\right] \end{array} \right\}$$

$$\eta_A^{[DFST]} = -\frac{1}{2}\int_{N_v-1}^{N_v+1} d\chi_D^{[DFST]} = \frac{1}{4}\left\{ \begin{array}{l} \frac{4\left[C_A\left(1+a-N_v^2\right)-2bN_v\right]}{(1+a)^2 + 2(a-1)N_v^2 + N_v^4} + \frac{1}{\sqrt{a}}\left[\arctan\left(\frac{N_v-2}{\sqrt{a}}\right) + \arctan\left(\frac{N_v+2}{\sqrt{a}}\right)\right] \\ - \frac{2}{\sqrt{a}}\left[\arctan\left(\frac{N_v-1}{\sqrt{a}}\right) + \arctan\left(\frac{N_v}{\sqrt{a}}\right) - \arctan\left(\frac{N_v+1}{\sqrt{a}}\right)\right] \end{array} \right\}$$

$$L(\mathbf{r}) = \frac{\nabla\rho(\mathbf{r})\cdot[-\nabla V(\mathbf{r})]}{[-\nabla V(\mathbf{r})]^2}$$
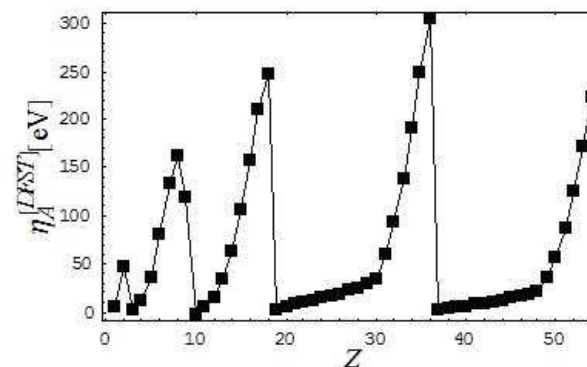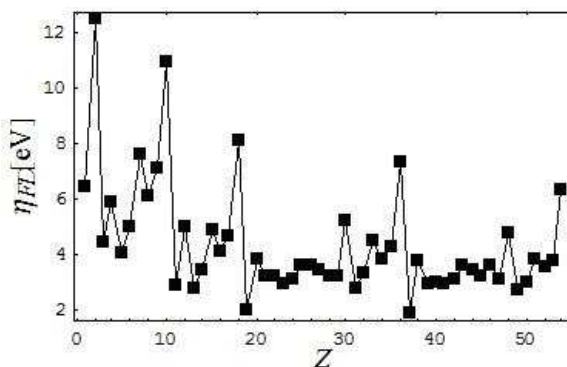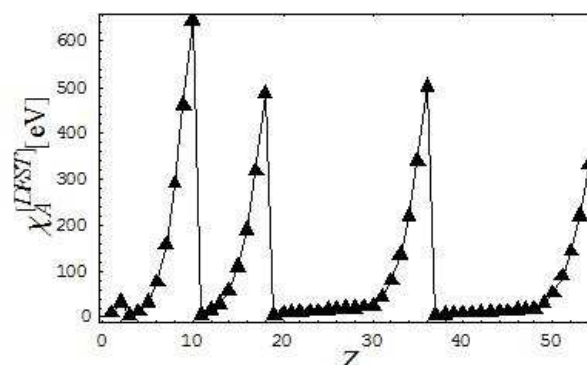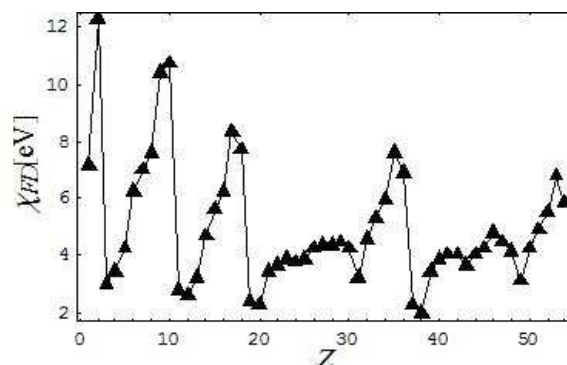
$$a \equiv \int L(\mathbf{r})d\mathbf{r}$$

$$b \equiv \int L(\mathbf{r})V(\mathbf{r})d\mathbf{r}$$

$$C_A \equiv \int \rho(\mathbf{r})V(\mathbf{r})d\mathbf{r}$$

$$S = a + N^2$$

$$s(\mathbf{r}) = L(\mathbf{r}) + N\rho(\mathbf{r})$$

Putz M.V. (**2012**) Chemical reactivity and biological activity criteria from DFT parabolic dependency E=E(N). In: Theoretical and Computational Developments in Modern Density Functional Theory, Ed. Roy A.K., NOVA Science Publishers Inc.: New York (ISBN: 978-1-61942-779-2), Chapter 17.

COS1: Chemical Reactivity

Atomic Periodicity. Atomic Size-Dependent Properties

Boyd-Markus - BM (1981)

$$\chi_M = \frac{Z_{eff}}{r^2}(1 - \int \rho(r)dr)$$

Ghanty and Gosh -GG (1996)

$$\chi_M = -\frac{\nabla_r \rho(r)}{\rho(r)}$$

Ghosh and Biswas - GB (2002)

$$\nabla_r \left[4\pi r^2 \rho_{\mathbf{STO}}(r) \right]\Big|_{r=R} = 0$$

Putz (2003)

$$\chi_M = \frac{b(R_{DFT})+N-1}{2\sqrt{a(R_{DFT})}}\arctan\left(\frac{N-1}{\sqrt{a(R_{DFT})}}\right)$$

$$-\frac{b(R_{DFT})+N+1}{2\sqrt{a(R_{DFT})}}\arctan\frac{N+1}{\sqrt{a(R_{DFT})}} + \frac{C_A(R_{DFT})-1}{4}\ln\left(\frac{a(R_{DFT})+(N-1)^2}{a(R_{DFT})+(N+1)^2}\right)$$

$$a(R_{DFT}) \equiv \int_{\infty}^{R} L(r)dr\Big|_{R\to 0} \qquad b(R_{DFT}) \equiv \int_{\infty}^{R} L(r)V(r)dr\Big|_{R\to 0}$$

$$C_A(R_{DFT}) \equiv \int_{\infty}^{R} 4\pi r^2 \rho_{\mathbf{STO}}(r)V(r)dr\Big|_{R\to 0}$$

Boyd R. J.; Markus, G. E. (**1981**) Electronegativities of the elements from a nonempirical electrostatic model. *J. Chem. Phys. 75*, 5385-5389; **Ghanty T.K.; Ghosh S.K.** (**1996**) New scale of atomic orbital radii and its relationships with polarizability, electronegativity, other atomic properties, and bond energies of diatomic molecules. *J. Phys. Chem. 100*, 17429-17433; **Ghosh D.C.; Biswas R.** (**2002**) Theoretical calculation of absolute radii of atoms and ions. Part 1. The atomic radii. *Int. J. Mol. Sci. 3*, 87-113.
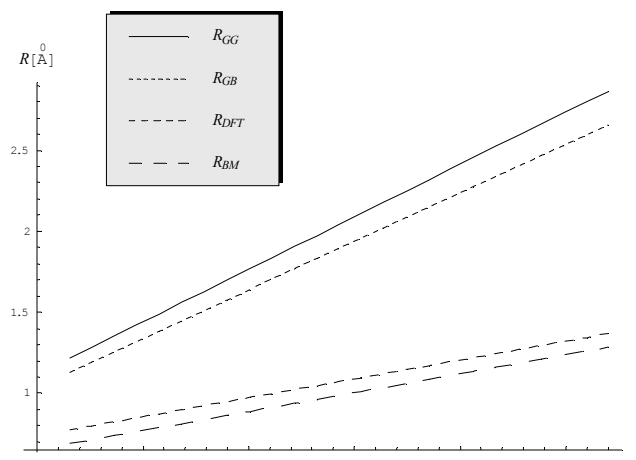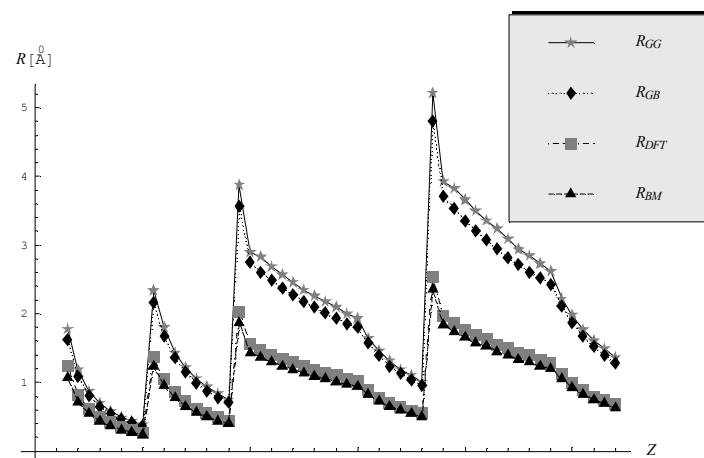
Putz M.V.; Russo N.; Sicilia E. (**2003**) Atomic radii scale and related size properties from density functional electronegativity formulation. *J. Phys. Chem. A* 107(28), 5461-5465.
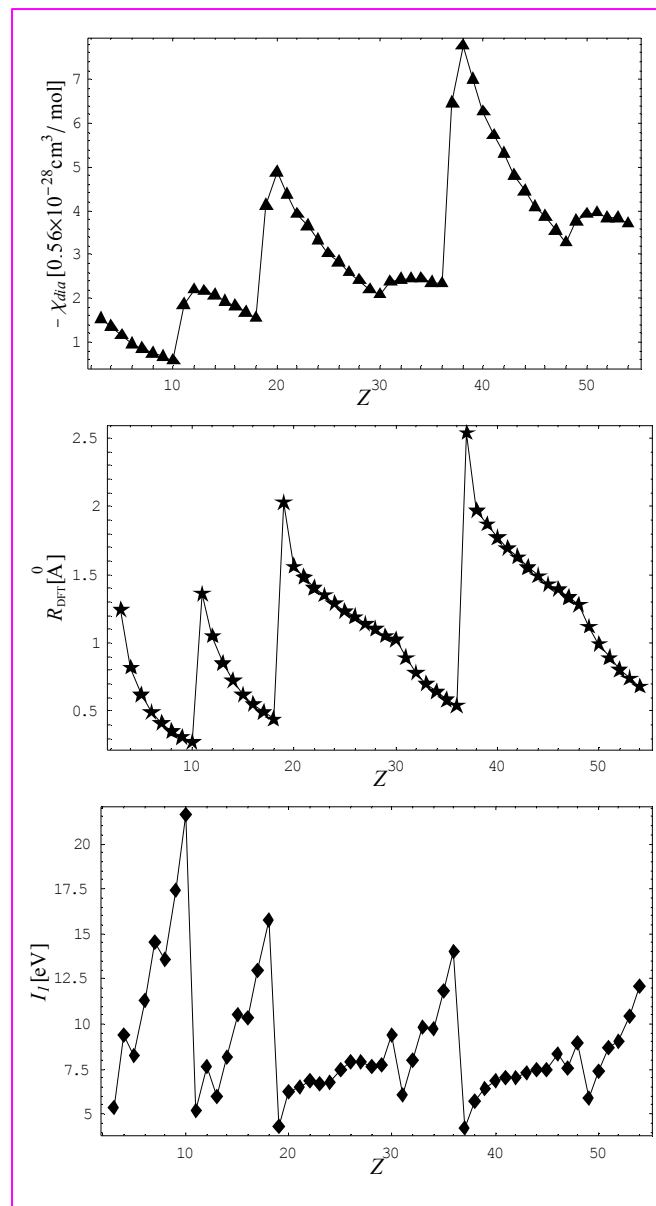
COS1: Chemical Reactivity
Atomic Periodicity. Atomic Size-Dependent Properties

$$f\left(N, Z, \langle g(r) \rangle\right) \to f\left(N_{outer}, Z_{eff}, g(R)\right)$$

diamagnetic susceptibility (Putz et al., 2003; Putz, 2012)

$$\chi_{dia} = -\frac{z\,e^2\,\mu_0}{6m}\,N\langle r^2 \rangle$$

$$\chi_{dia} = -N_{outer}R^2\,[0.56 \times 10^{-28}\,\mathrm{cm^3/mol}]$$

Putz M.V. (**2012**) Nanoroots of quantum chemistry: atomic radii, periodic behavior, and bondons. In: Nanoscience and Advancing Computational Methods in Chemistry, Eds. Castro, E.A., Haghi A.K., IGI Global: Pasadena (ISBN: 978-1-46661-607-3), 103-143.

COS1: Chemical Reactivity

atomic static dipole polarizability (Putz et al., 2003)

$$\alpha = \frac{2}{Z}\langle r^3 \rangle = \frac{2}{Z_{eff}} R^3 [10^{-24} \mathbf{cm^3}]$$

Putz M.V.; Russo N.; Sicilia E. (**2003**) Atomic radii scale and related size properties from density functional electronegativity formulation. *J. Phys. Chem. A* 107(28), 5461-5465.

the chemical hardness as the inverse of the global softness, *S* (Berkowitz & Parr, 1988)

$$\eta_S = \frac{1}{2S} = \frac{Z}{8\langle r \rangle} = \frac{Z_{eff}}{8R}[eV] = \frac{Z_{eff}^{2/3}}{2^{8/3}\alpha^{1/3}}$$
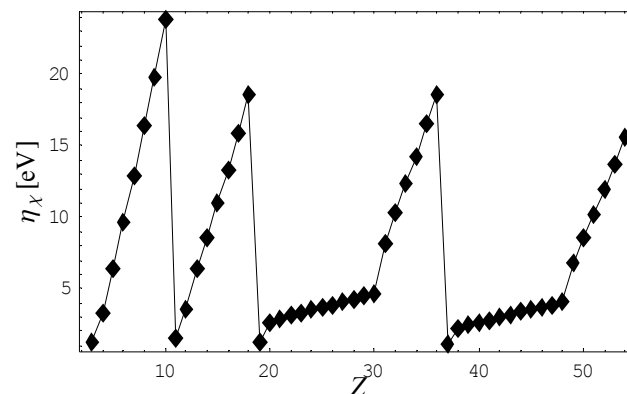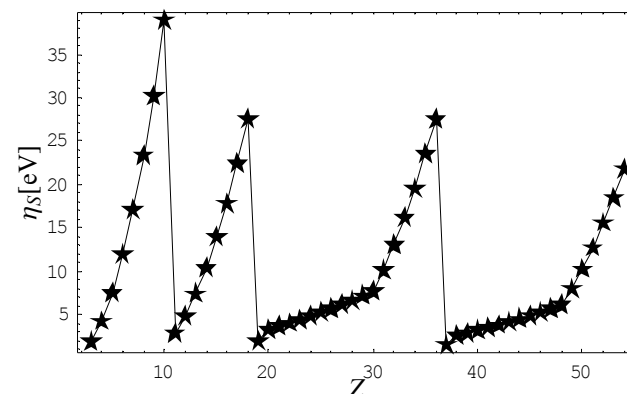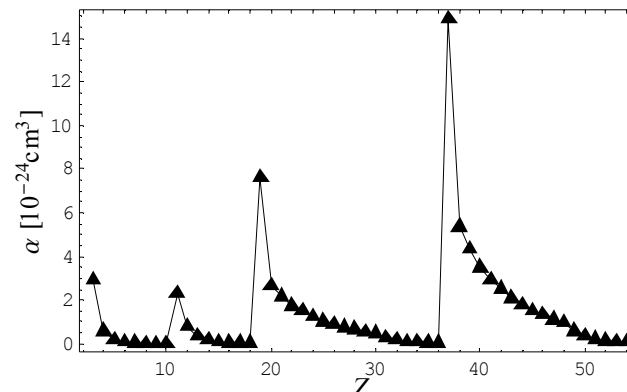
Berkowitz M.; Parr R.G. (**1988**) Molecular hardness and softness, local hardness and softness, hardness and softness kernels, and relations among these quantities. *J. Chem. Phys. 88*, 2554-2557.

chemical hardness in DFT

$$\eta_\chi = -\frac{1}{2}\left(\frac{\partial \chi}{\partial N}\right)_V$$

$$\eta_\chi = \frac{2\sqrt{a}\left[C_A(1+a-N^2)+2N\right]+\left[(1+a)^2+2(a-1)N^2+N^4\right]\left[\arctan\left(\frac{N+1}{\sqrt{a}}\right)-\arctan\left(\frac{N-1}{\sqrt{a}}\right)\right]}{4\sqrt{a}\left[a+(N-1)^2\right]\left[a+(N+1)^2\right]}$$

$$a = \frac{4}{Z}\langle r \rangle = \frac{4}{Z_{eff}} R \qquad\qquad C_A = -Z\left\langle\frac{1}{r}\right\rangle = -Z_{eff}\frac{1}{R}$$

COS1: Chemical Reactivity
The Sharing-Reactive Ansatz of Bonding

electronic covariance D(A,B) between of the electronic populations of atoms *A* and *B* (Fradera & Solà, 2002; Matito et al., 2007)

$$D(A,B) = 2\iint_{A\,B}\int \rho_{XC}(\mathbf{r},\mathbf{r'})d\mathbf{r'}\,d\mathbf{r}$$

Fradera X.; Solà M. (**2002**) Electron localization and delocalization in open-shell molecules. *J. Comp. Chem. 23,* 1347-1356. **Matito E.; Solà M.; Salvador P.; Duran M.** (**2007**) Electron sharing indexes at the correlated level. Application to aromaticity calculations. *Faraday Discuss. 135*, 325–345.

exchange-correlation density

the second-order density matrix   integrates in specific Löwdin manner

$$\rho_{XC}(\mathbf{r},\mathbf{r'}) = \rho(\mathbf{r})\rho(\mathbf{r'}) - \rho_2(\mathbf{r},\mathbf{r'}) \quad \iint_{A\,A}\rho_{XC}(\mathbf{r},\mathbf{r'})d\mathbf{r'}\,d\mathbf{r} = N_A \qquad \iint_{A\,A}\rho_2(\mathbf{r},\mathbf{r'})d\mathbf{r'}\,d\mathbf{r} = N_A(N_A - 1)$$

the delocalization electronic ansatz (Putz, 2011)

$$\frac{1}{2}D(A,B) \equiv \Delta N_{AB}$$

Putz M.V. (**2011**) On relationship between electronic sharing in bonding and electronegativity equalization of atoms in molecules. *Int. J. Chem. Model.* 3(4), 371-384.

the recently proposed softness kernel (Matito & Putz, 2011)

$$s(\mathbf{r},\mathbf{r'}) = -\left(\frac{\partial\rho_{XC}(\mathbf{r},\mathbf{r'})}{\partial\chi}\right)_{V(\mathbf{r})}$$

Matito E.; Putz M.V. (**2011**) New link between conceptual density functional theory and electron delocalization. *J. Phys. Chem. A* 115(45), 12459-12462.

$$\iint s(\mathbf{r},\mathbf{r'})d\mathbf{r}d\mathbf{r'} = -\int\left(\frac{\partial}{\partial\chi}\int\rho_{XC}(\mathbf{r},\mathbf{r'})d\mathbf{r'}\right)_{V(\mathbf{r})}d\mathbf{r} = -\int\left(\frac{\partial\rho(\mathbf{r})}{\partial\chi}\right)_{V(\mathbf{r})}d\mathbf{r} = \int s(\mathbf{r})d\mathbf{r} = S$$

$$\iint_{A\,B}s(\mathbf{r},\mathbf{r'})d\mathbf{r}d\mathbf{r'} = -\left(\frac{\partial}{\partial\chi}\iint_{A\,B}\rho_{XC}(\mathbf{r},\mathbf{r'})d\mathbf{r}d\mathbf{r'}\right)_{V(\mathbf{r})} = -\frac{1}{2}\left(\frac{\partial D(A,B)}{\partial\chi_{AB}}\right)_{V(\mathbf{r})}$$

$$-\frac{1}{2}\left(\frac{\partial D(A,B)}{\partial\chi_{AB}}\right)_A \equiv S_B$$

COS1: Chemical Reactivity
Additive Model of Atoms in Molecules

$$N = N_{\langle A \rangle} + N_{\langle B \rangle} \qquad N_{\langle A \rangle} = N_A + dN_{\langle A \rangle} \qquad N_{\langle B \rangle} = N_B - dN_{\langle B \rangle}$$

$$E = E_{\langle A \rangle} + E_{\langle B \rangle} \qquad E_{\langle\,\rangle}(N_{\langle\,\rangle}) \cong E_{\langle\,\rangle}(N) + \left(\frac{\partial E_{\langle\,\rangle}}{\partial N_{\langle\,\rangle}}\right)_0 (N_{\langle\,\rangle} - N) + \frac{1}{2}\left(\frac{\partial^2 E_{\langle\,\rangle}}{\partial N_{\langle\,\rangle}^2}\right)_0 (N_{\langle\,\rangle} - N)^2$$

$$E_{\langle\,\rangle}(N_{\langle\,\rangle}) \equiv E_{\langle\,\rangle}(N) - \chi \Delta N + \eta (\Delta N)^2$$

$$\left(\frac{\partial E_{\langle A \rangle}}{\partial N_{\langle A \rangle}}\right)_{N_{\langle B \rangle}, R_{AB}} = \left(\frac{\partial E_{\langle B \rangle}}{\partial N_{\langle B \rangle}}\right)_{N_{\langle A \rangle}, R_{AB}}$$

$$\chi_{\langle A \rangle} = \chi_A - 2\eta_A \Delta N = \chi_{\langle B \rangle} = \chi_B + 2\eta_B \Delta N = \chi_{AB}$$

$$\boxed{\Delta N = \frac{\chi_A - \chi_B}{2(\eta_A + \eta_B)}} \qquad \chi_{AB} \equiv \overline{\chi} = \frac{\eta_A \chi_B + \eta_B \chi_A}{\eta_A + \eta_B} \qquad \chi_{AIM} = \frac{n_{AIM}}{\sum_A \dfrac{n_A}{\chi_A}} \qquad \begin{array}{l} \chi_A = \theta\, \eta_A \\[4pt] \chi_B = \theta\, \eta_B \\[4pt] \chi_{AB} = \theta\, \eta_{AB} \end{array}$$

$$\eta_{AB} \equiv \overline{\eta} = 2\frac{\eta_A \eta_B}{\eta_A + \eta_B} \qquad \eta_{AIM} = \frac{n_{AIM}}{\sum_A \dfrac{n_A}{\eta_A}} \qquad \sum_A n_A = n_{AIM}$$

$$\boxed{\frac{1}{2} D(A,B) = \frac{\chi_A - \chi_B}{2(\eta_A + \eta_B)}}$$

$$-\frac{1}{2}\left(\frac{\partial D(A,B)}{\partial \chi_{AB}}\right)_A = -\left(\frac{1}{2}\frac{\partial D(A,B)}{\partial \chi_A}\right)\left(\frac{\partial \chi_A}{\partial \chi_{AB}}\right) = -\frac{1}{2(\eta_A + \eta_B)}\frac{2(\eta_A + \eta_B)}{\eta_B} = -\frac{1}{\eta_B} \equiv -2 S_B$$

$$-\frac{1}{2}\left(\frac{\partial D(A,B)}{\partial \chi_{AB}}\right)_B = +\frac{1}{\eta_A} \equiv +2 S_A$$

COS1: Chemical Reactivity
Geometric Model of Atoms in Molecules

$$\chi_{AB} = \chi_{\langle A \rangle} = \chi_{\langle A \rangle}(N_A + \Delta N)$$

$$\chi_{AB} = \chi_{\langle B \rangle} = \chi_{\langle B \rangle}(N_B - \Delta N)$$

$$\chi^2_{AB} = \chi_{\langle A \rangle}\chi_{\langle B \rangle} = \chi_{\langle A \rangle}(N_A + \Delta N)\chi_{\langle B \rangle}(N_B - \Delta N)$$

$$\chi^2_{AB} = \chi_A \chi_B$$

$$\chi_{\langle \rangle} = \chi \exp[-\gamma \, \Delta N] = \chi \exp[-\gamma(N_{\langle \rangle} - N)]$$

$$\Delta N = \begin{cases} + \Delta N ... for\ A \\ - \Delta N ... for\ B \end{cases}$$

$$2\eta_{\langle \rangle} = -\frac{\partial \chi_{\langle \rangle}}{\partial N_{\langle \rangle}} = \gamma \chi \exp[-\gamma \, \Delta N] = \gamma \chi_{\langle \rangle} \qquad \gamma = \frac{2\eta_{\langle \rangle}}{\chi_{\langle \rangle}}$$

$$\boxed{\chi_{\langle A \rangle} = \chi_{\langle B \rangle}} \qquad \boxed{\Delta N = -\frac{1}{2\gamma}\ln\left(\frac{\chi_B}{\chi_A}\right)}$$

$$\frac{1}{2}D(A,B) \equiv \Delta N = \frac{1}{2\gamma}\ln\left(\frac{\chi_A}{\chi_B}\right)$$

$$-\frac{1}{2}\left[\frac{D(A,B)}{\partial \chi_{\langle \rangle}}\right]_A = -\frac{1}{2}\left[\frac{\partial D(A,B)}{\partial \chi_A}\right]\left(\frac{\partial \chi_A}{\partial \chi_{\langle \rangle}}\right) = -\frac{1}{2\gamma\chi_A \exp[-\gamma \, \Delta N]} = -\frac{1}{2\gamma\chi_{\langle \rangle}} = -\frac{1}{4\eta_{\langle \rangle}} = -\frac{1}{2}S_{\langle \rangle}$$

$$-\frac{1}{2}\left[\frac{D(A,B)}{\partial \chi_{\langle \rangle}}\right]_B = +\frac{1}{2}S_{\langle \rangle}$$

COS1: Chemical Reactivity
Reactivity indices up to Spectral Like Resolution

$$-\chi = \frac{\partial E}{\partial N}\bigg|_{|N\rangle}$$

$$\cong a_1 \frac{E_{N+1} - E_{N-1}}{2} + b_1 \frac{E_{N+2} - E_{N-2}}{4} + c_1 \frac{E_{N+3} - E_{N-3}}{6}$$

$$- \alpha_1 \left(\frac{\partial E}{\partial N}\bigg|_{|N-1\rangle} + \frac{\partial E}{\partial N}\bigg|_{|N+1\rangle} \right) - \beta_1 \left(\frac{\partial E}{\partial N}\bigg|_{|N-2\rangle} + \frac{\partial E}{\partial N}\bigg|_{|N+2\rangle} \right)$$

$$\chi_{CFD} = -\left[a_1(1-\alpha_1) + \frac{1}{2}b_1 + \frac{1}{3}c_1 \right] \frac{\varepsilon_{HOMO(1)} + \varepsilon_{LUMO(1)}}{2}$$

$$-\left[b_1 + \frac{2}{3}c_1 - 2a_1(\alpha_1 + \beta_1) \right] \frac{\varepsilon_{HOMO(2)} + \varepsilon_{LUMO(2)}}{4}$$

$$-\left(c_1 - 3a_1\beta_1 \right) \frac{\varepsilon_{HOMO(3)} + \varepsilon_{LUMO(3)}}{6}$$

$$2\eta = \frac{\partial^2 E}{\partial N^2}\bigg|_{|N\rangle}$$

$$\cong 2a_2 \frac{E_{N+1} - 2E_N + E_{N-1}}{2} + b_2 \frac{E_{N+2} - 2E_N + E_{N-2}}{4} + c_2 \frac{E_{N+3} - 2E_N + E_{N-3}}{9}$$

$$- \alpha_2 \left(\frac{\partial^2 E}{\partial N^2}\bigg|_{|N-1\rangle} + \frac{\partial^2 E}{\partial N^2}\bigg|_{|N+1\rangle} \right) - \beta_2 \left(\frac{\partial^2 E}{\partial N^2}\bigg|_{|N-2\rangle} + \frac{\partial^2 E}{\partial N^2}\bigg|_{|N+2\rangle} \right)$$

$$\eta_{CFD} = \left[a_2(1-\alpha_2 + 2\beta_2) + \frac{1}{4}b_2 + \frac{1}{9}c_2 \right] \frac{\varepsilon_{LUMO(1)} - \varepsilon_{HOMO(1)}}{2}$$

$$+ \left[\frac{1}{2}b_2 + \frac{2}{9}c_2 + 2a_2(\beta_2 - \alpha_2) \right] \frac{\varepsilon_{LUMO(2)} - \varepsilon_{HOMO(2)}}{4}$$

$$+ \left[\frac{1}{3}c_2 - 3a_2\beta_2 \right] \frac{\varepsilon_{LUMO(3)} - \varepsilon_{HOMO(3)}}{6}$$

Putz M.V.; Russo N.; Sicilia E. (**2004**) On the application of the HSAB principle through the use of improved computational schemes for chemical hardness evaluation. *J. Comp. Chem.* 25(7), 994-1003; **Putz M.V.** (**2011**) Quantum parabolic effects of electronegativity and chemical hardness on carbon π-systems. In: Carbon Bonding and Structures: *Advances in Physics and Chemistry*, Ed. Putz M.V., Springer Verlag: London (ISBN: 978-94-007-1732-9), 1-32.

COS1: Chemical Reactivity

## Reactivity indices up to Spectral Like Resolution

| Scheme	Electronegativity					Chemical Hardness				
	a1	b1	c1	α1	β1	a2	b2	c2	α2	β2
2C	1	0	0	0	0	1	0	0	0	0
4C	$\frac{4}{3}$	$-\frac{1}{3}$	0	0	0	$\frac{4}{3}$	$-\frac{1}{3}$	0	0	0
6C	$\frac{3}{2}$	$-\frac{3}{5}$	$\frac{1}{10}$	0	0	$\frac{12}{11}$	$\frac{3}{11}$	0	$\frac{2}{11}$	0
SP	$\frac{5}{3}$	$\frac{1}{3}$	0	$\frac{1}{2}$	0	$\frac{6}{5}$	0	0	$\frac{1}{10}$	0
6T	$\frac{14}{9}$	$\frac{1}{9}$	0	$\frac{1}{3}$	0	$\frac{3}{2}$	$-\frac{3}{5}$	$\frac{1}{5}$	0	0
8T	$\frac{19}{12}$	$\frac{1}{6}$	0	$\frac{3}{8}$	0	$\frac{147}{152}$	$\frac{51}{95}$	$-\frac{23}{760}$	$\frac{9}{38}$	0
8P	$\frac{40}{27}$	$\frac{25}{54}$	0	$\frac{4}{9}$	$\frac{1}{36}$	$\frac{320}{393}$	$\frac{310}{393}$	0	$\frac{344}{1179}$	$\frac{23}{2358}$
10P	$\frac{17}{12}$	$\frac{101}{150}$	$\frac{1}{100}$	$\frac{1}{2}$	$\frac{1}{20}$	$\frac{1065}{1798}$	$\frac{1038}{899}$	$\frac{79}{1798}$	$\frac{334}{899}$	$\frac{43}{1798}$
SLR	1.303	0.994	0.038	0.577	0.09	0.216	1.723	0.177	0.502	0.056

COS1: Chemical Reactivity

Introducing Absolute Aromaticity

$$A_{\Delta\Pi} = \Pi_{AIM} - \Pi_{MOL}...\begin{cases} > 0...AIM...prevails \\ < 0...MOL...prevails \\ = 0...transition...states \end{cases}$$

Atoms-in-Molecule   **Molecular Orbitals**   **Absolute Aromaticity**
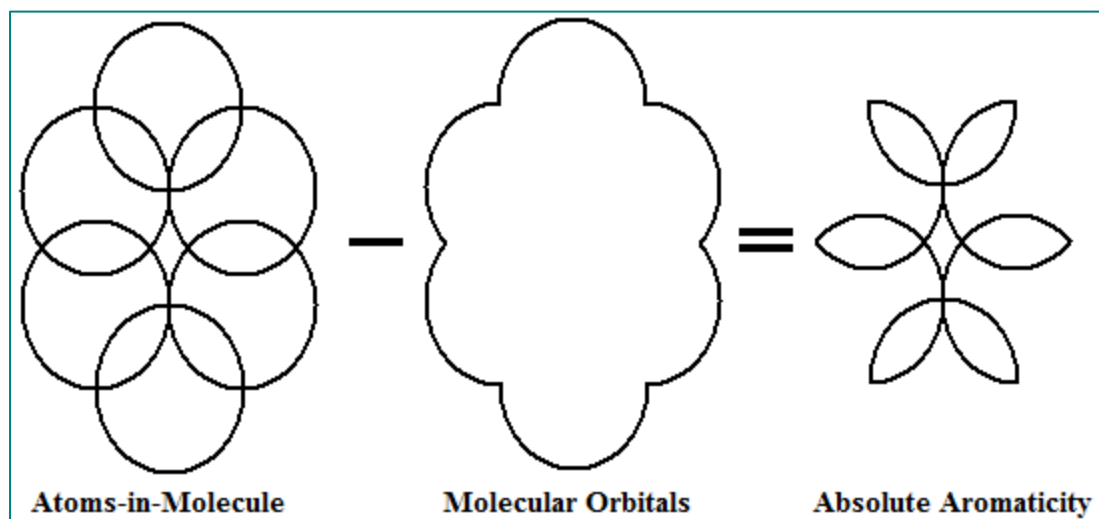
$$A^{\chi} = \chi_{AIM} - \chi_{CFD}$$

$$A^{\eta} = \eta_{AIM} - \eta_{CFD}$$

Putz M.V. (**2010**) On absolute aromaticity within electronegativity and chemical hardness reactivity pictures. MATCH Commun. Math. Comput. Chem. 64(2), 391-418.

COS1: Chemical Reactivity

Introducing Absolute Aromaticity

1	Benzene
2	Naphthalene
3	Anthracene
4	Phenanthrene
5	Pyrene
6	Naphthacene
7	Benz[a]anthracene
8	Chrysene
9	Triphenylene
10	Perylene
11	Benzo[e]pyrene
12	Benzo[a]pyrene
13	Pentacene
14	Benzo[a]naphthacene
15	Dibenz[a,h]anthracene
16	Benzo[b]chrysene
17	Picene
18	Benzo[ghi]perylene
19	Anthanthrene
20	Naphtho[2,1,8-qra]naphthacene
21	Benzo[a]perylene
22	Benzo[b]perylene
23	Coronene
24	Zethrene
25	Benzo[a]pentacene
26	Dibenzo[b,k]chrysene
27	Naphtho[2,3-g]chrysene
28	Naphtho[8,1,2-bcd]perylene
29	Dibenzo[cd,lm]perylene
30	Dibenzo[a,f]perylene
31	Phenanthro[1,10,9,8-opqra]perylene
32	Dibenzo[de,op]pentacene
33	Dibenzo[a,l]pentacene
34	Benzo[2,1-a:3,4,-a']dianthracene
35	Naphtho[2,1,8-yza]hexacene
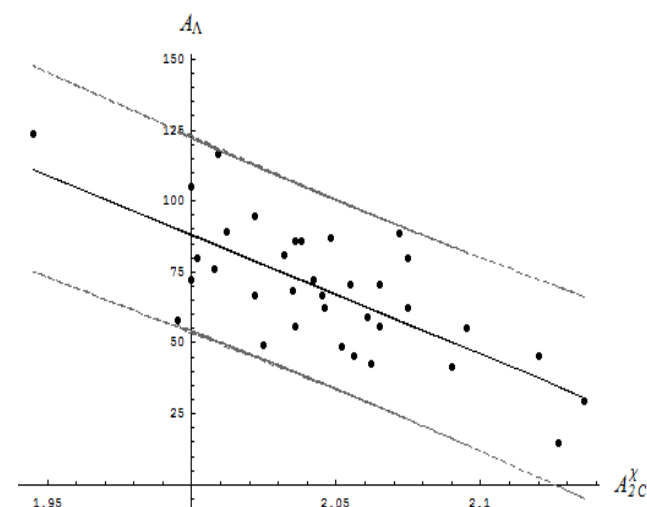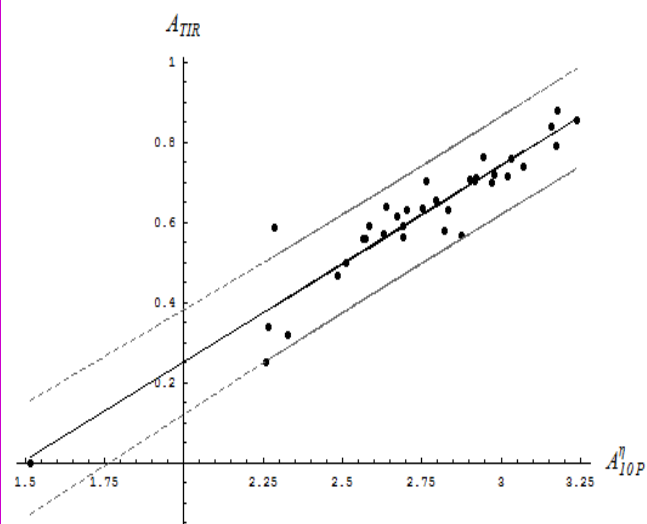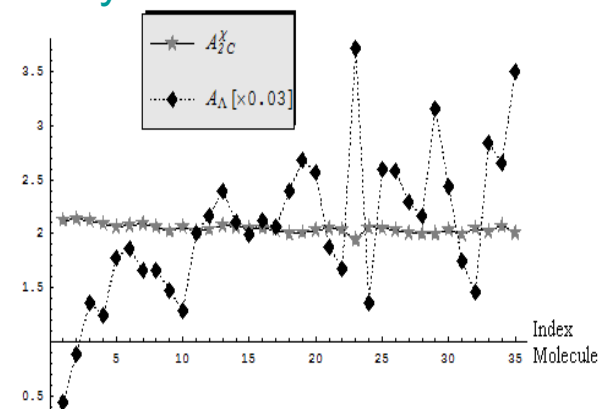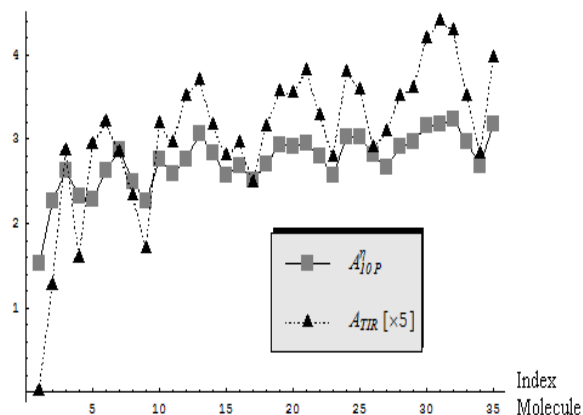
topological index of reactivity –TIR (Ciesielski et al., 2009)

exaltation magnetic susceptibility Λ [cgs-ppm] (Ciesielski et al., 2009)

Ciesielski A.; Krygowski T.M.; Cyranski M.K.; Dobrowolski M.A.; Balaban A.T. (**2009**) Are thermodynamic and kinetic stabilities correlated? A topological index of reactivity toward electrophiles used as a criterion of aromaticity of polycyclic benzenoid hydrocarbons. *J. Chem. Inf. Model. 49*, 369–376; Putz M.V. (**2010**) On absolute aromaticity within electronegativity and chemical hardness reactivity pictures. *MATCH Commun. Math. Comput. Chem.* 64(2), 391-418.

COS1: Chemical Reactivity

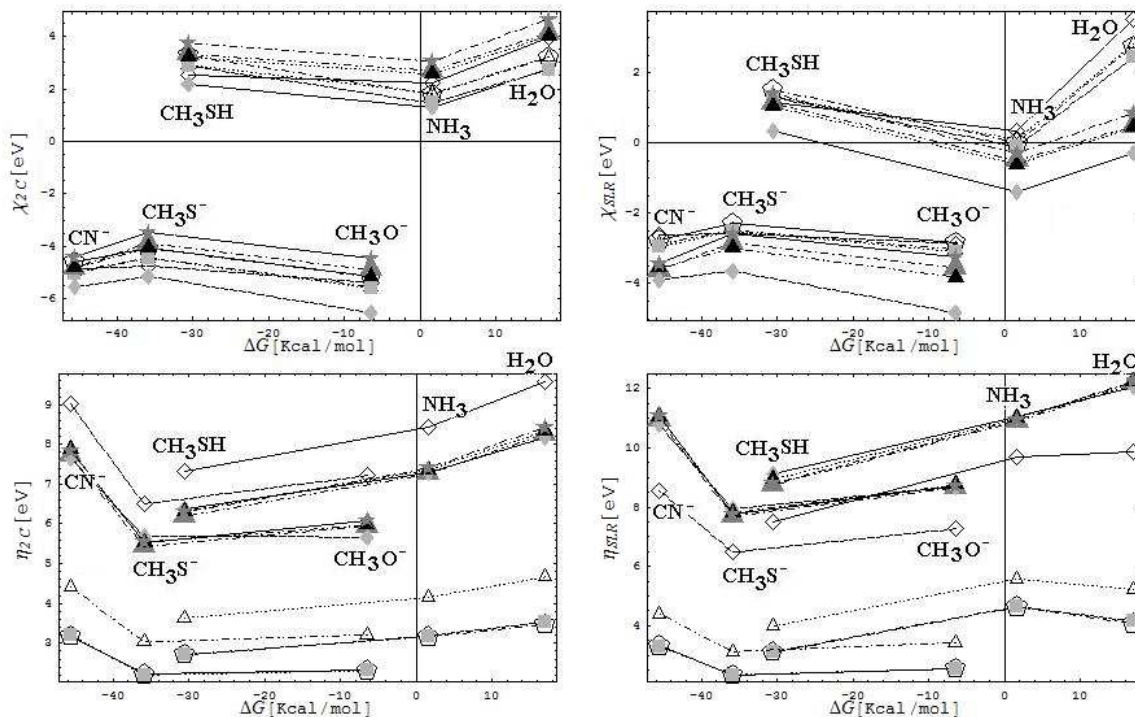## Orthogonal χ-η Patterns in (Solvent) Reactivity by HSAB Principle

acid + base ↔ salt + water

$$h_1 - s_1 + s_2 - h_2 \leftrightarrow h_1 - h_2 + s_2 - s_1$$

acid 1 + base 2 ↔ acid 2 + base 1

$$H\text{-}X^+ + HO\text{-}OH \leftrightarrow HO\text{-}X^+ + H\text{-}OH$$

X= NH_3, CH_3O^-, H_2O, CN^-, CH_3S^- and CH_3SH

Putz M.V. (**2011**) Electronegativity and chemical hardness: different patterns in quantum chemistry. Curr. Phys. Chem. 1(2), 111-139.

Maximum Hardness (MH) Index Y

$$1 = HSAB + MH$$

$$1 = \frac{S}{\eta} + Y$$

$$Y = \frac{\eta - S}{\eta} = \frac{\eta}{\eta} - \frac{S}{\eta}$$

Putz M.V. (**2008**) Maximum hardness index of quantum acid-base bonding. *MATCH Commun. Math. Comput. Chem.* 60(3), 845-868.
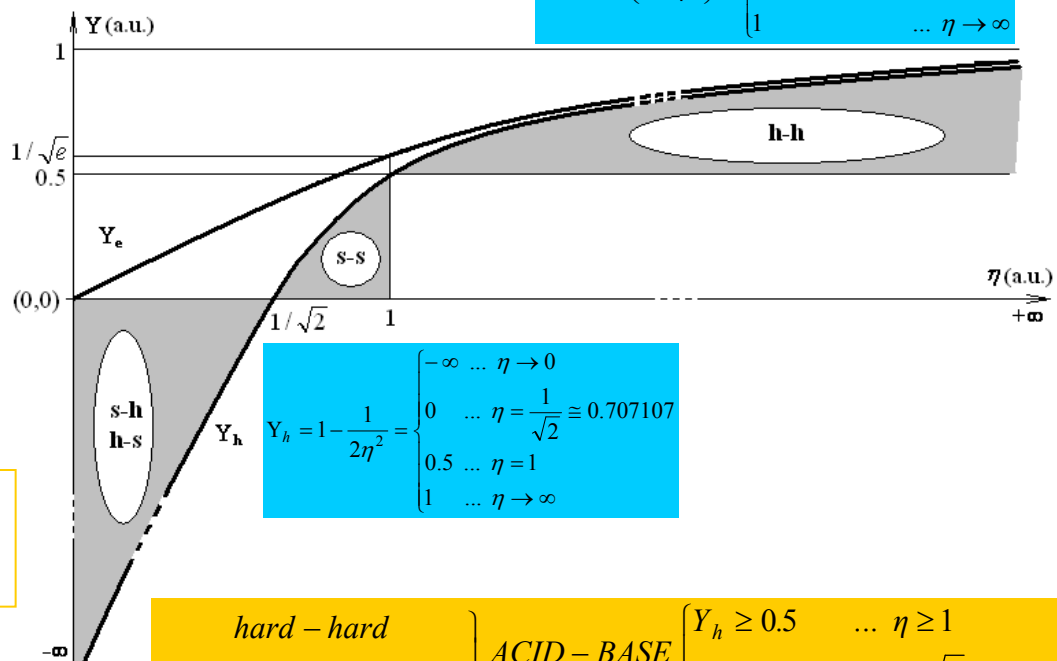
Qualitative Pearson classification

Lewis acids

Soft			Borderline			Hard		
CH_2	$GaCl_3$	BH_3	SO_2	GaH_3	$B(CH_3)_3$	SO_3	$AlCl_3$	BCl_3

Lewis bases

Soft			Borderline			Hard		
CH_3SH	CO	C_6H_6	N_2	C_5H_5N	$C_6H_5NH_2$	H_2O	N_2H_4	NH_3

$$Y_e = \exp\left(-\frac{1}{2\eta^2}\right) = \begin{cases} 0 & \dots \ \eta \to 0 \\ \dfrac{1}{\sqrt{e}} \cong 0.606531 & \dots \ \eta = 1 \\ 1 & \dots \ \eta \to \infty \end{cases}$$

$$Y_h = 1 - \frac{1}{2\eta^2} = \begin{cases} -\infty & \dots \ \eta \to 0 \\ 0 & \dots \ \eta = \dfrac{1}{\sqrt{2}} \cong 0.707107 \\ 0.5 & \dots \ \eta = 1 \\ 1 & \dots \ \eta \to \infty \end{cases}$$

$$\left.\begin{array}{l} hard - hard \\ soft - soft \\ hard - soft \ (soft - hard) \end{array}\right\} \ \begin{array}{c} ACID - BASE \\ BONDING \end{array} \ \begin{cases} Y_h \geq 0.5 & \dots \ \eta \geq 1 \\ 0 \leq Y_h < 0.5 & \dots \ 1/\sqrt{2} \leq \eta < 1 \\ Y_h < 0 & \dots \ 0 < \eta < 1/\sqrt{2} \end{cases}$$
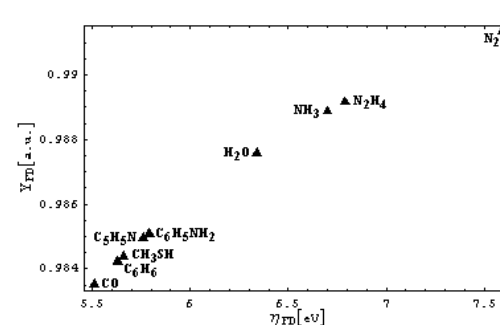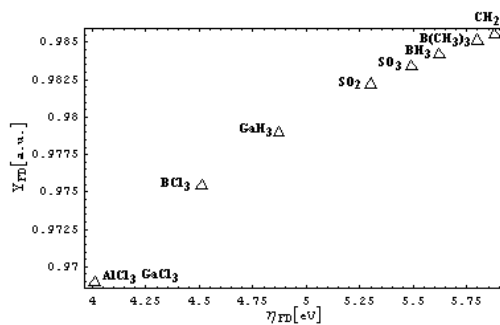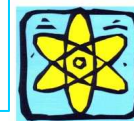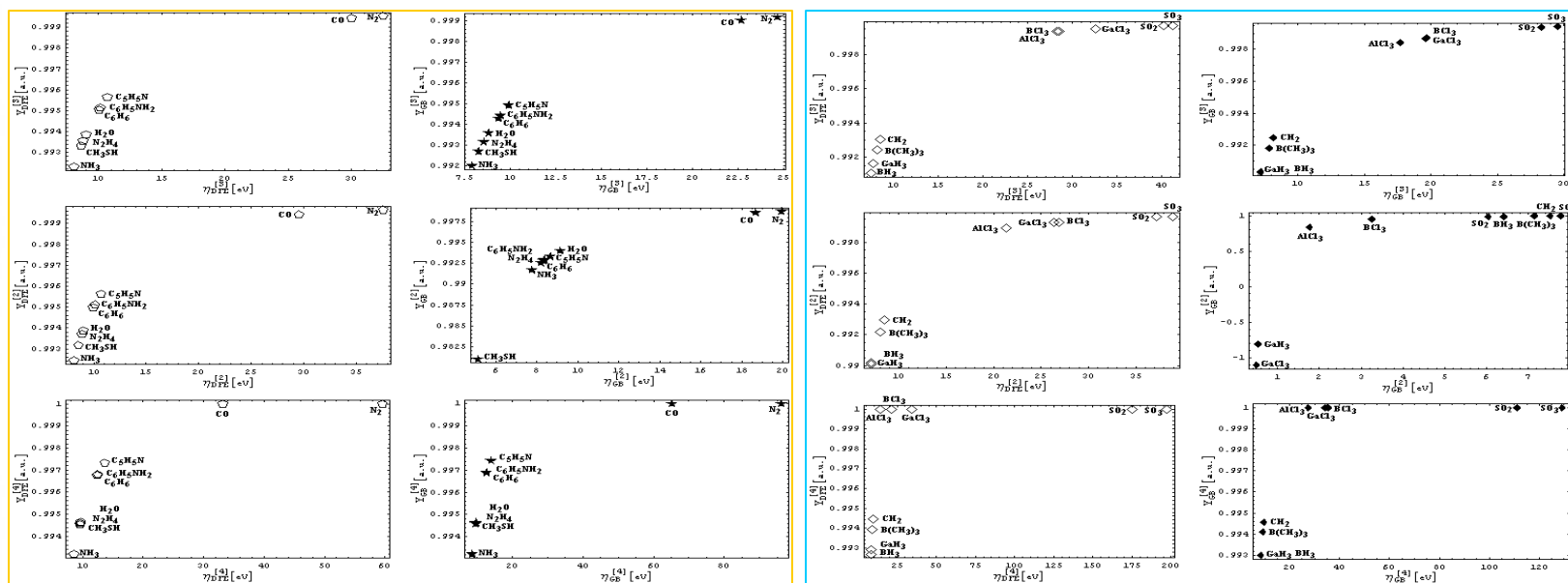
COS1: Chemical Reactivity

Maximum Hardness (MH) Index Υ

Electronegativity Source	Chemical Hardness Functionals
$d\chi = d\chi[dN]$	$\eta_A^{[1]} = \dfrac{1}{2\sqrt{a}}\left[\arctan\left(\dfrac{N_v+1}{\sqrt{a}}\right) - \arctan\left(\dfrac{N_v-1}{\sqrt{a}}\right)\right]$
$d\chi = d\chi[dN, dNdN]$	$\eta_A^{[2]} = \dfrac{1}{4\sqrt{a}}\left\{ \begin{array}{l} \arctan\left(\dfrac{N_v-2}{\sqrt{a}}\right) + \arctan\left(\dfrac{N_v+2}{\sqrt{a}}\right) \\ -2\left[\arctan\left(\dfrac{N_v-1}{\sqrt{a}}\right) + \arctan\left(\dfrac{N_v}{\sqrt{a}}\right) - \arctan\left(\dfrac{N_v+1}{\sqrt{a}}\right)\right] \end{array}\right\}$
$d\chi = d\chi[dN, \delta V(r)]$	$\eta_A^{[3]} = \dfrac{1}{2}\left\{ \dfrac{2\left[C_A\left(1+a-N_v^2\right)-2bN_v\right]}{(1+a)^2 + 2(a-1)N_v^2 + N_v^4} + \dfrac{1}{\sqrt{a}}\left[\arctan\left(\dfrac{N_v+1}{\sqrt{a}}\right) - \arctan\left(\dfrac{N_v-1}{\sqrt{a}}\right)\right]\right\}$
$d\chi = d\chi[dN, dNdN, \delta V(r)]$	$\eta_A^{[4]} = \dfrac{1}{4}\left\{ \begin{array}{l} \dfrac{4\left[C_A\left(1+a-N_v^2\right)-2bN_v\right]}{(1+a)^2 + 2(a-1)N_v^2 + N_v^4} \\ +\dfrac{1}{\sqrt{a}}\left[\arctan\left(\dfrac{N_v-2}{\sqrt{a}}\right) + \arctan\left(\dfrac{N_v+2}{\sqrt{a}}\right)\right] \\ -\dfrac{2}{\sqrt{a}}\left[\arctan\left(\dfrac{N_v-1}{\sqrt{a}}\right) + \arctan\left(\dfrac{N_v}{\sqrt{a}}\right) - \arctan\left(\dfrac{N_v+1}{\sqrt{a}}\right)\right] \end{array}\right\}$

Putz M.V. (**2008**) Maximum hardness index of quantum acid-base bonding. *MATCH Commun. Math. Comput. Chem.* 60(3), 845-868.

Putz M.V. (**2011**) Quantum and electrodynamic versatility of electronegativity and chemical hardness. In: Quantum Frontiers of Atoms and Molecules, Ed. Putz M.V., NOVA Science Publishers: New York, Inc. (ISBN: 978-1-61668-158-6), 251-270.

$$\eta^S = \frac{Z_{eff}}{2R}\,(a.u.)$$

COS1: Chemical Reactivity-Perspectives

Golden Ratio Driving Chemical Reactivity

"*WAVE $\otimes$ PARTICLE = constant*"

$$WAVE \otimes PARTICLE = n_{W/P}h$$

$$\boxed{\Delta O \times O = n_o h}$$

$$\Delta O = \frac{\Delta N}{Z} = \frac{N-Z}{Z} \qquad\qquad O = \frac{N}{Z}$$

Heisenberg imbalance equation for *valence atoms*

$$\boxed{\frac{N-Z}{Z} \times \frac{N}{Z} = 1}$$

$$Z = \frac{-N + \sqrt{N^2 + 4N^2}}{2} = N\tau \qquad\qquad \tau = \frac{-1+\sqrt{5}}{2} = 0.6180$$

$$\boxed{\frac{Z}{N} = \begin{cases} 1 ... STABLE\,(PHYSICAL)\,ATOM \\ \tau ... REACTIVE\,(CHEMICAL)\,ATOM \end{cases}}$$
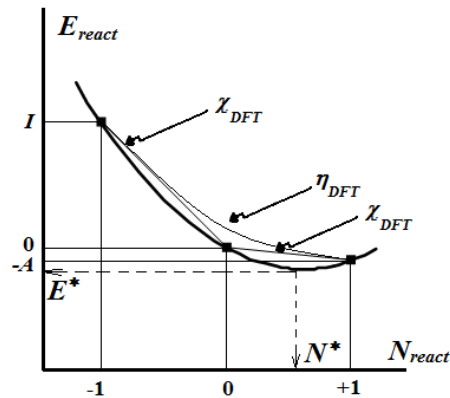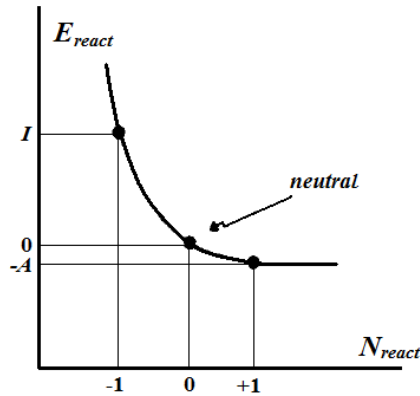
Golden Ratio Driving Chemical Reactivity

$$\rho(r,\xi) = N\frac{\xi^3}{\pi}\exp[-2\xi r]$$

$$E[\xi] = T[\xi] + V_{ee}[\xi] + V_{ne}[\xi] = N\frac{\xi^2}{2} + (N^2 - N)\frac{5}{16}\xi - N\xi$$

$$\frac{\partial E[\xi]}{\partial \xi} = 0 \quad \xi = \frac{21 - 5N}{16}$$

$$E_{Q1}(a.u.) = \frac{25}{512}N^2 - \frac{105}{256}N + \frac{441}{512} = \frac{1}{512}(21-5N)^2 = \frac{5^2}{512}(6.80\tau - N)^2$$

$$N = 6.80\tau \qquad N = 6.80\frac{Z}{N} \qquad N_{REACT} \equiv N^{**} = 2.60768\sqrt{Z}$$

$$\chi^{**} = -\left(\left(\left(\frac{\partial E_{Q1}}{\partial N}\right)_{N=2.60768\sqrt{Z}}\right)_{Z=\tau N}\right)_{N=1}$$
$$= 0.209963(a.u.) = 5.713(eV)$$

$$\eta^{**} = \frac{1}{2}\left(\frac{\partial^2 E_{Q1}}{\partial N^2}\right)$$
$$= \frac{25}{512}(a.u.) = 1.3286(eV)$$

Atom	Z	I[eV]	A[eV]	N*	N**
H	1	13.595	0.7542	0.558735	0.607681
Li	3	5.390	0.620	0.629979	0.516636
B	5	8.296	0.278	0.534672	0.830952
C	6	11.256	1.268	0.626952	0.387488
O	8	13.614	1.462	0.620309	0.375636
F	9	17.42	3.399	0.742422	0.823043
Na	11	5.138	0.546	0.618902	0.648699
Al	13	5.984	0.442	0.579755	0.402127
Si	14	8.149	1.385	0.70476	0.757049
P	15	10.484	0.7464	0.576651	0.0995049
S	16	10.357	2.0772	0.750876	0.430724
Cl	17	13.01	3.615	0.884779	0.751744
K	19	4.339	0.5012	0.630596	0.366618
V	23	6.74	0.526	0.584648	0.505999
Cr	24	6.763	0.667	0.609416	0.774976
Fe	26	7.90	0.164	0.5212	0.296616
Co	27	7.86	0.662	0.59197	0.549908
Ni	28	7.633	1.157	0.67866	0.798551
Cu	29	7.724	1.226	0.688673	0.0427917
Se	34	9.75	2.0206	0.761417	0.205262
Br	35	11.84	3.364	0.896885	0.427249
Rb	37	4.176	0.4860	0.631707	0.861904
Zr	40	6.84	0.427	0.566584	0.492423
Nb	41	6.88	0.894	0.649348	0.697305
Mo	42	7.10	0.747	0.617582	0.899704
Rh	45	7.46	1.138	0.680006	0.492856
Pd	46	8.33	0.558	0.571796	0.686153
Ag	47	7.574	1.303	0.707782	0.87736
Sn	50	7.342	1.25	0.705187	0.439089
Sb	51	8.639	1.05	0.638358	0.622567
Te	52	9.01	1.9708	0.779975	0.804255
I	53	10.454	3.061	0.91404	0.984204

special charge wave function based on their difference on the golden ratio scale

$$NC^* = 0.677771 - 0.193006\, Z + 0.104303\, Z^2$$
$$- 0.0242757\, Z^3 + 0.00302359\, Z^4$$
$$- 0.000220204\, Z^5 + 9.79371 \cdot 10^{-6}\, Z^6$$
$$- 2.6894 \cdot 10^{-7}\, Z^7 + 4.4448 \cdot 10^{-9}\, Z^8$$
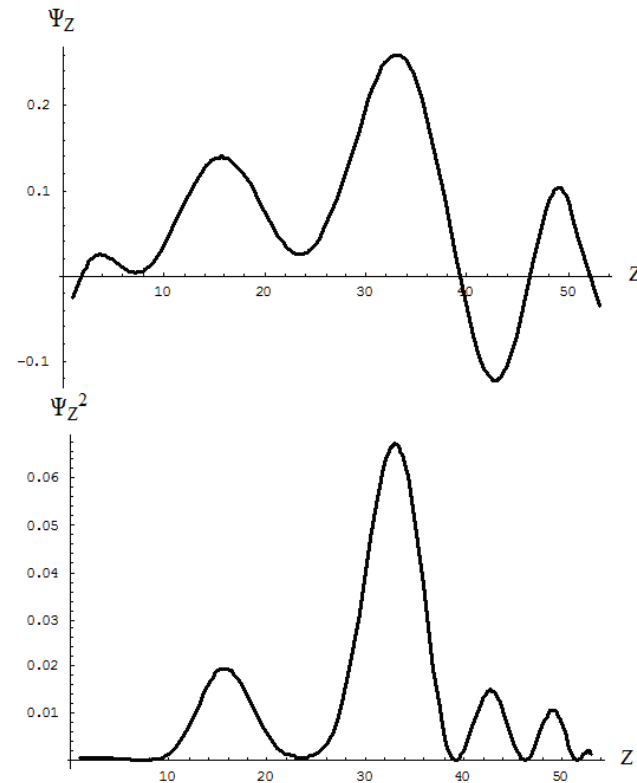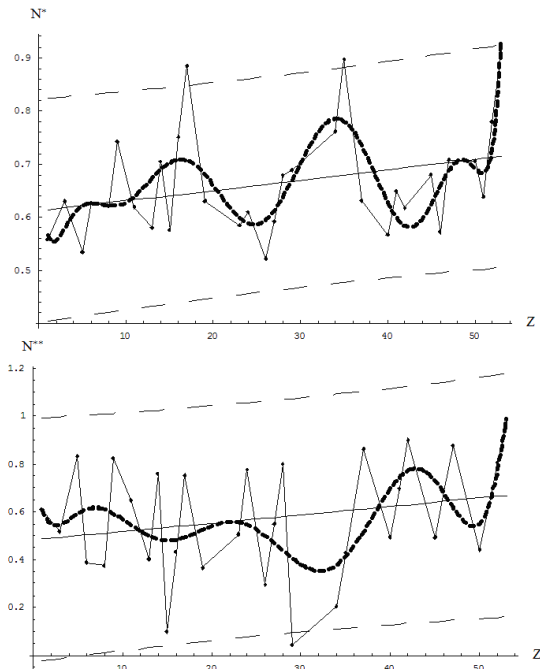$$- 4.05002 \cdot 10^{-11}\, Z^9 + 1.56254 \cdot 10^{-13}\, Z^{10}$$

$$NC^{**} = 0.768074 - 0.224502\, Z + 0.076654\, Z^2$$
$$- 0.0107337\, Z^3 + 0.000667575\, Z^4$$
$$- 0.000012746\, Z^5 - 6.0246 \cdot 10^{-7}\, Z^6$$
$$+ 4.01411 \cdot 10^{-8}\, Z^7 - 9.49568 \cdot 10^{-10}\, Z^8$$
$$+ 1.05449 \cdot 10^{-11}\, Z^9 - 4.58533 \cdot 10^{-14}\, Z^{10}$$

$$\Psi_Z = \tau\left(NC_Z^* - NC_Z^{**}\right)$$

$$\int_1^{53} |\Psi_Z|^2\, dZ = 0.667233 \approx \tau$$

$$\int_1^{53} \left(NC_Z^* - NC_Z^{**}\right)^2 dZ \approx \frac{1}{\tau} = 1 + \tau$$

$$\sqrt{\int_1^{53} \left(NC_Z^* - NC_Z^{**}\right)^2 dZ} \approx 2\tau$$

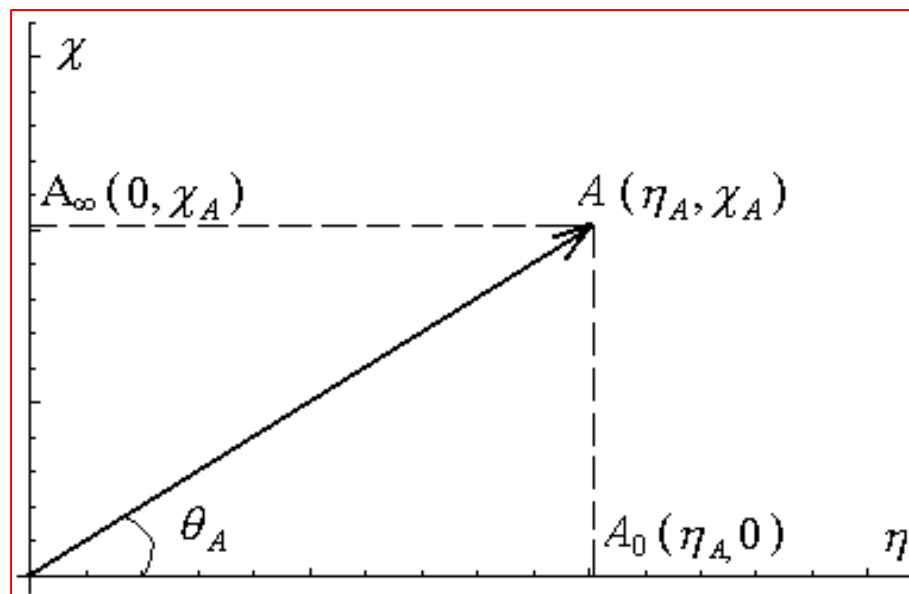## Chemical Power Index

$$C_\pi = \frac{1}{2}\frac{\chi}{\eta}$$

$$C_\pi = \frac{1}{2}\left(\frac{\chi}{\eta} - \frac{0}{\eta}\right)$$

$$\tan(\theta_A) = \frac{\chi_A}{\eta_A} = 2C_\pi(A)$$

$$C_\pi(A_0) = \frac{1}{2}\left(\frac{0}{\eta} - \frac{0}{\eta}\right) = 0$$

$$C_\pi(A_\infty) = \frac{1}{2}\left(\frac{\chi_A}{0} - \frac{0}{0}\right) = \infty - \frac{0}{0}$$

$$\omega = \frac{\chi^2}{2\eta} = \chi C_\pi$$

Putz M.V. (**2013**) Chemical orthogonal space of electronegativity and hardness. Introducing chemical power; *in preparation*.

COS1: Chemical Reactivity-Perspectives

Structural Coloring with Chemical Reactivity

Timisoara-Parma rules: the chemical descriptor (χ or η) values are distributed over all nodes of a molecule, which are grouped on successive reticules starting from the "central" most populated ones with bonding and nodal (frontier) electrons, while considering the equivalent/equidistant reticules until the molecular bonding space is fully described with parallel and decreasing CFD values of a descriptor (i.e., one common for all nodes of a reticule) and all of the CFD models have been used to consider all of the remaining equivalent reticules in the molecular space, if any.
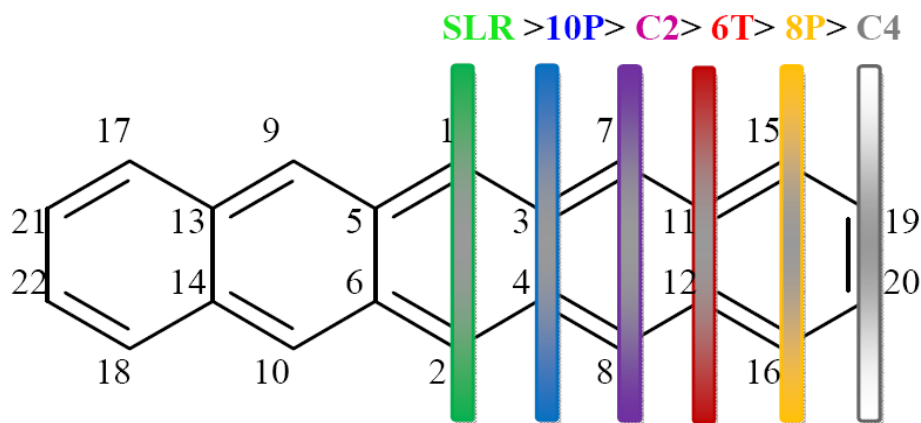
SLR >10P> C2> 6T> 8P> C4

$$W(\chi) = \det{}^{1/N_\pi} \left\| \widehat{W}_\chi \right\|$$

$$W(\eta) = \det{}^{1/N_\pi} \left\| \widehat{W}_\eta \right\|$$

Conclusions COS1:
Orthogonal Spaces of Chemical Reactivity

New Link between Conceptual Density Functional Theory and Electron Delocalization

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[‡]Laboratory of Computational and Structural Physical Chemistry, Chemistry Department, West University of Timisoara, Pestalozzi Str. 16, Timisoara, RO-300115, Romania

$$1 = \frac{S}{\eta} + Y$$

### MAXIMUM HARDNESS INDEX OF QUANTUM ACID-BASE BONDING

Mihai V. Putz

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REGULAR ARTICLE

Mihai V. Putz · Nino Russo · Emilia Sicilia

About the Mulliken electronegativity in DFT
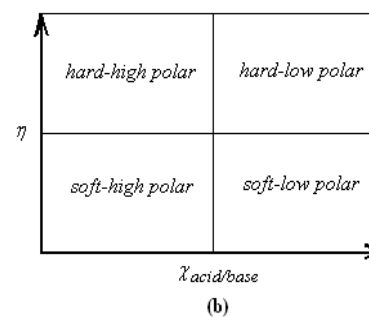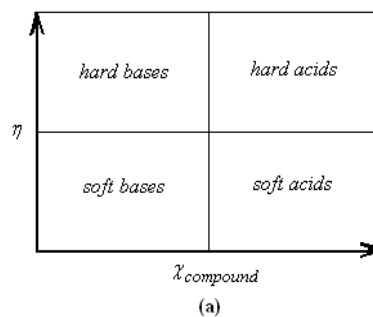
(a)

(b)

$$\eta \equiv \frac{1}{2}\left(\frac{\partial^2 E_N}{\partial N^2}\right)_{V(r)}$$

$$\chi \equiv -\left(\frac{\partial E_N}{\partial N}\right)_{V(r)}$$

Atomic Radii Scale and Related Size Properties from Density Functional Electronegativity Formulation

Mihai V. Putz,[†] Nino Russo,[*] and Emilia Sicilia

Dipartimento di Chimica and Centro di Calcolo ad Alte Prestazioni per Elaborazioni Parallele e Distribuite-Centro d'Eccellenza MIUR, Università della Calabria, Via Pietro Bucci, I-87030 Arcavacata di Rende (CS), Italy

RESEARCH ARTICLE — Open Access

Valence atom with bohmian quantum potential: the golden ratio approach

Mihai V Putz

On the Applicability of the HSAB Principle through the Use of Improved Computational Schemes for Chemical Hardness Evaluation

MIHAI V. PUTZ,[*] NINO RUSSO, EMILIA SICILIA

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SEMICLASSICAL ELECTRONEGATIVITY AND CHEMICAL HARDNESS

MIHAI V. PUTZ

ON ABSOLUTE AROMATICITY WITHIN ELECTRONEGATIVITY AND CHEMICAL HARDNESS REACTIVITY PICTURES

Mihai V. Putz

Electronegativity: Quantum Observable

MIHAI V. PUTZ

Laboratory of Computational and Structural Physical Chemistry, Chemistry Department, West University of Timisoara, Str. Pestalozzi No.16, Timisoara, RO-300115, Romania

COS2: Electronic Localization

Electronic localization function
defined as the "step" realization of *orthogonality*

$$ELF = \frac{1}{f\left(\frac{D_g(\rho(\mathbf{r}))}{D_h(\rho(\mathbf{r}))}\right)} \rightarrow \begin{cases} 0, \nabla\rho(\mathbf{r}) >> \rho(\mathbf{r}) \\ 1, \nabla\rho(\mathbf{r}) << \rho(\mathbf{r}) \end{cases}$$

density *gradient* component

$$D_g(\mathbf{r}) = \frac{1}{2}\sum_i |\nabla\phi_i(\mathbf{r})|^2 - \frac{1}{8}\frac{|\nabla\rho(\mathbf{r})|^2}{\rho(\mathbf{r})}$$

density *homogeneous* contribution

$$D_h(\mathbf{r}) = \frac{3}{10}(3\pi^2)^{2/3}[\rho(\mathbf{r})]^{5/3} = 2.871\rho(\mathbf{r})^{5/3}$$

Hartree-Fock (or Kohn-Sham) orbitals ϕ_i

D_g accounts for the excess of local kinetic energy density due to Pauli repulsion

D_h plays the role of the "renormalization" factor

Fokker-Planck path integral (Kleinert, Pelster & Putz, 2002) in atomic units

$$(x_b, t_b; x_a, t_a)_{FP} = \int_{x(t_a)=x_a}^{x(t_b)=x_b} D'x(t)\exp\left\{-\frac{1}{2}\int_{t_a}^{t_b} dt[\dot{x}(t) - K(x(t))]^2 - \frac{1}{2}\int_{t_a}^{t_b} dtK'(x(t))\right\}$$

the drift function

$$K(x(t)) = -\partial_x U(x)$$

$$h \rightarrow D_h(x_a)$$
$$g \rightarrow D_g(x_a)$$

anharmonic potential

$$K(x) = -hx - gx^3$$

Kleinert, H., Pelster, A., Putz M.V. (**2002**) Variational perturbation theory for Markov processes. *Phys. Rev. E* 65(6), 066128/1-7;
Putz M.V. (**2005**) Markovian approach of the electron localization functions. *Int. J. Quantum Chem.* 105(1), 1-11.

COS2: Electronic Localization
Electronic localization function algorithm

the *bilocal dependency*

$$U(x_a, x_b) = h(x_a)\frac{x_b^2}{2} + g(x_a)\frac{x_b^4}{4}$$

(i) Solving the path integral the *time-dependent (spin) conditioned probability is provided*

(ii) Stationary (spin) conditioned probability

$$\lim_{(t_b - t_a) \to +\infty} (x_b, t_b; x_a, t_a)^{x^4}_{FP} = (x_b, t_b; x_a, t_a)^{x^4}_{FP/\omega}$$

(ii) Adjusting the exchange (parallel spins) conditional probability
(Parr & Yang, 1989; Koch & Holthausen, 2000; Ayers & Levy, 2001)

(iv) Identification with conditioned pair probability (Becke, 1988; Putz, 2009)

$$P^{\sigma\sigma}(x_b; x_a) \cong A_{\sigma\sigma} x_b^2$$

density (radial) equation of Poisson type

$$\rho(x_b) = \nabla^2_{x_b} U(x_a, x_b) = h(x_a) + 3g(x_a) x_b^2$$

$$(x_b, t_b; x_a, t_a)^{x^4}_{FP}$$

$$(x_b, t_b; x_a, t_a)^{x^4}_{FP/\omega} = \sqrt{\frac{h}{\pi}} \exp\left[\frac{3}{8}\frac{g}{h^2} - hx_b^2 - \frac{g}{2}x_b^4\right]$$

$$\int_{-\infty}^{+\infty} (x_b, t_b; x_a, t_a)^{x^4/\sigma\sigma}_{FP/\omega} dx_b = -1$$

$$(x_b, t_b; x_a, t_a)^{x^4/\sigma\sigma}_{FP/\omega} = -\frac{1 - hx_b^2 - \frac{g}{2}x_b^4}{1 - \frac{3}{8}\frac{g}{h^2}}$$

$$x_b^4 + \left[\frac{2h}{g} + A_{\sigma\sigma}\left(\frac{3}{4}\frac{1}{h^2} - \frac{2}{g}\right)\right]x_b^2 - \frac{2}{g} = 0$$

Koch W.; Holthausen M.C. (**2002**) *A Chemist's Guide to Density Functional Theory* (2nd ed.). Wiley-VCH: Weinheim. **Ayers P.W.; Levy M.** (**2001**) Sum rules for exchange and correlation potentials. *J. Chem. Phys. 115*, 4438-4443; **Becke A.D.** (**1988**) Correlation energy of an inhomogeneous electron gas: A coordinate-space model. *J. Chem. Phys. 88*, 1053-1062. **Parr R.G.; Yang W.** (**1989**) *Density Functional Theory of Atoms and Molecules*. Oxford University Press: New York; **Putz M.V.** (**2009**) Path integrals for electronic densities, reactivity indices, and localization functions in quantum systems. *Int. J. Mol. Sci. 10*(11), 4816-4940.
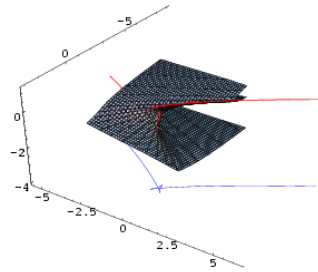
COS2: Electronic Localization
Markovian localization functions

Laplacian field: *M1: Markovian one*

$$ELF^{M1}(h, g, A_{\sigma\sigma}, x_b)$$

$$= \frac{1}{30} x_b^6 + \frac{1}{12}\left[\frac{2h}{g} + A_{\sigma\sigma}\left(\frac{3}{4}\frac{1}{h^2} - \frac{2}{g}\right)\right]x_b^4 - \frac{1}{g}x_b^2$$

butterfly elementary catastrophe

$$M1: \begin{cases} \Delta ELF^{M1} = 0 \\ \nabla ELF^{M1} = 0 \end{cases}$$

$$\Rightarrow \begin{cases} x_b^4 + \left[\frac{2h}{g} + A_{\sigma\sigma}\left(\frac{3}{4}\frac{1}{h^2} - \frac{2}{g}\right)\right]x_b^2 - \frac{2}{g} = 0 \\ \frac{1}{5}x_b^5 + \frac{1}{3}\left[\frac{2h}{g} + A_{\sigma\sigma}\left(\frac{3}{4}\frac{1}{h^2} - \frac{2}{g}\right)\right]x_b^3 - \frac{2}{g}x_b = 0 \end{cases}$$

$$x_b^{M1} = \pm\left(\frac{10}{-g}\right)^{1/4}$$

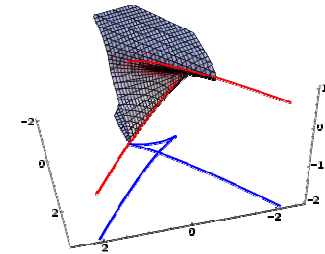$$ELF^{M1}(x) = \frac{1}{\left[g*\left(-D_g(x), D_h(x)\right)\right]^{3/2}}$$

gradient field: *M2: Markovian two*

$$ELF^{M2}(h, g, A_{\sigma\sigma}, x_b)$$

$$= \frac{1}{5} x_b^5 + \frac{1}{3}\left[\frac{2h}{g} + A_{\sigma\sigma}\left(\frac{3}{4}\frac{1}{h^2} - \frac{2}{g}\right)\right]x_b^3 - \frac{2}{g}x_b$$

swallow tail elementary catastrophe

$$M2: \begin{cases} \nabla ELF^{M2} = 0 \\ \Delta ELF^{M2} = 0 \end{cases}$$

$$\Rightarrow \begin{cases} x_b^4 + \left[\frac{2h}{g} + A_{\sigma\sigma}\left(\frac{3}{4}\frac{1}{h^2} - \frac{2}{g}\right)\right]x_b^2 - \frac{2}{g} = 0 \\ 4x_b^3 + 2\left[\frac{2h}{g} + A_{\sigma\sigma}\left(\frac{3}{4}\frac{1}{h^2} - \frac{2}{g}\right)\right]x_b = 0 \end{cases}$$

$$x_b^{M2} = \pm\left(\frac{2}{-g}\right)^{1/4}$$

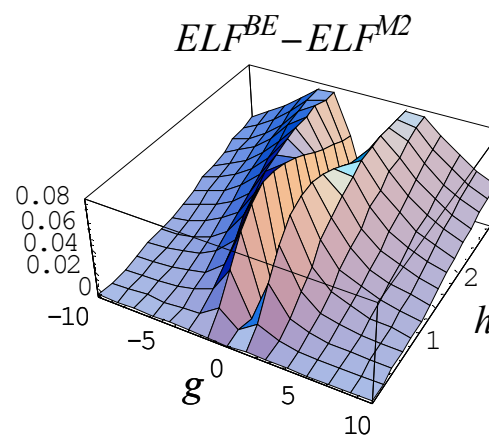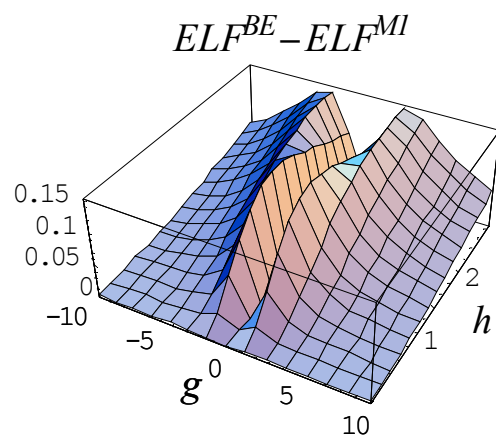$$ELF^{M2}(x) = \frac{1}{\left[g*\left(-D_g(x), D_h(x)\right)\right]^{5/2}}$$

$$ELF(x) \equiv \frac{1}{f\left(\frac{-g(x)}{h(x)}\right)} = \frac{1}{f\left(\frac{-D_g(x)}{D_h(x)}\right)}$$

$$-g \rightarrow g*(-g, h) > 0$$

COS2: Electronic Localization

Special Markovian Electronic Localization Forms

$$g*(-g,h) = 1 + \frac{(-g)^2}{h^2} = 1 + \left(\frac{g}{h}\right)^2 \rightarrow 1 + \left(\frac{D_g(x)}{D_h(x)}\right)^2 > 0$$

$$ELF^{M1}(x) = \left[\frac{1}{1 + \left(D_g(x)/D_h(x)\right)^2}\right]^{3/2} = \left[ELF^{BE}(x)\right]^{3/2}$$

$$ELF^{M2}(x) = \left[\frac{1}{1 + \left(D_g(x)/D_h(x)\right)^2}\right]^{5/4} = \left[ELF^{BE}(x)\right]^{5/4}$$

$$ELF^{BE} - ELF^{M1}$$

$$ELF^{BE} - ELF^{M2}$$

Putz M.V. (**2009**) Path integrals for electronic densities, reactivity indices, and localization functions in quantum systems. *Int. J. Mol. Sci.* 10(11), 4816-4940. **Becke A.D.; Edgecombe K.E.** (**1990**) A simple measure of electron localization in atomic and molecular systems. *J. Chem Phys.* 92, 5397–5403.
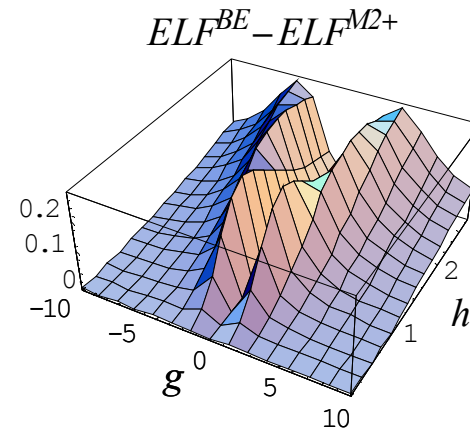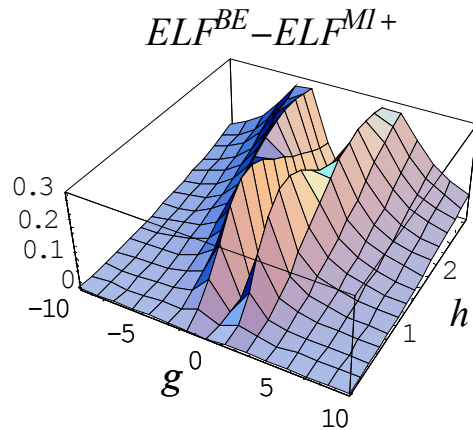
COS2: Electronic Localization

Special Markovian Electronic Localization Forms

$$g*(-g,h) = \exp\left[\left(\frac{-g}{h}\right)^2\right] \rightarrow \exp\left[\left(\frac{D_g(x)}{D_h(x)}\right)^2\right] > 0$$

$$ELF^{M1+}(x) = \exp\left[-\frac{3}{2}\left(\frac{D_g(x)}{D_h(x)}\right)^2\right]$$

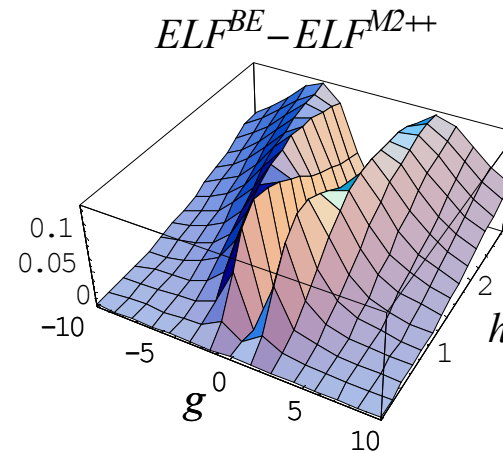$$ELF^{M2+}(x) = \exp\left[-\frac{5}{4}\left(\frac{D_g(x)}{D_h(x)}\right)^2\right]$$

$$ELF^{BE} - ELF^{M1+}$$

$$ELF^{BE} - ELF^{M2+}$$

COS2: Electronic Localization

Special Markovian Electronic Localization Forms

$$g*(-g,h) = \cosh\left[\sqrt{2}\,\frac{(-g)}{h}\right] \rightarrow \cosh\left[\sqrt{2}\,\frac{D_g(x)}{D_h(x)}\right] > 0$$

$$ELF^{M1++}(x) = \left\{\text{sech}\left[\sqrt{2}\,\frac{D_g(x)}{D_h(x)}\right]\right\}^{3/2}$$

$$ELF^{M2++}(x) = \left\{\text{sech}\left[\sqrt{2}\,\frac{D_g(x)}{D_h(x)}\right]\right\}^{5/4}$$

$ELF^{BE} - ELF^{M1++}$

$ELF^{BE} - ELF^{M2++}$
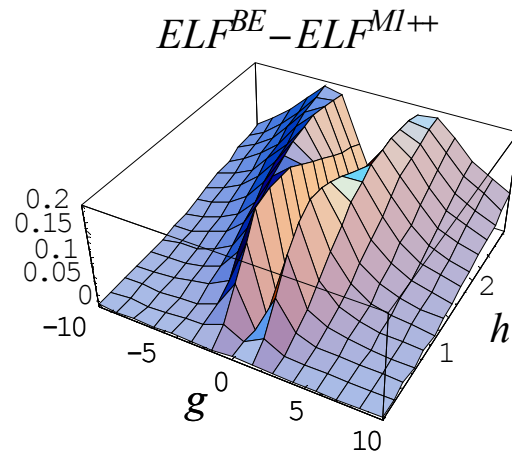
COS2: Electronic Localization

Atomic case

Hartree-Fock (HF) orbitals (Clementi & Roetti, 1974)

$$\varphi_{1s}^{HF}(r) = 5.97998e^{-15.5659r} + 54.4121e^{-9.48486r} + 0.864275e^{-7.79242r}$$
$$+ 0.116083e^{-4.8253r} - 0.00616627e^{-2.86423r} + 0.00316777e^{-1.96184r}$$

$$\varphi_{2s}^{HF}(r) = -4.69086e^{-15.5659r} - 49.4426e^{-9.48486r} - 18.169e^{-7.79242r}$$
$$+ 12.2167e^{-4.8253r} + 7.17766e^{-2.86423r} + 0.775679e^{-1.96184r}$$

$$\varphi_{2p}^{HF}(r) = r\begin{pmatrix} 5.45138e^{-9.13464r} + 16.1988e^{-4.48489r} \\ + 5.3916e^{-2.38168r} + 0.639566e^{-1.45208r} \end{pmatrix}$$

Clementi E.; Roetti C. (**1974**) Roothaan-Hartree-Fock atomic wavefunctions: Basis functions and their coefficients for ground and certain excited states of neutral and ionized atoms, Z≤54. *At. Data. Nucl. Data. Tables 14*, 177-478.

self-consistent field (Gombás & Szondy, 1970)
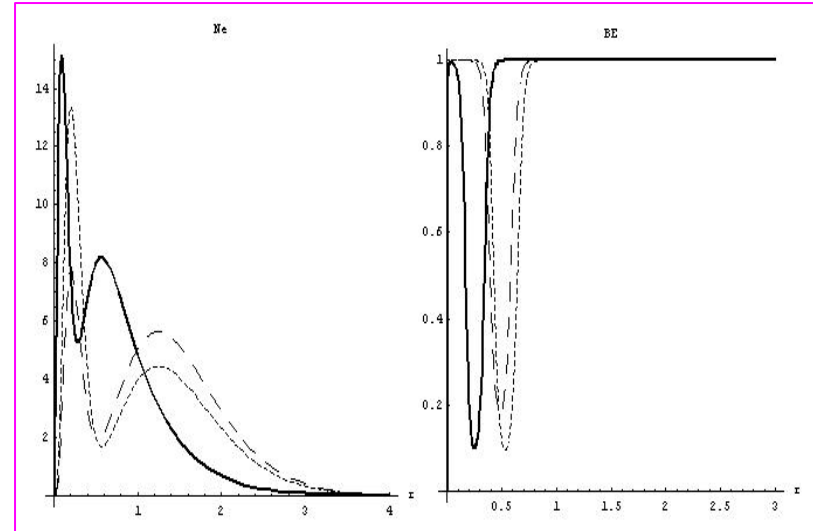
$$\varphi_K^{SCF1}(r) = 353.397e^{-9.87r}r$$

$$\varphi_L^{SCF1}(r) = 5.89511e^{-2.006r}r^{3/2}$$

$$\varphi_{1s}^{SCF2}(r) = 353.397e^{-9.87r}r$$

$$\varphi_{2s}^{SCF2}(r) = -307.024e^{-9.87r}r + 2.31275e^{-2.006r}r^{3/2}$$

$$\varphi_{2p}^{SCF2}(r) = 5.89511e^{-2.006r}r^{3/2}$$

Gombás P.; Szondy T. (**1970**) *Solutions of the Simplified Self-Consistent Field for All Atoms of the Periodic System of Elements from Z=2 to Z=92*. Adam Hilger Ltd: London.

$$r^2\rho(r) = \sum_{nl} q_{nl}\left|r\varphi_{nl}(r)\right|^2$$
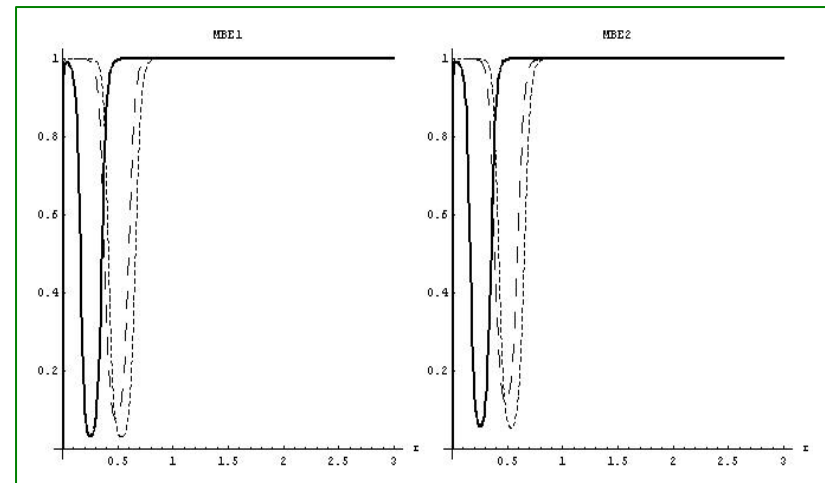
Putz M.V. (**2005**) Markovian approach of the electron localization functions. *Int. J. Quantum Chem.* 105(1), 1-11.

COS2: Electronic Localization

Atomic case

COS2: Electronic Localization

Atomic case
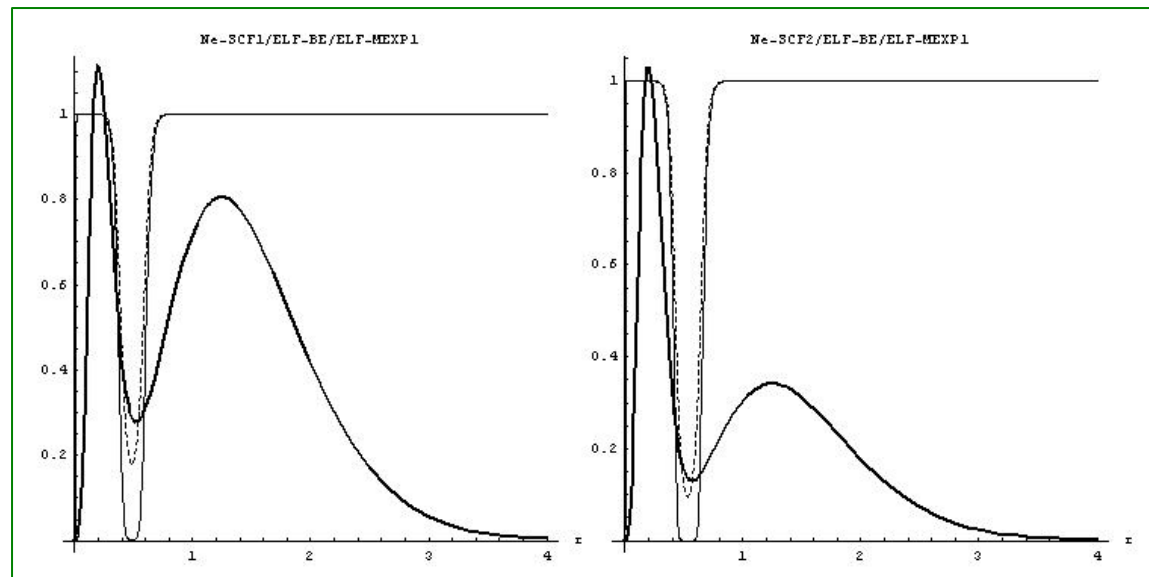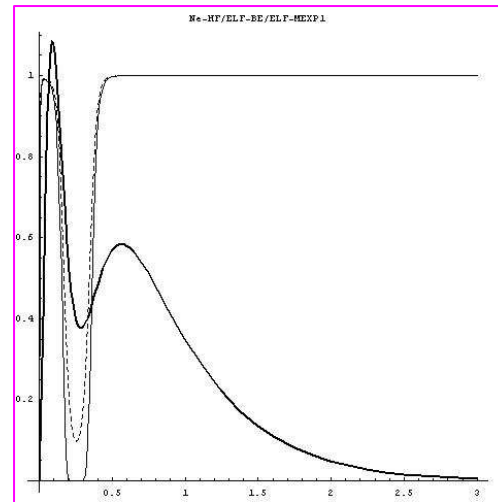
COS2: Electronic Localization

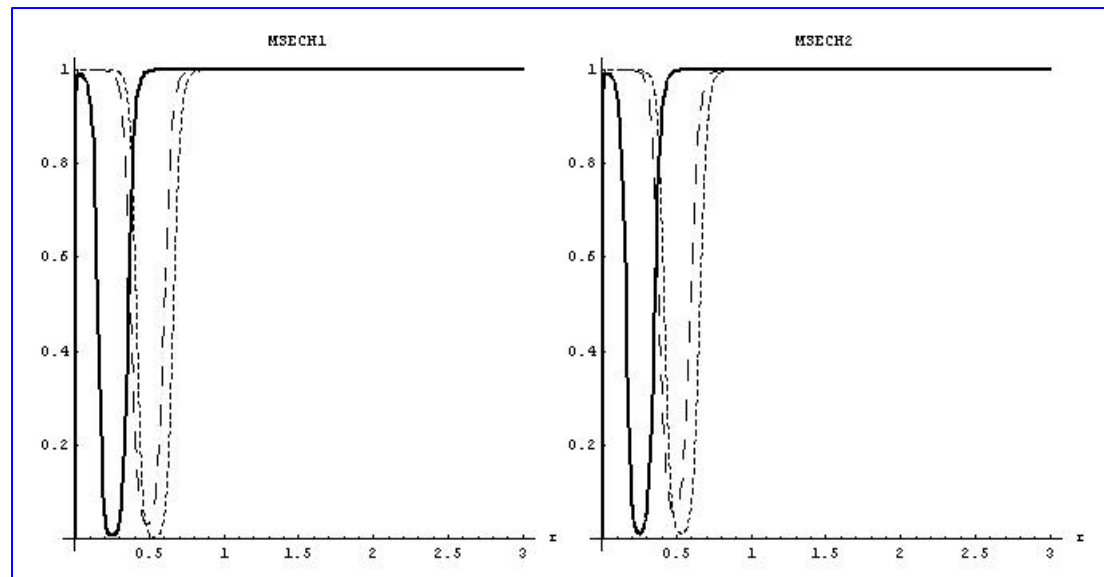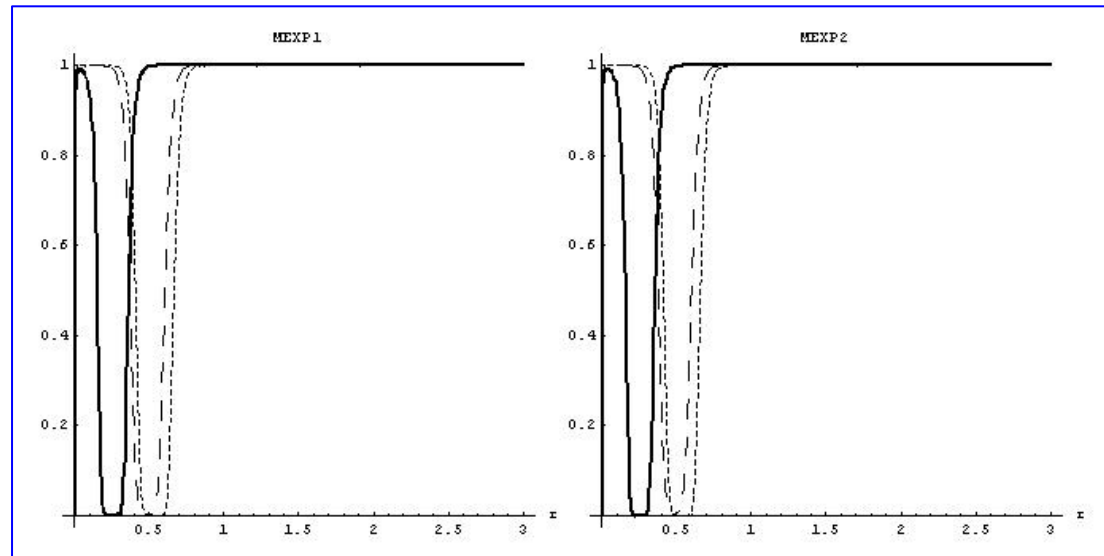## Molecular case

atomic functions (Gombás & Szondy, 1970)

$$f_1^{Li}(r) = 8.863248r \exp(-2.698r)$$

$$f_2^{Li}(r) = 0.369721r^{5/2} \exp(-0.797r)$$

$$\int_0^\infty \left[f_n^{Li}(r) \right]^2 dr = 1 , \; n = 1,2$$
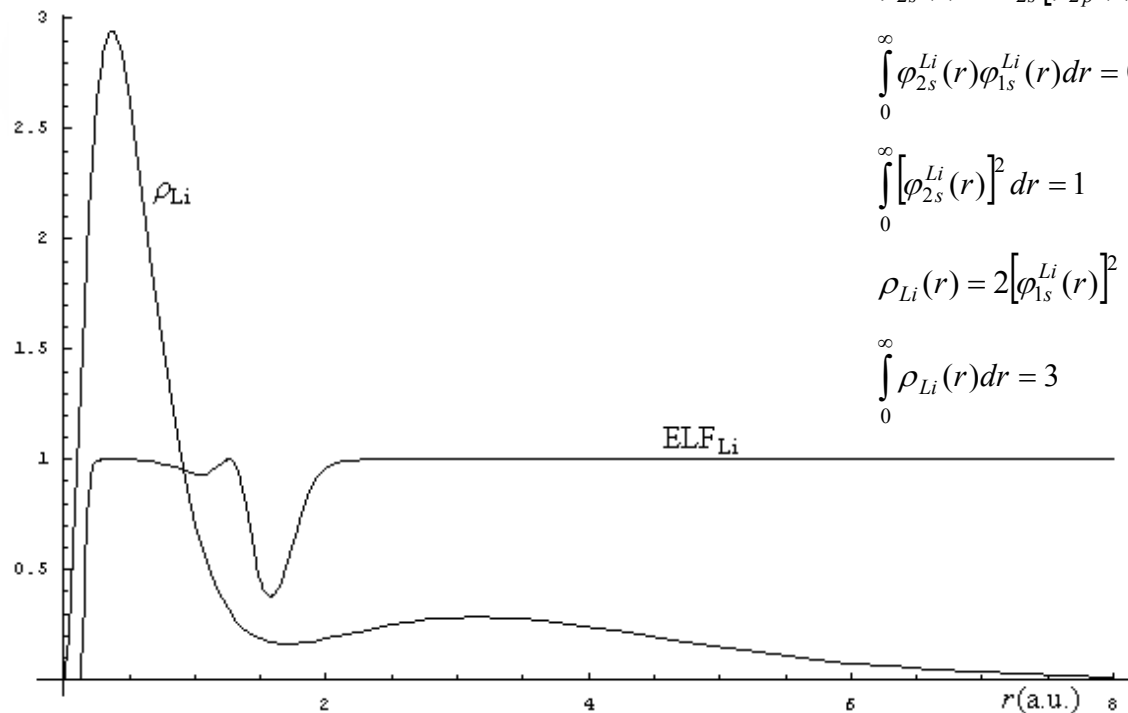
orthonormal orbital eigen-waves

$$\varphi_{1s}^{Li}(r) = f_1^{Li}(r)$$

$$\varphi_{2p}^{Li}(r) = f_2^{Li}(r)$$

$$\varphi_{2s}^{Li}(r) = C_{2s}^{Li}\left[\varphi_{2p}^{Li}(r) - \alpha \varphi_{1s}^{Li}(r) \right]$$

$$\int_0^\infty \varphi_{2s}^{Li}(r)\varphi_{1s}^{Li}(r)dr = 0$$

$$\int_0^\infty \left[\varphi_{2s}^{Li}(r) \right]^2 dr = 1$$

$$\rho_{Li}(r) = 2\left[\varphi_{1s}^{Li}(r) \right]^2 + \left[\varphi_{2s}^{Li}(r) \right]^2$$

$$\int_0^\infty \rho_{Li}(r)dr = 3$$

One can equally say that in the crossing vicinity of AIM-ELFs the electrons are at the same time completely localized (for bonding with $ELF_X - ELF_H \rightarrow 0$) and completely delocalized for atomic systems (with $ELF_{X,H} \rightarrow 1$), according to above the *ELF* definition and present signification.

In other words it can be alleged that *ELF application on chemical bond helps in identifying the molecular region where the electrons undergo the transition from the complete delocalization in atoms to localization in molecular bonding behavior*.
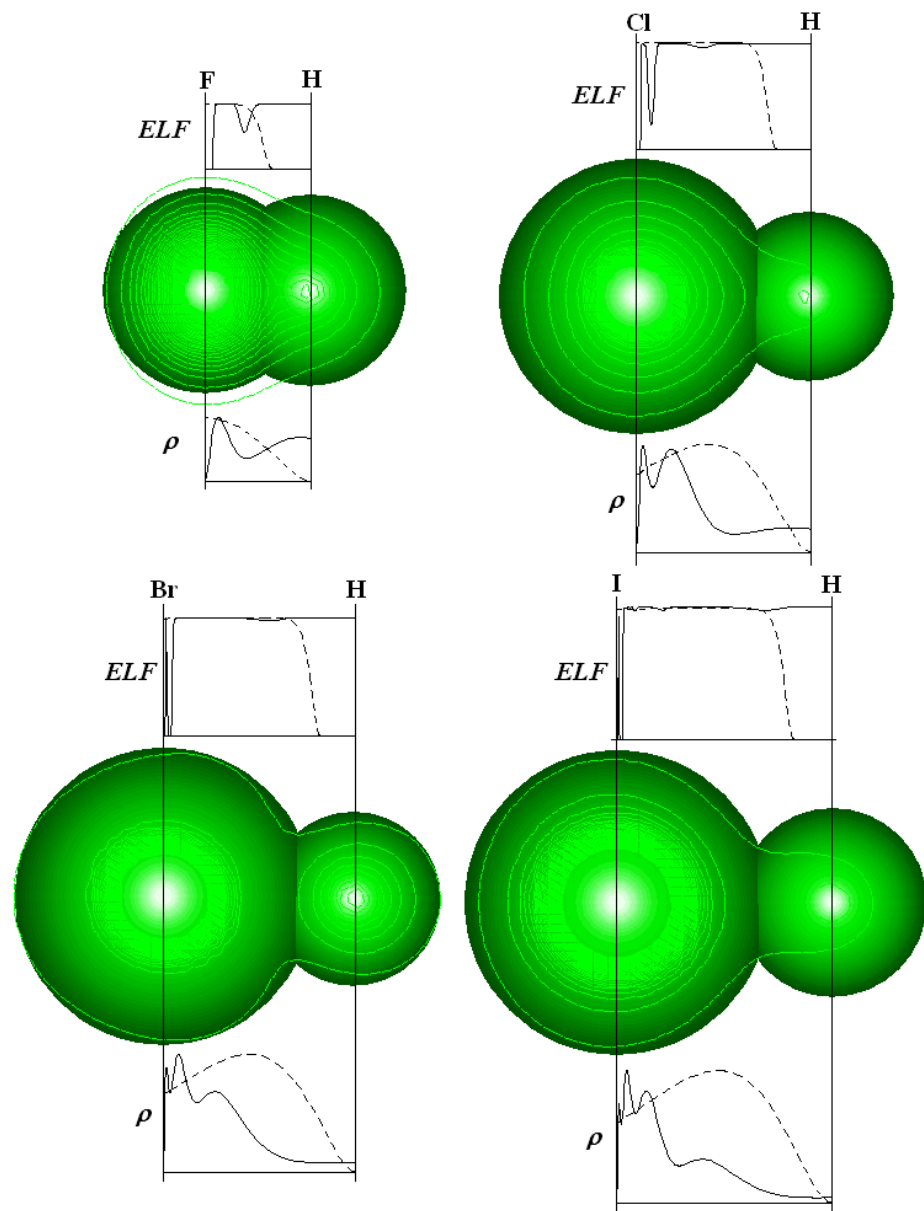
COS2: Electronic Localization-Perspectives

Electronic Density Derivatives

$$\frac{\delta^2 \rho(\mathbf{r}_1, \mathbf{r}_2)}{\delta N^2} = ?$$

two-points (non-local) chemical softness function

$$s(\mathbf{r}_1, \mathbf{r}_2) = -\left[\frac{\delta \rho^2(\mathbf{r}_1, \mathbf{r}_2)}{\delta \chi}\right]_V$$

the idempotency relationship

$$\int \rho^2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = \int \rho(\mathbf{r}_1, \mathbf{r}_2)\rho(\mathbf{r}_2, \mathbf{r}_1) d\mathbf{r}_2 = \rho(\mathbf{r}_1, \mathbf{r}_1) = \rho(\mathbf{r}_1)$$

fulfils the softness hierarchy

$$s(\mathbf{r}_1) = \int s(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2$$

the linear response function successively writes

$$\kappa(\mathbf{r}_1, \mathbf{r}_2) = \left(\frac{\delta \rho(\mathbf{r}_1)}{\delta V(\mathbf{r}_2)}\right)_N = -s(\mathbf{r}_1, \mathbf{r}_2) + \frac{s(\mathbf{r}_1)s(\mathbf{r}_2)}{S} = -\frac{1}{\eta}\left[\frac{\delta \rho^2(\mathbf{r}_1, \mathbf{r}_2)}{\delta N}\right]_V + \frac{f(\mathbf{r}_1)f(\mathbf{r}_2)}{\eta}$$

first order derivatives

$$\frac{\delta \rho^2(\mathbf{r}_1, \mathbf{r}_2)}{\delta N} = f(\mathbf{r}_1)f(\mathbf{r}_2) - \eta \kappa(\mathbf{r}_1, \mathbf{r}_2)$$

$$\frac{\delta \rho(\mathbf{r}_1, \mathbf{r}_2)}{\delta N} = \frac{f(\mathbf{r}_1)f(\mathbf{r}_2) - \eta \kappa(\mathbf{r}_1, \mathbf{r}_2)}{2\rho(\mathbf{r}_1, \mathbf{r}_2)}$$

second order derivatives

$$\frac{\delta^2 \rho^2(\mathbf{r}_1, \mathbf{r}_2)}{\delta N^2} = 2[\delta_N f(\mathbf{r}_1)]f(\mathbf{r}_2) - [\partial_N \eta]\kappa(\mathbf{r}_1, \mathbf{r}_2) - \eta[\delta_N \kappa(\mathbf{r}_1, \mathbf{r}_2)]$$

$$\frac{\delta^2 \rho(\mathbf{r}_1, \mathbf{r}_2)}{\delta N^2} = \frac{1}{2\rho^2(\mathbf{r}_1, \mathbf{r}_2)}\left\{\begin{array}{c}\rho(\mathbf{r}_1, \mathbf{r}_2)[\delta_N(f(\mathbf{r}_1)f(\mathbf{r}_2) - \eta\kappa(\mathbf{r}_1, \mathbf{r}_2))]\\ -\frac{(f(\mathbf{r}_1)f(\mathbf{r}_2) - \eta\kappa(\mathbf{r}_1, \mathbf{r}_2))^2}{2\rho(\mathbf{r}_1, \mathbf{r}_2)}\end{array}\right\}$$

Conclusions COS2:
Orthogonal Space of Electronic Localization

Markovian Approach of the Electron Localization Functions

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$$ELF = \frac{1}{f\left(\dfrac{g(\rho(\mathbf{r}))}{h(\rho(\mathbf{r}))}\right)} \rightarrow \begin{cases} 0, \nabla\rho(\mathbf{r}) >> \rho(\mathbf{r}) \\ 1, \nabla\rho(\mathbf{r}) << \rho(\mathbf{r}) \end{cases}$$

Path Integrals for Electronic Densities, Reactivity Indices, and Localization Functions in Quantum Systems

Mihai V. Putz

Variational perturbation theory for Markov processes

Hagen Kleinert,* Axel Pelster,† and Mihai V. Putz‡
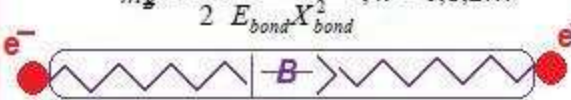*Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany*
(Received 16 August 2001; published 28 June 2002)

Most Expected Bosonic Nature of the Chemical Bond: The Bondon

Through performing the chemical field gauge algorithm, either by Schroedinger or Dirac quantum level analysis, one obtains the working expression for the bondonic ground state properties

$$m_B = \frac{\hbar^2}{2}\frac{(2\pi m + 1)^2}{E_{bond} X_{bond}^2}, \; n = 0,1,2\ldots$$

$$E_{bond}[kcal/mol] \times X_{bond}^0[\mathring{A}] = 182019$$

Bond Type	X_{bond} (Å)	E_{bond} (kcal/mol)	$\varsigma_m = \dfrac{m_B}{m_0}$	$\varsigma_v = \dfrac{v_B}{c}[\%]$	$\varsigma_e = \dfrac{e_B}{e}[\times 10^3]$	$t_B[\times 10^{15}]$ (seconds)
H–H	0.60	104.2	2.34219	3.451	0.3435	9.236
C–C	1.54	81.2	0.45624	6.890	0.687	11.894
C–C[(a)]	1.54	170.9	0.21678	14.385	1.446	5.743
C=C	1.34	147	0.33286	10.816	1.082	6.616
C≡C	1.20	194	0.31451	12.753	1.279	5.037
N≡N	1.10	225	0.32272	13.544	1.36	4.352
O=O	1.10	118.4	0.61327	7.175	0.716	8.160
F–F	1.28	37.6	1.42621	2.657	0.264	25.582
Cl–Cl	1.98	58	0.3864	6.330	0.631	16.639
I–I	2.66	36.1	0.3440	5.296	0.528	26.701
C–H	1.09	99.2	0.7455	5.961	0.594	9.724
N–H	1.02	93.4	0.9042	5.254	0.523	10.32
O–H	0.96	110.6	0.8620	5.854	0.583	8.721
C–O	1.42	82	0.5314	6.418	0.64	11.771
C=O[(b)]	1.21	166	0.3615	11.026	1.104	5.862
C=O[(c)]	1.15	191.6	0.3467	12.081	1.211	5.091
C–Cl	1.76	78	0.3636	7.560	0.754	12.394
C–Br	1.91	68	0.3542	7.155	0.714	14.208
C–I	2.10	51	0.3906	5.905	0.588	18.9131

(a) in diamond; (b) in CH₂O; (c) in O=C=O

$$\varsigma_m = \frac{m_B}{m_0} = \frac{87.8603}{\left(E_{bond}[kcal/mol]\right)\left(X_{bond}^0[\mathring{A}]\right)^2}$$

$$\varsigma_v = \frac{v_B}{c} = \sqrt{\frac{100}{1+\dfrac{3.27817\times 10^6}{\left(E_{bond}[kcal/mol]\right)^2\left(X_{bond}^0[\mathring{A}]\right)^2}}}[\%]$$

$$\varsigma_e = \frac{e_B}{e} \sim \frac{1}{32\pi}\frac{\left(E_{bond}[kcal/mol]\right)\left(X_{bond}^0[\mathring{A}]\right)}{\sqrt{3.27817\times 10^3}}$$

$$t_B = \frac{2\hbar}{m_B v_B^2} = \frac{2\hbar}{\left(m_0 \varsigma_m\right)\left(c\varsigma_v \cdot 10^{-2}\right)^2} = \frac{0.0257618}{\varsigma_m \varsigma_v^2}\times 10^{-15}[s]_{SI}$$

Chemical bond \ Property	ς_m	ς_v	ς_e	t_B
Covalence	>>	<<	<<	>>
Multiple bonds	<	>	>	<
Metallic	<<	>	>	<
Ionic	~>	~	~	~>

Putz M.V. (**2010**): The bondons: the quantum particles of the chemical bond. *Int. J. Mol. Sci.* 11(11), 4227-4256; **Putz M.V.** (**2012**) Quantum Theory: Density, Condensation, and Bonding. Apple Academic Press: New Jersey, USA (ISBN: 978-1-926895-14-7), pp. 240.

COS3: Bondonic Condensation of Chemical Bonding

Bosonic Condensation with Density Functional Pattern

$$N = \int \rho(\mathbf{r})d\mathbf{r} = \int |\psi(\mathbf{r})|^2 d\mathbf{r}$$

$$\rho(\mathbf{r}) = \rho_{CONDENSATE}(\mathbf{r}) + \rho_{CRITIC}(\mathbf{r})$$

$$= |\Psi(\mathbf{r})|^2 + \sum_{k \neq 0} |\varphi_k(\mathbf{r})|^2 \frac{1}{\exp(\beta E_k) - 1}$$

the *order parameter* and
the *super-fluidic density (Putz, 2012)*

$$\begin{cases} \Psi(\mathbf{r}) \equiv \langle \psi(\mathbf{r}) \rangle_T \\ \rho(\mathbf{r}) \equiv \langle \psi^+(\mathbf{r})\psi(\mathbf{r}) \rangle_T \end{cases}$$

$$\begin{cases} \rho(\mathbf{r}) \overset{!}{=} \rho_{KS}(\mathbf{r}) := \langle \psi^+(\mathbf{r})\psi(\mathbf{r}) \rangle_T^{KS} \\ \Psi(\mathbf{r}) \overset{!}{=} \Psi_{KS}(\mathbf{r}) := \langle \psi(\mathbf{r}) \rangle_T^{KS} \end{cases}$$
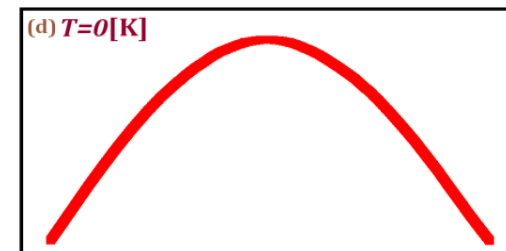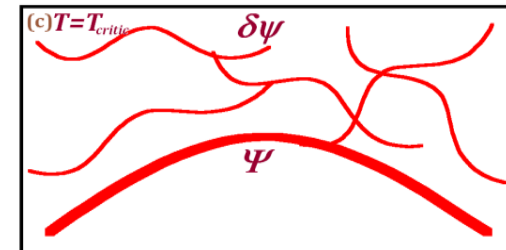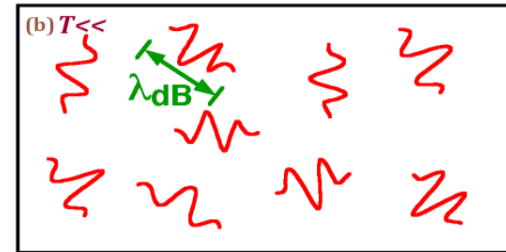
Landau energy functional (Huang, 2001)

$$E[\psi, \psi^+] = \int d\mathbf{r} \left[\frac{\hbar^2}{2m_B} |\nabla \psi(\mathbf{r})|^2 + (V(\mathbf{r}) - \mu)\psi^+(\mathbf{r})\psi(\mathbf{r}) + \frac{g}{2} (\psi^+(\mathbf{r})\psi(\mathbf{r}))^2 \right]$$

Gross-Pitaevsky (1961) equation

$$0 = \frac{\partial E}{\partial \psi^+}$$

$$\left[-\frac{\hbar^2}{2m_B} \nabla^2 + V(\mathbf{r}) + g|\psi|^2 \right] \psi = \mu \psi$$

(a) $T >>$

(b) $T <<$ — λ_{dB}

(c) $T = T_{critic}$ — $\delta\psi$ — Ψ

(d) $T = 0[K]$
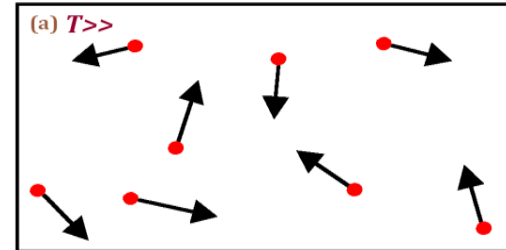
Huang K. (**2001**) *Introduction to Statistical Physics*. London: Taylor and Francis.; **Gross E.P.** (**1961**) Structure of a quantized vortex in boson systems. *Nuovo Cimento 20*, 454-477; **Pitaevsky L.P.** (**1961**) Vortex lines in an imperfect Bose gas. *Sov. Phys. - JETP 13*, 451-454; **Putz M.V.** (**2012**) Conceptual density functional theory: from inhomogeneous electronic gas to Bose-Einstein condensates. In: Chemical Information and Computational Challenges in 21st, Ed. Putz M.V., NOVA Science Publishers, Inc.: New York (ISBN: 978-1-61209-712-1).

Ketterle W. (**2002**) Nobel Lecture: when atoms behave as waves: Bose-Einstein condensation and the atom laser, *Rev. Mod. Phys. 74*, 1131–1151.

COS3: Bondonic Condensation of Chemical Bonding

Working BEC Connections with Density Functional Theory

Thomas-Fermi approximation: the kinetic energy can be neglected in the stationary Gross-Pitaevsky equation

$$\left|\psi\right|^2 \cong \frac{1}{g}\left[\mu - V(\mathbf{r})\right]$$

$$\mu = V(\mathbf{r}) + \frac{\delta F_{HK}[\rho]}{\delta\rho(\mathbf{r})}$$

$$\left|\psi\right|^2 \cong \frac{1}{g}\left[\frac{\delta F_{HK}[\rho]}{\delta\rho(\mathbf{r})}\right]_{V(\mathbf{r})}$$

$$\int d\mathbf{r}\left|\psi(\mathbf{r})\right|^4 \cong \frac{1}{g^2}\int d\mathbf{r}\left[\mu - V(\mathbf{r})\right]^2 = \frac{1}{g^2}\int d\mathbf{r}\left[\nabla_\rho F_{HK}\right]^2$$

$$\int d\mathbf{r}\left|\psi(\mathbf{r})\right|^4 \cong -\frac{F_{HK}\eta}{g^2}$$

$$E[\rho] = \int d\mathbf{r}V(\mathbf{r})\rho(\mathbf{r}) + E_{kin}[\rho] + E_{Coub}[\rho] + E_{XC}[\rho] = C_A[\rho] + F_{HK}[\rho]$$

"more is different" (Anderson, 1972)
"infinite more is the same" (Kadanoff, 2009)

Anderson P. (**1972**) More is different. *Sci. New Ser.* 177, 393–396; Kadanoff L.P. (**2009**) More is the same; mean field theory and phase transitions. *J. Stat. Phys.* 137, 777-797. **Putz M.V.** (2012) From Kohn-Sham to Gross-Pitaevsky equation within Bose-Einstein condensation ψ-theory. *Int. J. Chem. Model.* 4(1), 1-11.

➤ "few electrons is different"
➤ "pairing electrons is the same"

Glaum K., Kleinert H., Pelster A. (**2007**) Condensation of ideal Bose gas confined in a box within a canonical ensemble. *Phys. Rev. A* 76, 063604.

• BEC with finite numbers of bosons' interaction, as is the practical case;
• Chemical Bonding with single bosonic (bondonic) appearance.

COS3: Bondonic Condensation of Chemical Bonding

Homopolar Chemical Bonding by Bosonic-Bondons

$$\underbrace{\psi_{BB}(\mathbf{r})}_{BONDONIC} = \underbrace{c_A\psi_A(\mathbf{r}) + c_B\psi_B(\mathbf{r})}_{FERMIONIC\ SUPERPOSITION}$$

$$\hat{H}_{FB} = \hat{H}_F + \hat{H}_B$$

consider the Gross-Pitaevsky stationary Hamiltonian that can be projected for chemical bond on *orthogonal* fermionic-bondonic (FB) contributions

$$\hat{H}_F = -\frac{\hbar^2}{2m_0}\nabla^2 + V(\mathbf{r})$$

$$\hat{H}_B = g|\psi|^2$$

$$m_B = \frac{\hbar^2}{2}\frac{1}{E_{bond}R_{bond}^2}$$

$$\left\langle \hat{H}_{FB}\right\rangle = \left\langle \hat{H}_F\right\rangle_{\substack{FERMIONIC\\SIDE}} + \left\langle \hat{H}_B\right\rangle_{\substack{BOSONIC\\SIDE}}$$

bondonic bosonic strength, at chemical bonding level

$$= \frac{\int d\mathbf{r}(c_A\psi_A(\mathbf{r}) + c_B\psi_B(\mathbf{r}))^* \hat{H}_F(c_A\psi_A(\mathbf{r}) + c_B\psi_B(\mathbf{r})) + g\int d\mathbf{r}|\psi_{BB}(\mathbf{r})|^4}{\int d\mathbf{r}(c_A\psi_A(\mathbf{r}) + c_B\psi_B(\mathbf{r}))^*(c_A\psi_A(\mathbf{r}) + c_B\psi_B(\mathbf{r}))}$$

$$g_B = \frac{4\pi a_B\hbar^2}{m_B}\bigg|_{a_B\to R_{bond}} = 8\pi E_{bond}R_{bond}^3$$

$$\left\langle \hat{H}_{FB}\right\rangle \cong \frac{1}{c_A^2 + c_B^2 + 2c_Ac_B S}\left\{(c_A^2 + c_B^2)H_{11} + 2c_Ac_B H_{12} - \frac{F_{HK}\eta_{Molec}}{g_B}\right\}$$

$$R_{bond}^3 = V_{bond} = \frac{N_{bondons}}{\rho_{bodnons}(\mathbf{r})}\underset{(bosons)}{} \overset{(simple\ bonding:\ one\ bondon)}{=} \frac{1}{|\langle\psi(\mathbf{r})\rangle|^2}$$

Hohenberg-Kohn functional

$$g_B = \frac{8\pi E_{bond}}{|\langle\psi(\mathbf{r})\rangle|^2}$$

$$\begin{aligned}F_{HK} &= \left\langle \hat{H}_{FB}\right\rangle - C_A\\
&= \left\langle \hat{H}_{FB}\right\rangle - \int d\mathbf{r} V(\mathbf{r})\left[(c_A\psi_A(\mathbf{r}) + c_B\psi_A(\mathbf{r}))^*(c_A\psi_A(\mathbf{r}) + c_B\psi_A(\mathbf{r}))\right]\\
&= \left\langle \hat{H}_{FB}\right\rangle - (c_A^2 + c_B^2)V_{11} - 2c_Ac_B V_{12}\end{aligned}$$

Putz M.V. (**2011**) Hidden side of chemical bond: the bosonic condensate. In: Advances In Chemistry Research. Volume 10, Ed. Taylor J.C., NOVA Science Publishers, Inc.: New York (ISBN: 978-1-61324-018-2), 261-298.

COS3: Bondonic Condensation of Chemical Bonding

Homopolar Chemical Bonding by Bosonic-Bondons

$$\left\langle \hat{H}_{FB} \right\rangle \cong \frac{\left(c_A^2 + c_B^2\right)\left(H_{11} + \dfrac{\eta_{Molec}}{g_B} V_{11}\right) + 2c_A c_B \left(H_{12} + \dfrac{\eta_{Molec}}{g_B} V_{12}\right)}{c_A^2 + c_B^2 + 2c_A c_B S + \dfrac{\eta_{Molec}}{g_B}}$$

- *intra-atomic* $H_{11} = \int d\mathbf{r}\, \psi_A^*(\mathbf{r}) \hat{H}_F \psi_A(\mathbf{r}) = \int d\mathbf{r}\, \psi_B^*(\mathbf{r}) \hat{H}_F \psi_B(\mathbf{r})$
- *inter-atomic* $H_{12} = \int d\mathbf{r}\, \psi_A^*(\mathbf{r}) \hat{H}_F \psi_B(\mathbf{r}) = \int d\mathbf{r}\, \psi_B^*(\mathbf{r}) \hat{H}_F \psi_A(\mathbf{r})$
- *overlapping* $S = \int d\mathbf{r}\, \psi_A^*(\mathbf{r}) \psi_B(\mathbf{r}) = \int d\mathbf{r}\, \psi_B^*(\mathbf{r}) \psi_A(\mathbf{r})$
- *Coulombic* $V_{11} = \int d\mathbf{r}\, \psi_A^*(\mathbf{r}) V(\mathbf{r}) \psi_A(\mathbf{r}) = \int d\mathbf{r}\, \psi_B^*(\mathbf{r}) V(\mathbf{r}) \psi_B(\mathbf{r})$
- *exchange* $V_{12} = \int d\mathbf{r}\, \psi_A^*(\mathbf{r}) V(\mathbf{r}) \psi_B(\mathbf{r}) = \int d\mathbf{r}\, \psi_B^*(\mathbf{r}) V(\mathbf{r}) \psi_A(\mathbf{r})$

$$\begin{cases} \dfrac{\partial}{\partial c_A}\left\langle \hat{H}_{FB}\right\rangle = 0 \\ \dfrac{\partial}{\partial c_B}\left\langle \hat{H}_{FB}\right\rangle = 0 \end{cases}$$

single chemical bond assumed

$$1 = \int d\mathbf{r}[\psi_{BB}(\mathbf{r})]^2$$

antibonding

$$\begin{cases} \left\langle \hat{H}_{FB}\right\rangle^\alpha \equiv E^+ = \dfrac{H_{11} + H_{12}}{1+S} + \dfrac{\eta_{Molec}}{g_B}\dfrac{V_{11} + V_{12}}{1+S} \\ \psi_{BB}^\alpha(\mathbf{r}) = \dfrac{1}{\sqrt{2+2S}}\left[\psi_A(\mathbf{r}) + \psi_A(\mathbf{r})\right] \end{cases}$$

bonding

$$\begin{cases} \left\langle \hat{H}_{FB}\right\rangle^\beta \equiv E^- = \dfrac{H_{11} - H_{12}}{1-S} + \dfrac{\eta_{Molec}}{g_B}\dfrac{V_{11} - V_{12}}{1-S} \\ \psi_{BB}^\beta(\mathbf{r}) = \dfrac{1}{\sqrt{2-2S}}\left[\psi_A(\mathbf{r}) - \psi_A(\mathbf{r})\right] \end{cases}$$

in the limit of small bosonic interaction

$$\langle\psi\rangle \to 0$$

$$E_{bond}^\pm = \frac{H_{11} \pm H_{12}}{1 \pm S} + \left|\langle\psi(\mathbf{r})\rangle\right|^2 \frac{\eta_{Molec}}{8\pi E_{bond}^\pm} \frac{V_{11} \pm V_{12}}{1 \pm S}$$

$$E_{bond-BEC-I}^\pm = -\left|\langle\psi(\mathbf{r})\rangle\right|^2 \frac{\eta_{Molec}}{8\pi} \frac{V_{11} \pm V_{12}}{H_{11} \pm H_{12}}$$

$$E_{bond-BEC-II}^\pm = \frac{H_{11} \pm H_{12}}{1 \pm S} + \left|\langle\psi(\mathbf{r})\rangle\right|^2 \frac{\eta_{Molec}}{8\pi} \frac{V_{11} \pm V_{12}}{H_{11} \pm H_{12}}$$

physical- and chemical- bonding condensates

COS3: Bondonic Condensation of Chemical Bonding

Homopolar Chemical Bonding by Bosonic-Bondons H_2 &vs. He_2

$$V(A,B) = -\frac{2}{r_A} - \frac{2}{r_B} + \frac{1}{R}$$

$$\begin{cases} \langle \psi_A | \psi_A \rangle = \langle \psi_B | \psi_B \rangle = N_0 \\ N_0 = 1, 2 \end{cases}$$
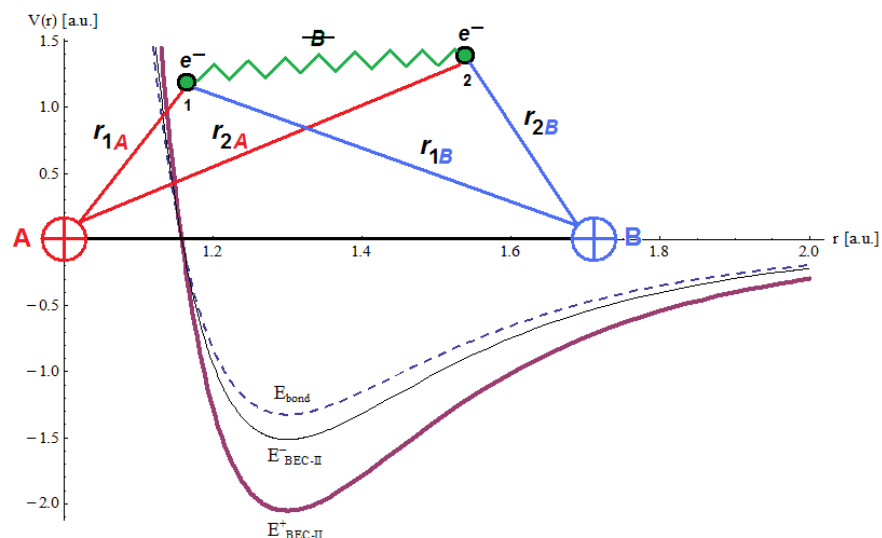
special 1s atomic orbitals, suitable for modeling the bosonic interaction

$$\psi(r) = \sqrt{\frac{\gamma}{\pi}} \exp(-\alpha r)$$

$\alpha = \xi$

$\gamma = N_0 \xi^3$

$\xi = \dfrac{21 - 5N_0}{16}$

$$V^{12-6}(r) = -E_{bond}\left[\left(\frac{R}{r}\right)^{12} - 2\left(\frac{R}{r}\right)^{6}\right]$$

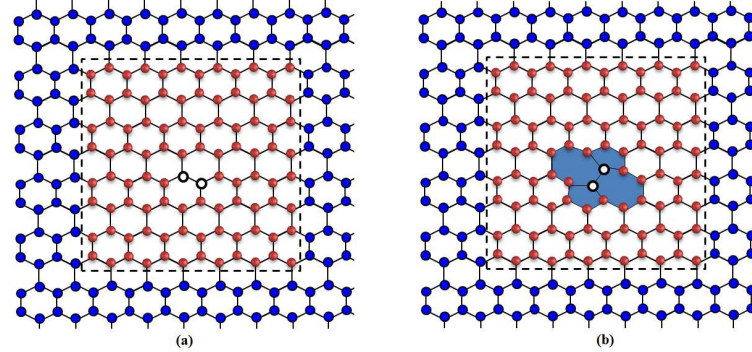| Atoms	N_0	η	E_0	Molecules	R	E_{bond}	E_{+BEC-I}	E_{-BEC-I}	$E_{+BEC-II}$	$E_{-BEC-II}$
H	1	0.237	-0.5	H-H	1.3[c)]	-1.324	-0.011	-0.017	-2.054	-1.513
He	2	0.458	-2.9	He-He	5.67	-2.85×10^{-5}	-8.15×10^{-3}	-1.3×10^{-2}	-3.695	-4.072

COS3: Bondonic Condensation of Chemical Bonding-Perspectives

Bondonic Characterization of Extended Nanosystems: Graphene

$$M_B = \frac{\hbar^2}{2 E_{bond} X_{bond}^2}$$

$$E_{bond}[kcal/mol] X_{Bond}[\overset{o}{A}] = a, \quad a = 182,019$$

$$\bar{x} = (x_a + x_b)/2 \qquad \Delta x = x_b - x_a$$

(a)   (b)

$$(x_b \hbar \beta; x_a 0) = \sqrt{\frac{M}{2\pi\hbar^2\beta}} \exp\left\{ -\frac{M}{2\hbar^2\beta}(\Delta x)^2 - \beta V(\bar{x}) \right\}$$
$$\times \left\{ 1 - \frac{\hbar^2\beta^2}{12M}\nabla^2 V(\bar{x}) - \frac{\beta}{24}(\Delta x\nabla)^2 V(\bar{x}) + \frac{\hbar^2\beta^3}{24M}[\nabla V(\bar{x})]^2 \right\}$$

$$z(\beta) = \int (x_b \hbar\beta; x_a 0)\Big|_{x_a = x_b = \bar{x}} d\bar{x}$$
$$= \sqrt{\frac{M}{2\pi\hbar^2\beta}} \int \exp\left[-\beta V(\bar{x}) - \frac{\hbar^2\beta^2}{24M}\nabla^2 V(\bar{x}) \right] d\bar{x}$$

$$z_B(\beta, X_{bond}, E_{bond}) = \frac{1}{2X_{bond}}\sqrt{\frac{1}{\pi E_{bond}\beta}} \int \exp\left[-\beta V(\bar{x}) - \frac{\beta^2}{12}E_{bond}\bar{x}^2\nabla^2 V(\bar{x}) \right] d\bar{x}$$

$$V(\bar{x}) \rightarrow \Xi$$
$$\nabla^2 V(\bar{x}) \rightarrow \Xi^{[2]}$$

$$z_B^{[0]}(\beta, E_{bond}) = \frac{1}{2X_{bond}}\sqrt{\frac{1}{\pi E_{bond}\beta}} \int_0^{X_{bond}} \exp[-\beta\Xi]d\bar{x} = \frac{1}{2}\sqrt{\frac{1}{\pi E_{bond}\beta}}\exp[-\beta\Xi]$$

$$\langle E_{Bond}\rangle[kcal/mol] = -\frac{\partial \ln z_B^{[0]}(\beta, E_{bond})}{\partial\beta} = \frac{1}{2\beta} + \Xi = \begin{cases} \Xi, ... \beta \rightarrow \infty (T \rightarrow 0K) \\ \infty, ... \beta \rightarrow 0 (T \rightarrow \infty K) \end{cases}$$

$$\langle X_{Bond}\rangle[\overset{o}{A}] = \frac{2a\beta}{1 + 2\beta\Xi} = \begin{cases} \dfrac{a}{\Xi}, ... \beta \rightarrow \infty (T \rightarrow 0K) \\ 0, ... \beta \rightarrow 0 (T \rightarrow \infty K) \end{cases}$$

Bondonic Characterization of Extended Nanosystems: Graphene

transition between two phases of a nanosystem, e.g. an ideal and a modified (with defects) ones, as follows:

$$C_{\mathcal{B}}\left(\beta_{CRITIC}, \Xi_0\right)\Big|_{IDEAL} = C_{\mathcal{B}}\left(\beta_{CRITIC}, \Xi_D\right)\Big|_{DEFECTS}$$

$$N^{-1}\left\langle E_{Bond}^N \right\rangle[kcal/mol] = -\frac{\partial}{\partial\beta}\ln\left\{\frac{z_{\mathcal{B}}^N(\beta)_{\langle X_{bond}\rangle,\Xi,\Xi^{[2]}}}{N!}\right\} = \frac{3}{2\beta} + \Xi + \frac{1}{\beta+2\beta^2}$$

$$C_{\mathcal{B}}(N,\beta) = k_B\beta^2\frac{\partial^2}{\partial\beta^2}\ln\left\{\frac{z_{\mathcal{B}}^N(\beta)_{\langle X_{bond}\rangle,\Xi,\Xi^{[2]}}}{N!}\right\} = \frac{5+4\beta\Xi(5+3\beta\Xi)}{2(1+2\beta\Xi)^2}Nk_B$$
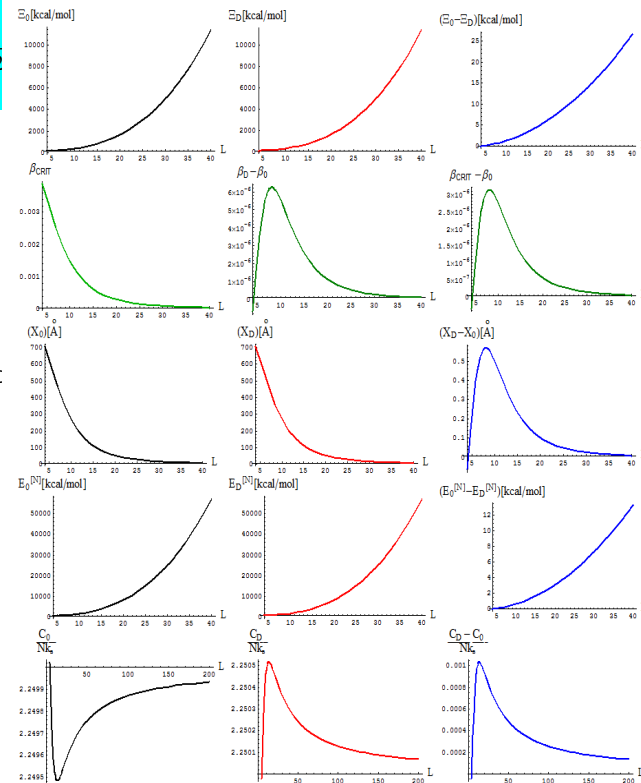
$5Nk_B/2$ *bondonic Dulong-Petit* limit $\quad \beta \vee \Xi \to 0$

$3Nk_B/2$ maximum topological potential $\quad \beta \vee \Xi \to \infty$

$$|\beta_{CRITIC}| = \frac{\Xi_0 + \Xi_D}{4\Xi_0\Xi_D} = \begin{cases} \dfrac{1}{2\Xi_0} & ...\Xi_0 = \Xi_D \\ \infty & ...\Xi_0 \to 0 \vee \Xi_D \to 0 \end{cases}$$

$$\delta = \beta/\beta_{CRITIC} \qquad \sigma = \Xi_0/\Xi_D$$

$$\frac{C_{\mathcal{B}}(\sigma,\delta)}{Nk_B} = \frac{3}{2} + \frac{1+\delta\sigma(1+\sigma)}{(1+0.5\delta\sigma(1+\sigma))^2} \xrightarrow{\delta\&\sigma\to1} \frac{43}{18} \cong 2.38889$$

Conclusions COS3:
Orthogonal Space of Bondonic Condensation of Chemical Bonding

Article

The Bondons: The Quantum Particles of the Chemical Bond

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Fax: ++40-256-592-620; Web: www.mvputz.iqstorm.ro

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Bondonic characterization of extended nanosystems: Application to graphene's nanoribbons

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$$N = \int \rho(\mathbf{r})d\mathbf{r} = \int |\psi(\mathbf{r})|^2 d\mathbf{r}$$

$$m_B = \frac{\hbar^2}{2}\frac{(2\pi n+1)^2}{E_{bond}X_{bond}^2}$$

$$\left\langle \hat{H}_{FB} \right\rangle = \left\langle \hat{H}_F \right\rangle_{\substack{FERMIONIC\\SIDE}} + \left\langle \hat{H}_B \right\rangle_{\substack{BOSONIC\\SIDE}}$$

Density Functional Theory of Bose–Einstein Condensation: Road to Chemical Bonding Quantum Condensate

Mihai V. Putz

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Taylor & Francis Group

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It is agreed on this   day of   , 2013, by and between **Chapter Author(s):**

Mihai V. PUTZ, Ottorino ORI and Mircea V. DIUDEA

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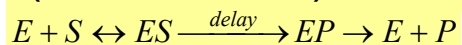Title: Bondonic electronic properties of 2D graphenic lattices with structural defects   Chapter No.:   xx
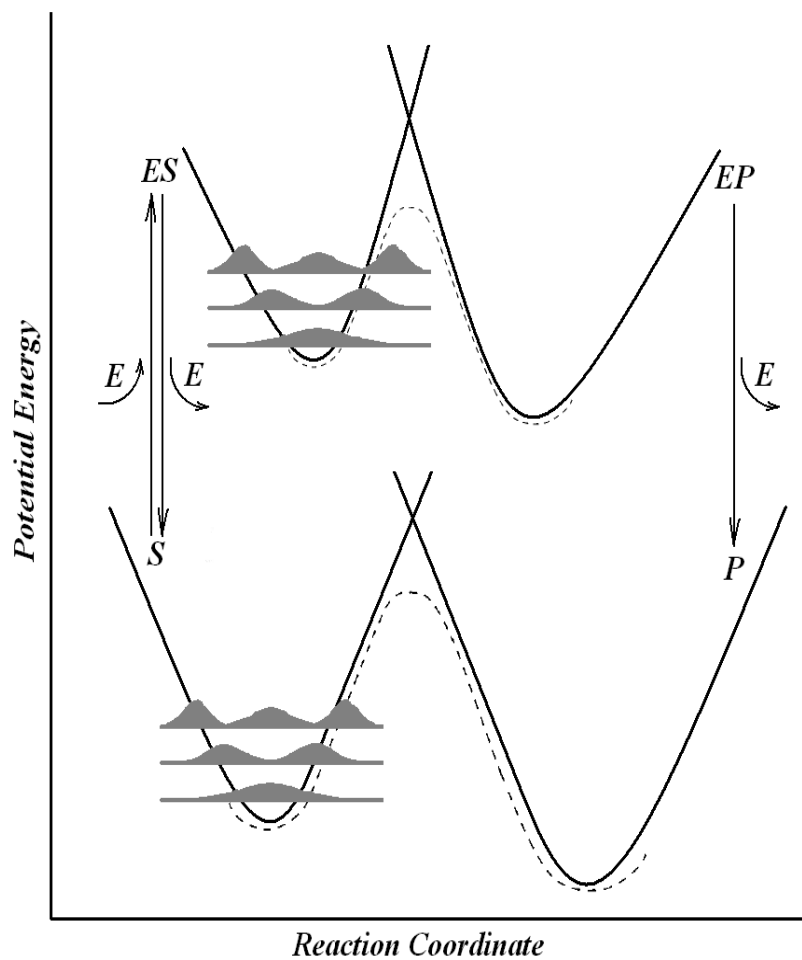
COS4: Enzyme-Substrate Interaction's Logistics

Enzyme Kinetics as Quantum Delayed Tunnelling Phenomena

Brownian enzymic reaction (Brown, 1902)

Brown A.J. (**1902**) Enzyme action. *J. Chem. Soc. Trans. 81*, 373-388; Michaelis L.; Menten M.L. (**1913**) Die kinetik der invertinwirkung. *Biochem. Z. 49*, 333-369.

$$E + S \leftrightarrow ES \xrightarrow{delay} EP \to E + P$$

Michaelis-Menten (1913)

$$E + S \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} ES \overset{k_2}{\to} E + P$$

Putz M.V.; Putz A.M. (**2011**) Logistic vs. W-Lambert information in quantum modeling of enzyme kinetics. Int. J. Chemoinf. Chem. Eng. 1(1), 42-60.
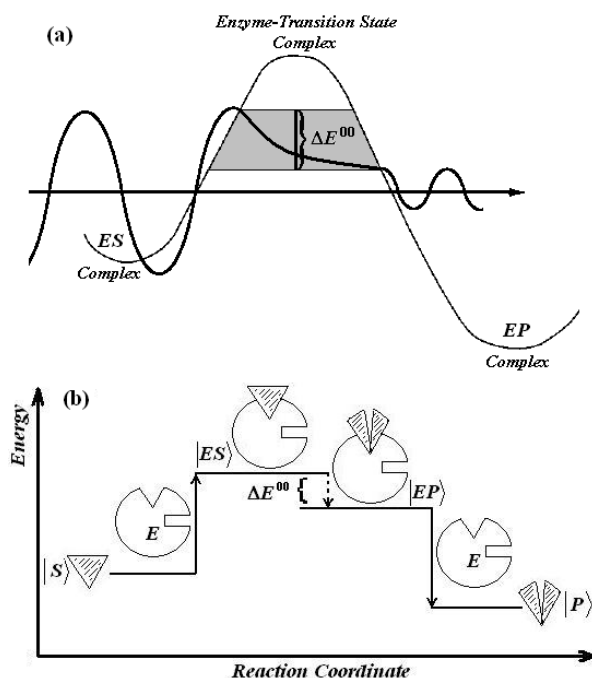
COS4: Enzyme-Substrate Interaction's Logistics

Logistic Enzyme Kinetics

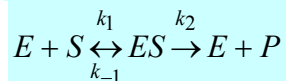One considers the *orthogonal* completion of the substrate probability binding space within the enzymic complexes in a probabilistic form

$$1 = P_{\text{REACT}}([S]_{bind}) + P_{\text{UNREACT}}([S]_{bind})$$

$$P_{\text{REACT}}([S]_{bind}) = \begin{cases} 0 & , & [S]_{bind} \to 0 \\ 1 & , & [S]_{bind} \gg 0 \end{cases}$$

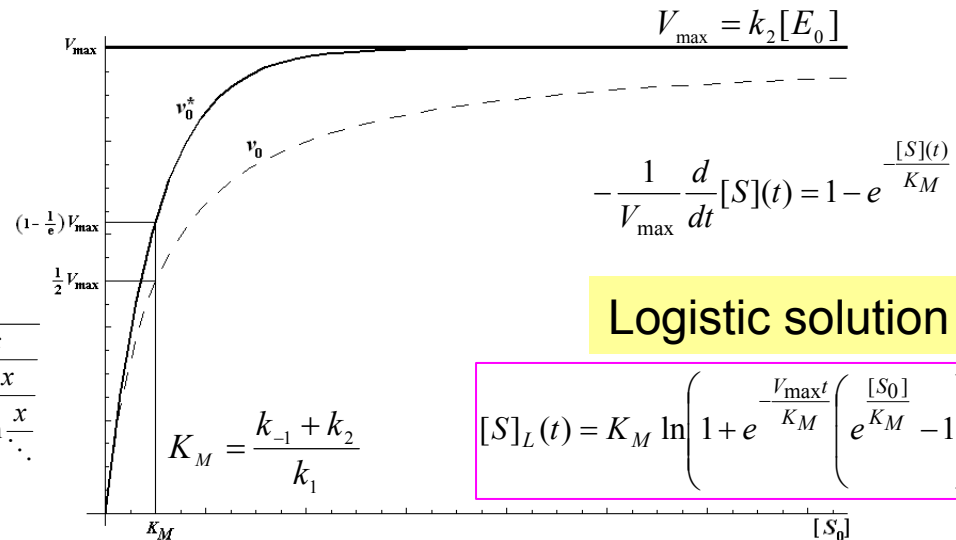$$P_{\text{REACT}}([S](t)) = \frac{v(t)}{V_{\max}} = -\frac{1}{V_{\max}}\frac{d}{dt}[S](t)$$

$$P_{\text{UNREACT}}([S]_{bind}) = \begin{cases} 1 & , & [S]_{bind} \to 0 \\ 0 & , & [S]_{bind} \gg 0 \end{cases}$$

$$P_{\text{UNREACT}}([S](t))^* = \frac{1}{e^{\frac{[S](t)}{K_M}}} \overset{[S](t)\to 0}{\cong} \frac{1}{1+\frac{[S](t)}{K_M}} = P_{\text{UNREACT}}([S](t))^{\text{MM}}$$

$$V_{\max} = k_2[E_0]$$

W-Lambert solution

$$[S]_W(t) = K_M W\left(\frac{[S_0]}{K_M} e^{\frac{[S_0]-V_{\max}t}{K_M}}\right)$$

$$W(x) = \ln\frac{x}{\ln(W(x))} = \ln\frac{x}{\ln\dfrac{x}{\ln(W(x))}} = \ldots = \ln\frac{x}{\ln\dfrac{x}{\ln\dfrac{x}{\ln\dfrac{x}{\ln\frac{x}{\ddots}}}}}$$

$$K_M = \frac{k_{-1}+k_2}{k_1}$$

$$-\frac{1}{V_{\max}}\frac{d}{dt}[S](t) = 1 - e^{\frac{[S](t)}{K_M}}$$

Logistic solution

$$[S]_L(t) = K_M \ln\left(1 + e^{-\frac{V_{\max}t}{K_M}}\left(e^{\frac{[S_0]}{K_M}} - 1\right)\right)$$

Schnell S.; Mendoza C. (1997) Closed form solution for time-dependent enzyme kinetics. *J. Theor. Biol. 187*, 207-212.

Putz M.V.; Lacrămă A.-M.; Ostafe, V. (2007) Introducing logistic enzyme kinetics. J. Optoelectron. Adv. Mater. 9(9), 2910 – 2916.
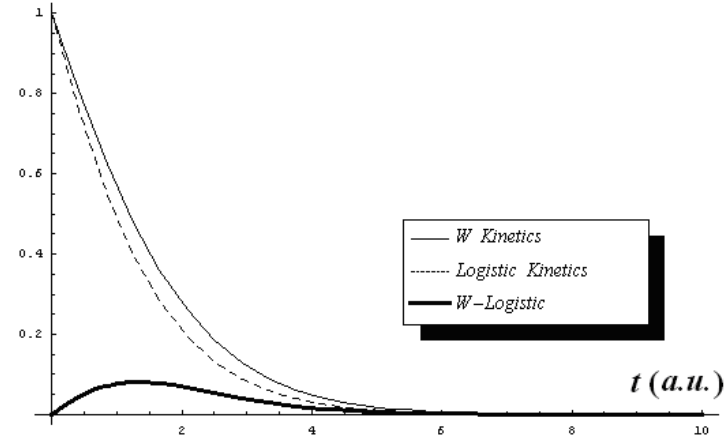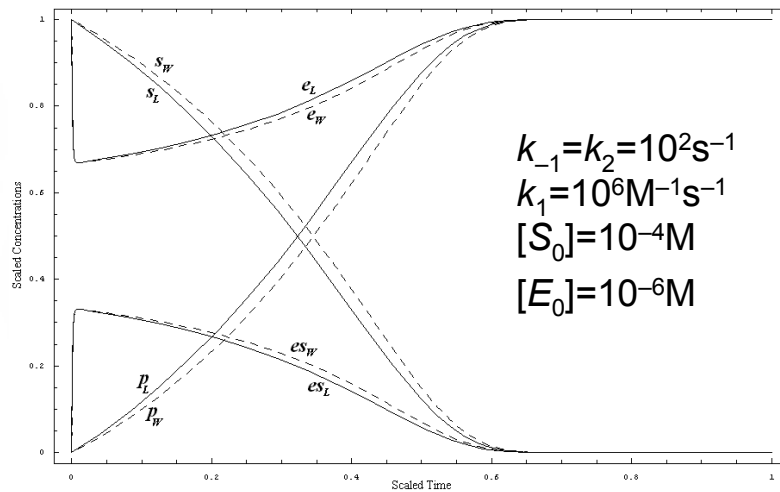
COS4: Enzyme-Substrate Interaction's Logistics

Solving the Enzyme-Substrate Kinetics' Paradox

the logistic transformation

$$f_1 W\left(f_2 e^{f_2} e^{-f_3 t}\right) \rightarrow f_1 \ln\left(1 + \left(e^{f_2} - 1\right) e^{-f_3 t}\right)$$

Putz M.V., Lacrămă, A.-M., Ostafe, V. (**2006**) Full analytic progress curves of the enzymic reactions in vitro. *Int. J. Mol. Sci.* 7(11), 469-484.

$$k_{-1} = k_2 = 10^2 s^{-1}$$
$$k_1 = 10^6 M^{-1} s^{-1}$$
$$[S_0] = 10^{-4} M$$
$$[E_0] = 10^{-6} M$$

the adapted Beer-Lambert law:

$$A_S(t) = a_M l[S](t) \qquad A_0 = a_M l[S]_0$$

the normal absorptivity:

$$a_S(t) = \frac{A_S(t)}{A_0} = \frac{[S](t)}{[S]_0} \qquad a_P(t) = \frac{A_P(t)}{A_0} = \frac{[P](t)}{[S]_0}$$

in vitro:
$$10^{-7} < \varepsilon \equiv \frac{[E]_0}{[S]_0} < 10^{-2}$$

$$a_P(t) = 1 - a_S(t) - \frac{\varepsilon[S](t)}{[S](t) + K_M}$$

in vivo:
$$\varepsilon \geq 10^{-2}$$

$$\Delta a(t) = a_S^W(t) - a_S^{Log}(t) \cong a_P^{Log}(t) - a_P^W(t)$$

COS4: Enzyme-Substrate Interaction's Logistics

Solving the Enzyme-Substrate Kinetics' Paradox

velocity of enzyme reaction $V_{max}=10^{-4}M{\cdot}s^{-1}$ and the Michaelis constant $K_M=2{\cdot}10^{-4}M$
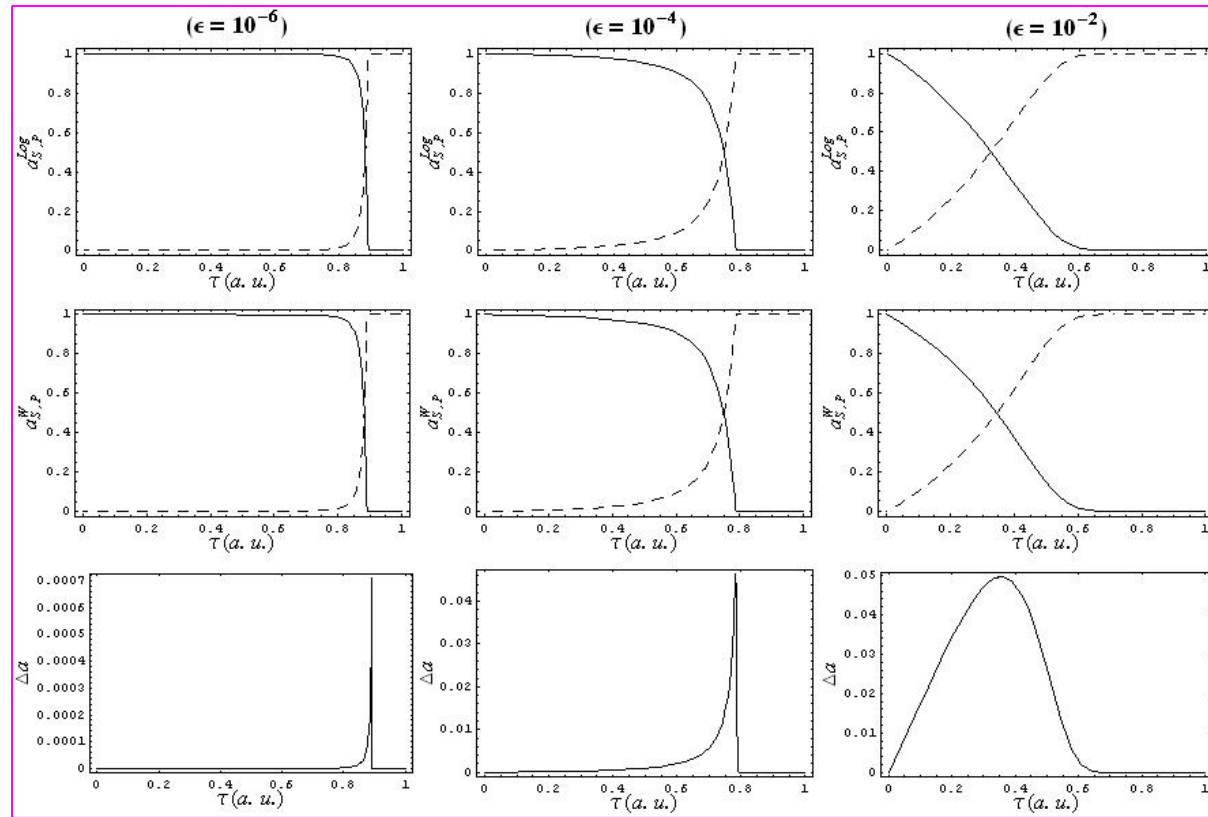
$$\tau = 1 - \frac{1}{\ln(t+e)}$$

$$t = e^{\frac{1}{1-\tau}} - e \rightarrow \begin{cases} 0...\tau \rightarrow 0 \\ \infty...\tau \rightarrow 1 \end{cases}$$

Putz M.V.; Lacrămă A.-M. (**2007**) Enzymatic control of the bio-inspired nanomaterials at the spectroscopic level. J. Optoelectron. Adv. Mater. 9(8), 2529-2534.

COS4: Enzyme-Substrate Interaction's Logistics
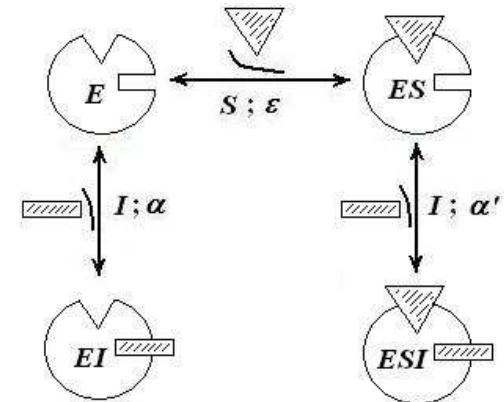
Application to Mixed Inhibition

$$[S](t)^W = \frac{\alpha}{\alpha'} K_M W\left(\frac{\alpha'[E]_0}{\alpha\varepsilon K_M} \exp\left(\frac{\alpha'[E]_0}{\alpha\varepsilon K_M} \right) \exp\left(-\frac{tV_{max}}{\alpha K_M} \right) \right)$$

$$[S]^{Log}(t) = \frac{\alpha}{\alpha'} K_M \ln\left(1 + \left(\exp\left(\frac{\alpha'[E]_0}{\alpha\varepsilon K_M} \right) - 1 \right) \exp\left(-\frac{V_{max}}{\alpha K_M} t \right) \right)$$

$$K_I = \frac{[E][I]_0}{[EI]} \qquad K_{IS} = \frac{[ES][I]_0}{[ESI]}$$

$$\alpha = 1 + \frac{[I]_0}{K_I} \qquad \alpha' = 1 + \frac{[I]_0}{K_{IS}}$$

| *competitive inhibition* | *uncompetitive inhibition* |
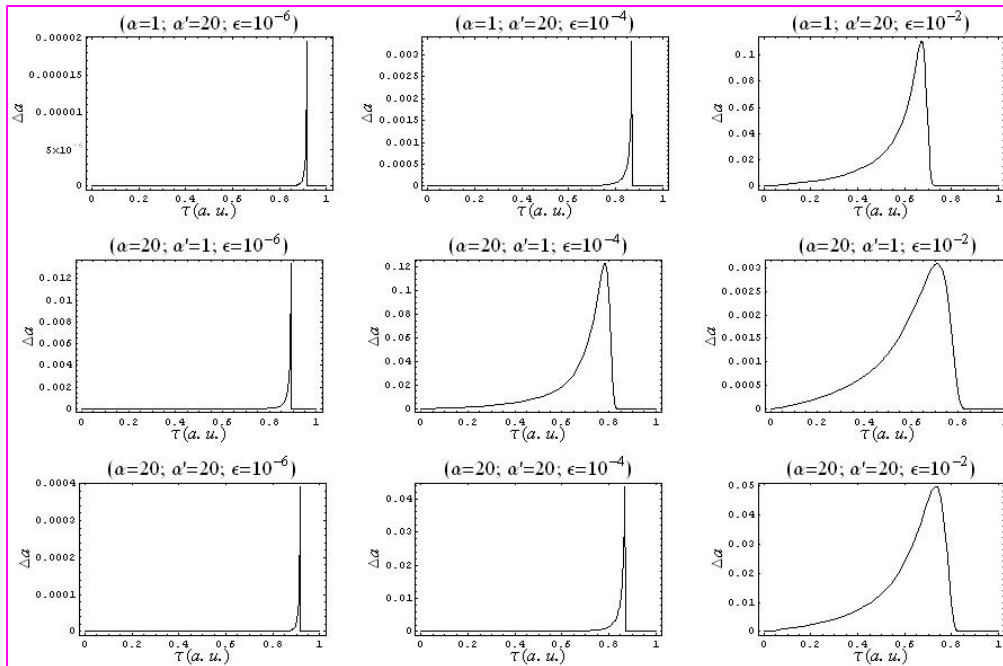
$$\varepsilon \in \left(10^{-6}, 10^{-4}\right) \qquad \Delta\tau^{0\alpha'} < \Delta\tau^{\alpha\alpha'} < \Delta\tau^{00} < \Delta\tau^{\alpha 0}$$

$$\varepsilon \geq 10^{-2} \qquad \Delta\tau^{\alpha 0} < \Delta\tau^{\alpha\alpha'} < \Delta\tau^{00} < \Delta\tau^{0\alpha'}$$

COS4: Enzyme-Substrate Interaction's Logistics

*Quantum in vitro (a) and in vivo (b) energetic diagrams
of the generalized Brownian enzyme-catalyzed reaction*

Relationship between the reaction
rate and the turnover number or
the effective time of reaction (Δt)
via Heisenberg relation

$$\frac{1}{k_{cat}} \propto \Delta t \cong \frac{\hbar}{\Delta E_{tunnelling}} = \frac{\hbar}{k_B T}$$

$$\varepsilon \in \left(10^{-6}, 10^{-4}\right)$$

$$\Delta E^{0\alpha'} > \Delta E^{\alpha\alpha'} > \Delta E^{00} > \Delta E^{\alpha 0}$$

$$\varepsilon \geq 10^{-2}$$

$$\Delta E^{\alpha 0} > \Delta E^{\alpha\alpha'} > \Delta E^{00} > \Delta E^{0\alpha'}$$
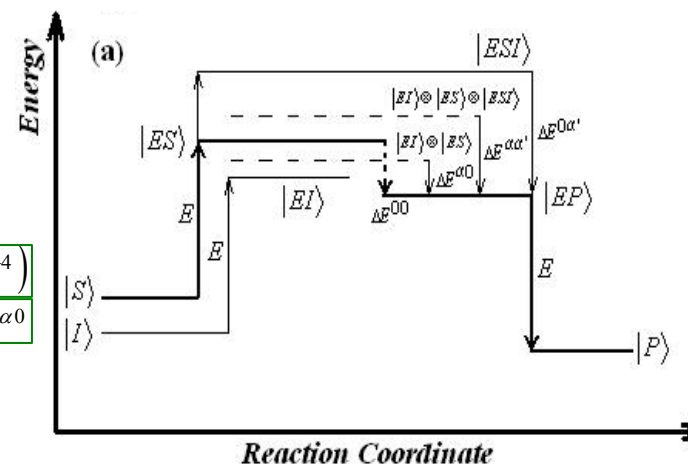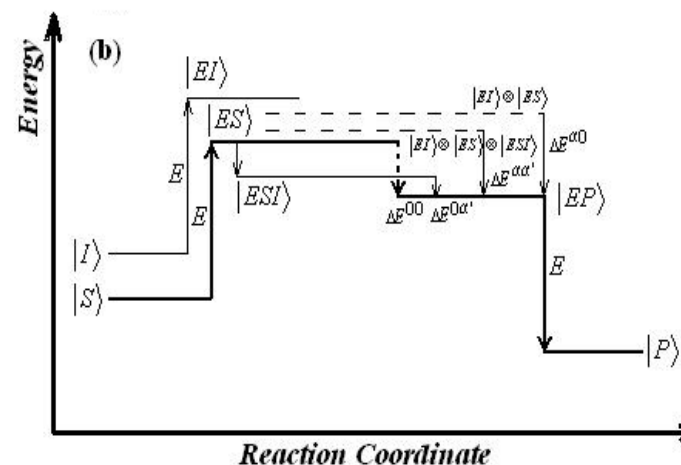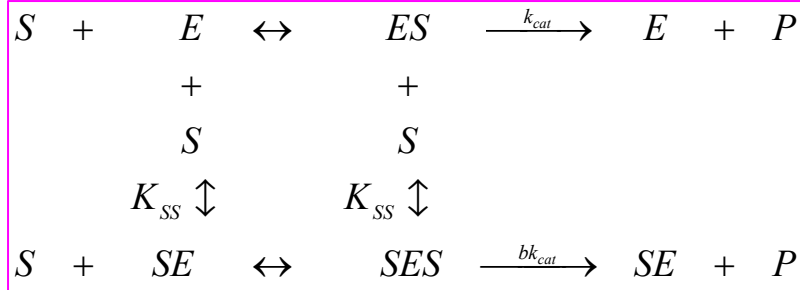
COS4: Enzyme-Substrate Interaction's Logistics

On Haldane-Radić Logistic Enzyme Kinetics

$$S + E \leftrightarrow ES \xrightarrow{k_{cat}} E + P$$
$$+ \qquad +$$
$$S \qquad S$$
$$K_{SS} \updownarrow \qquad K_{SS} \updownarrow$$
$$S + SE \leftrightarrow SES \xrightarrow{bk_{cat}} SE + P$$

$$K_{SS} \to \infty \Leftrightarrow b \to 1$$

$$E + S \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} ES \xrightarrow{k_2} E + P$$

hydrolysis of various concentrations of butyrylthiocholine by a fixed concentration of butyrylcholinesterase

$$K_M = \frac{[E]\cdot[S]}{[ES]} = \frac{[SE]\cdot[S]}{[SES]}, K_{SS} = \frac{[SE]\cdot[S]}{[SES]} = \frac{[E]\cdot[S]}{[SE]}$$

$$V_{max} = k_{cat}[E_0]$$

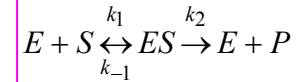$$v = k_{cat}[ES] + bk_{cat}[SES]$$

$$v = k_{cat} \frac{[E_0]\left(1 + \frac{b[S]}{K_{SS}}\right)}{\left(1 + \frac{K_M}{[S]}\right)\left(1 + \frac{[S]}{K_{SS}}\right)} = \frac{V_{max}[S]}{K_M + [S]} \frac{(K_{SS} + b[S])}{(K_{SS} + [S])}$$

$$[S]_L^{HR}(t) = \frac{K_{SS}}{1 - b + K_{SS}/K_M} \ln\left(1 + \left(e^{\left(\frac{1}{K_M} + \frac{1-b}{K_{SS}}\right)[S_0]} - 1\right)e^{-\frac{V_{max}}{K_M}t}\right)$$

$$[S]_L^{HR}(t) = \begin{cases} [S_0], & t \to 0 \\ 0, & t \to \infty \end{cases}$$
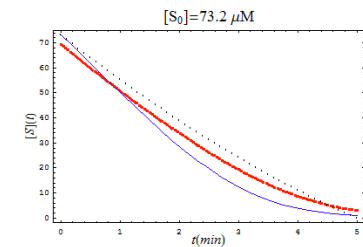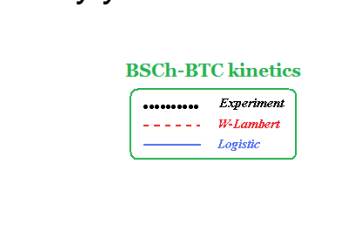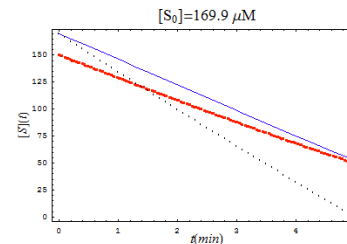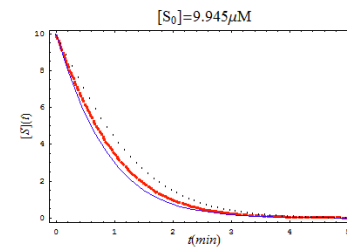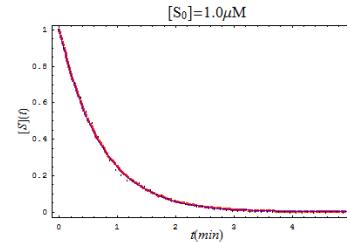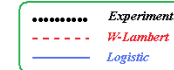
Putz M.V. (**2011**) On reducible character of Haldane-Radić enzyme kinetics to conventional and logistic Michaelis-Menten models. *Molecules* 16(4), 3128-3145.

[S_0]=1.0μM

BSCh-BTC kinetics
- .... Experiment
- - - - - W-Lambert
- —— Logistic

[S_0]=9.945μM

[S_0]=73.2 μM

[S_0]=169.9 μM

[S_0]=176.86 μM

$K_M = 7.5 μM$; $K_{SS} = 8700 μM$; $V_{max} = 7.2 μM/min$; $b = 3$

COS4: Enzyme-Substrate Interaction's Logistics-Perspectives

Chemical Reactivity Logistical Driving Biological Activity

$$A = \ln\left(\frac{1}{EC_{50}}\right)$$

$$EC_{50} = \exp(-\|A\|)$$

$$S_0 = \exp(-\|A^*\|)$$

"receptor time"

$$\tau = 1/2 \qquad \Delta t_\infty = 4e^2$$

$$v = -\frac{d}{dt}S(t) \rightarrow -\frac{S_t - S_0}{\Delta t} \qquad v_{max} = \frac{S_0}{\Delta t_\infty}$$

$$v_{max} = \frac{1}{4}\exp(-\|A^*\| - 2) = \frac{S_0}{4e^2}$$

$$[S]_L(t) = e^{-\|A\|}\ln\left(1 + e^{-\frac{\exp(\|A\|-\|A^*\|)}{4e^2}t}\left(e^{\exp(\|A\|-\|A^*\|)} - 1\right)\right)$$

Activity	Structural predictor variables					
$\lvert A_{OBS(ERVED)}\rangle$	$\lvert X_0\rangle$	$\lvert X_1\rangle$	$\cdots$	$\lvert X_k\rangle$	$\cdots$	$\lvert X_M\rangle$
$A_{1\text{-}OBS}$	1	x_{11}	$\cdots$	x_{1k}	$\cdots$	x_{1M}
$A_{2\text{-}OBS}$	1	x_{21}	$\cdots$	x_{2k}	$\cdots$	x_{2M}
$\vdots$	$\vdots$	$\vdots$		$\vdots$		$\vdots$
$A_{N\text{-}OBS}$	1	x_{N1}	$\cdots$	x_{Nk}	$\cdots$	x_{NM}

$$\lvert A^*\rangle^{ENDPOINT} = B_0\lvert X_0\rangle + B_1\lvert X_1\rangle + \ldots + B_M\lvert X_M\rangle$$

$$\|A^*\| = \sqrt{\langle A^* \mid A^*\rangle} = \sqrt{\sum_{k=0}^{M} B_k^2 \langle X_k \mid X_k\rangle} = \sqrt{\sum_{k=0}^{M} B_k^2\left(\sum_{j=1}^{N} x_{kj}^2\right)} = \sqrt{\sum_{j=1}^{N}\left(A_j^*\right)^2}$$
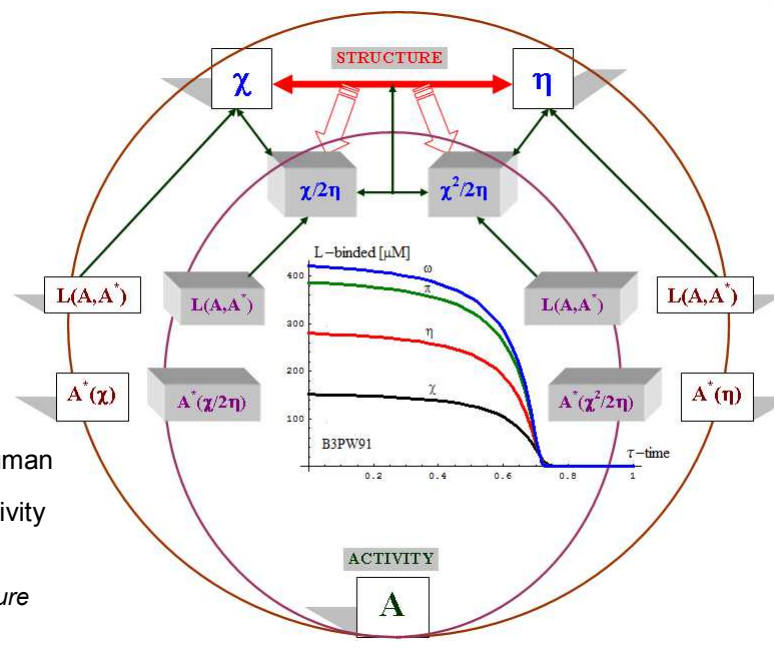

Example: chlorinated polycyclic aromatic hydrocarbon action on human breast cancer MCF-7 cells as measured by EROD/P450 (CYP) activity

Putz M.V., Putz A.M. (**2013**) DFT Chemical Reactivity Driven by Biological Activity: Applications for the Toxicological Fate of Chlorinated PAHs. *Structure and Bonding* 150, 181–232; DOI: 10.1007/978-3-642-32750-6_6

Conclusions COS4:
Orthogonal Space of Enzyme-Substrate Interaction's Logistics

Full Analytic Progress Curves of Enzymic Reactions in Vitro

Mihai V. Putz [1],*, Ana-Maria Lacrămă [2] and Vasile Ostafe [2]

Enzymatic control of the bio-inspired nanomaterials at the spectroscopic level

M. V. PUTZ*, A.-M. LACRĂMĂ[a]

$$1 = P_{\text{REACT}}([S]_{bind}) + P_{\text{UNREACT}}([S]_{bind})$$

$$f_1 W\left(f_2 e^{f_2} e^{-f_3 t}\right) \rightarrow f_1 \ln\left(1 + \left(e^{f_2} - 1\right)e^{-f_3 t}\right)$$

Article

On the Reducible Character of Haldane-Radić Enzyme Kinetics to Conventional and Logistic Michaelis-Menten Models

Mihai V. Putz

DFT Chemical Reactivity Driven by Biological Activity: Applications for the Toxicological Fate of Chlorinated PAHs

Mihai V. Putz and Ana-Maria Putz

COS5: Chemical Structure-Biological Activity Correlation

OECD-QSAR Principles:

OECD-QSAR-1: a defined endpoint
OECD-QSAR-2: an unambiguous algorithm
OECD-QSAR-3: a defined domain of applicability
OECD-QSAR-4: appropriate measures of goodness-of–fit, robustness and predictivity
OECD-QSAR-5: a mechanistic interpretation, if possible
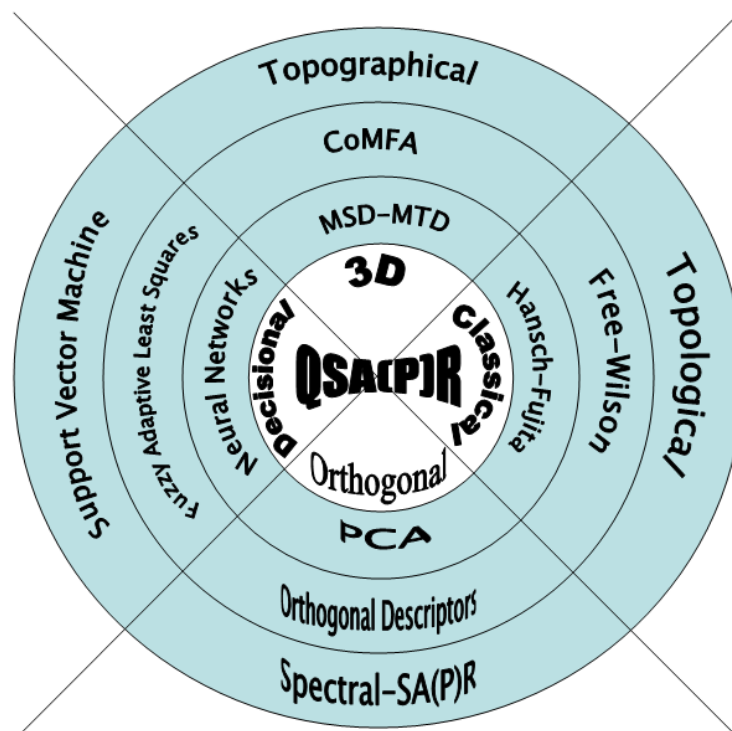
Putz M.V. Editor (**2012**) QSAR & SPECTRAL-SAR in Computational Ecotoxicology. Apple Academic Press: New Jersey, USA (ISBN: 978-1-926895-13-0), pp. 256; **Putz M.V.; Putz A.M.; Barou R.** (**2011**) Spectral-SAR realization of OECD-QSAR principles. *Int. J. Chem. Model.* 3(3), 173-190.

OECD-QSAR-2: Spectral-SAR Algorithm on Chemical Hilbert Space

Activity	Structural predictor variables				
$\left\|Y_{OBS(ERVED)}\right\rangle$	$\left\|X_0\right\rangle$	$\left\|X_1\right\rangle$ $\cdots$	$\left\|X_k\right\rangle$	$\cdots$	$\left\|X_M\right\rangle$
$y_{1\text{-}OBS}$	1	x_{11} $\cdots$	x_{1k}	$\cdots$	x_{1M}
$y_{2\text{-}OBS}$	1	x_{21} $\cdots$	x_{2k}	$\cdots$	x_{2M}
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
$y_{N\text{-}OBS}$	1	x_{N1} $\cdots$	x_{Nk}	$\cdots$	x_{NM}

The *orthogonalization feature* of quantum states

$$\left\langle Y_{PRED} \mid prediction\ error \right\rangle = 0$$

$$\left\langle X_{i=\overline{0,M}} \mid prediction\ error \right\rangle = 0$$

The (quantum) *superposition principle*

$$\left\|Y_{OBS(ERVED)}\right\rangle = \left\|Y_{PRED(ICTED)}\right\rangle + \left\|prediction\ error\right\rangle$$

$$= B_0\left\|X_0\right\rangle + B_1\left\|X_1\right\rangle + ... + B_k\left\|X_k\right\rangle + ... + B_M\left\|X_M\right\rangle + \left\|prediction\ error\right\rangle$$

$$
\begin{vmatrix}
\left\|Y_{PRED}\right\rangle & \omega_0 & \omega_1 & \cdots & \omega_k & \cdots & \omega_M \\
\left\|X_0\right\rangle & 1 & 0 & \cdots & 0 & \cdots & 0 \\
\left\|X_1\right\rangle & r_0^1 & 1 & \cdots & 0 & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & & \vdots \\
\left\|X_k\right\rangle & r_0^k & r_1^k & \cdots & 1 & \cdots & 0 \\
\vdots & \vdots & \vdots & \vdots & \vdots & & \vdots \\
\left\|X_M\right\rangle & r_0^M & r_1^M & \cdots & r_k^M & \cdots & 1
\end{vmatrix} = 0
$$

Gram-Schmidt orthogonalization

$$\left\|\Omega_0\right\rangle = \left\|X_0\right\rangle$$

$$\left\|\Omega_k\right\rangle = \left\|X_k\right\rangle - \sum_{i=0}^{k-1} r_i^k \left\|\Omega_i\right\rangle \qquad r_i^k = \frac{\left\langle X_k \mid \Omega_i \right\rangle}{\left\langle \Omega_i \mid \Omega_i \right\rangle} \qquad k = \overline{1,M}$$

$$\left\|Y_{PRED}\right\rangle = \omega_0\left\|\Omega_0\right\rangle + \omega_1\left\|\Omega_1\right\rangle + ... + \omega_k\left\|\Omega_k\right\rangle + ... + \omega_M\left\|\Omega_M\right\rangle$$

$$\omega_k = \frac{\left\langle \Omega_k \mid Y \right\rangle}{\left\langle \Omega_k \mid \Omega_k \right\rangle} \qquad k = \overline{0,M}$$

$$
\begin{cases}
\left\|Y_{PRED}\right\rangle = \omega_0\left\|\Omega_0\right\rangle + \omega_1\left\|\Omega_1\right\rangle + ... + \omega_k\left\|\Omega_k\right\rangle + ... + \omega_M\left\|\Omega_M\right\rangle \\
\left\|X_0\right\rangle = 1\cdot\left\|\Omega_0\right\rangle + 0\cdot\left\|\Omega_1\right\rangle + ... + 0\cdot\left\|\Omega_k\right\rangle + ... + 0\cdot\left\|\Omega_M\right\rangle \\
\left\|X_1\right\rangle = r_0^1\left\|\Omega_0\right\rangle + 1\cdot\left\|\Omega_1\right\rangle + ... + 0\cdot\left\|\Omega_k\right\rangle + ... + 0\cdot\left\|\Omega_M\right\rangle \\
\cdots \\
\left\|X_k\right\rangle = r_0^k\left\|\Omega_0\right\rangle + r_1^k\left\|\Omega_1\right\rangle + ... + 1\cdot\left\|\Omega_k\right\rangle + ... + 0\cdot\left\|\Omega_M\right\rangle \\
\cdots \\
\left\|X_M\right\rangle = r_0^M\left\|\Omega_0\right\rangle + r_1^M\left\|\Omega_1\right\rangle + ... + r_k^M\left\|\Omega_k\right\rangle + ... + 1\cdot\left\|\Omega_M\right\rangle
\end{cases}
$$

Putz M.V., Lacrămă, A.-M. (**2007**) Introducing Spectral Structure Activity Relationship (S-SAR) analysis. Application to ecotoxicology. *Int. J. Mol. Sci.* 8(5), 363-391.

COS5: Chemical Structure-Biological Activity Correlation

OECD-QSAR3: Extending Spectral-SAR to composed structures

The four most important classes of ionic liquids based on the reference cation:

(1) imidazolium, (2) pyridinium-, (3) phosphonium-, (4) ammonium-

Lacrămă, A.-M., Putz M.V., Ostafe, V. (2007) A Spectral-SAR model for the anionic-cationic interaction in ionic liquids: application to Vibrio fischeri ecotoxicity. *Int. J. Mol. Sci.* 8(8), 842-863.
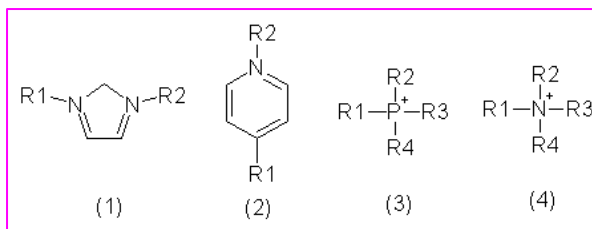
Putz A.M., Putz M.V. (2013) "Spectral-Structure Activity Relationship (Spectral-SAR) Assessment of Ionic Liquids' in Silico Ecotoxicity", in "*IONIC LIQUIDS - NEW ASPECTS FOR THE FUTURE*", Jun-ichi Kadokawa (Ed.), InTech, Inc., Rijeka-New York-Shanghai, Croatia-USA-China, ISBN: 978-953-51-0937-2, Chapter 4 (DOI:10.5772/51657), pp. 85-126

|0+> model

$$\left|Y_{AC}\right\rangle^{0+} = \hat{O}_{S-SAR}\left|0+\right\rangle = \hat{O}_{S-SAR}\, f\left(\{X_A\}, \{X_C\}\right)$$

Hansch specification of the spectral vectors:

$$f\left(LogP_A, LogP_C\right) \equiv LogP_{AC} = \log\left(e^{LogP_A} + e^{LogP_C}\right) \in \{X_{1AC}\}$$

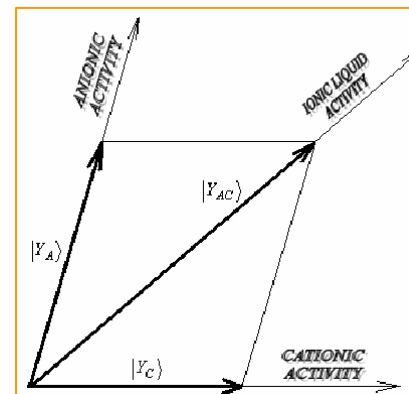$$f\left(POL_A, POL_C\right) \equiv POL_{AC} = \left(POL_A^{1/3} + POL_C^{1/3}\right)^3 \in \{X_{2AC}\}$$

$$f\left(E_A, E_C\right) \equiv E_{AC} = E_A + E_C - 627.71\frac{q_A q_C}{POL_{AC}^{1/3}} \in \{X_{3AC}\} \quad \text{[kcal/mol]}$$

$$\cos\theta_{AC} = \frac{\langle Y_C | Y_A\rangle}{\|Y_C\rangle\|\|Y_A\rangle\|} = \frac{\sum\limits_{i=1}^{N} y_{iC} y_{iA}}{\sqrt{\sum\limits_{i=1}^{N} y_{iC}^2 \sum\limits_{i=1}^{N} y_{iA}^2}} \begin{cases} \geq 0.707107 \dots |0+\rangle\ MODEL \\ < 0.707107 \dots |1+\rangle\ MODEL \end{cases}$$

|1+> model

$$\left|Y_{AC}\right\rangle^{1+} = \left|1+\right\rangle = \left|Y_A\right\rangle + \left|Y_C\right\rangle = \hat{O}_{S-SAR}\left[g\left(\{X_A\}\right) + g\left(\{X_C\}\right)\right]$$

$$\{X_{A,C}\} = \{LogP_{A,C}, POL_{A,C}, E_{TOT(A,C)}\}$$

COS5: Chemical Structure-Biological Activity Correlation

OECD-QSAR4: Algebraic Correlation Factor

Timişoara Theorem on the Algebraic Spectral-SAR correlation

$$Y_{i-OBS} = Y_{i-PRED} + pe_i$$

$$Y_{i-OBS}^2 = Y_{i-PRED}^2 + pe_i^2 + 2Y_{i-PRED} \cdot pe_i$$

$$\sum_{i=1}^{N} Y_{i-OBS}^2 = \sum_{i=1}^{N} Y_{i-PRED}^2 + \sum_{i=1}^{N} pe_i^2 + 2\sum_{i=1}^{N} Y_{i-PRED} \cdot pe_i$$

$$\sum_{i=1}^{N} Y_{i-PRED} \cdot pe_i = \langle Y_{PRED} | pe \rangle = 0$$

$$\sum_{i=1}^{N} Y_{i-OBS}^2 = \sum_{i=1}^{N} Y_{i-PRED}^2 + \sum_{i=1}^{N} pe_i^2$$

$$\sum_{i=1}^{N} Y_{i-OBS}^2 = \sum_{i=1}^{N} Y_{i-PRED}^2 + \sum_{i=1}^{N} (Y_{i-OBS} - Y_{i-PRED})^2$$

$$\sum_{i=1}^{N} Y_{i-PRED}^2 = \sum_{i=1}^{N} Y_{i-OBS} \cdot Y_{i-PRED}$$

$$\left\| Y_{PRED} \rangle \right\|^2 = \langle Y_{OBS} | Y_{PRED} \rangle$$

$$\left\| Y_{PRED} \rangle \right\|^2 \leq \left\| Y_{OBS} \rangle \right\| \cdot \left\| Y_{PRED} \rangle \right\|$$

$$\left\| Y_{PRED} \rangle \right\| \leq \left\| Y_{OBS} \rangle \right\|$$

$$RA \equiv r_{ALGEBRAIC} = \frac{\left\| Y_{PRED} \rangle \right\|}{\left\| Y_{OBS} \rangle \right\|} \leq 1$$

$$r_{S-SAR}^{ALGEBRAIC} \geq r_{QSAR}^{STATISTIC}$$

Proof:

$$\frac{\langle Y_{PRED} | Y_{PRED} \rangle}{\langle Y_{OBS} | Y_{OBS} \rangle} \geq 1 - \frac{\langle Y_{OBS} - Y_{PRED} | Y_{OBS} - Y_{PRED} \rangle}{\langle Y_{OBS} - \overline{Y}_{OBS} | Y_{OBS} - \overline{Y}_{OBS} \rangle}$$

$$\overline{Y}_{OBS} = \frac{1}{N} \sum_{i=1}^{N} y_{i-OBS} \qquad \left| \overline{Y}_{OBS} \rangle = \left(\frac{1}{N} \sum_{i=1}^{N} y_{i-OBS} \right) \right| 1\,1\,\ldots\,1_N \rangle$$

$$\langle Y_{PRED} | Y_{PRED} \rangle \langle Y_{OBS} - \overline{Y}_{OBS} | Y_{OBS} - \overline{Y}_{OBS} \rangle$$
$$> \langle Y_{OBS} | Y_{OBS} \rangle \left[\langle Y_{OBS} - \overline{Y}_{OBS} | Y_{OBS} - \overline{Y}_{OBS} \rangle - \langle Y_{OBS} - Y_{PRED} | Y_{OBS} - Y_{PRED} \rangle \right]$$

$$2\langle Y_{PRED} | Y_{PRED} \rangle \langle Y_{OBS} | Y_{OBS} \rangle - 2\langle Y_{OBS} | Y_{OBS} \rangle \underbrace{\langle Y_{OBS} | Y_{PRED} \rangle}_{\langle Y_{PRED} | Y_{PRED} \rangle}$$
$$+ \underbrace{\left[\langle Y_{OBS} | Y_{OBS} \rangle - \langle Y_{PRED} | Y_{PRED} \rangle \right]}_{\geq 0} \left[2\langle Y_{OBS} | \overline{Y}_{OBS} \rangle - \langle \overline{Y}_{OBS} | \overline{Y}_{OBS} \rangle \right] > 0$$

$$2\langle Y_{OBS} | \overline{Y}_{OBS} \rangle > \langle \overline{Y}_{OBS} | \overline{Y}_{OBS} \rangle$$

$$2\sum_{i=1}^{N} \left(y_{i-OBS} \frac{1}{N} \sum_{i=1}^{N} y_{i-OBS} \right) > \sum_{i=1}^{N} \left(\frac{1}{N} \sum_{i=1}^{N} y_{i-OBS} \right) \left(\frac{1}{N} \sum_{i=1}^{N} y_{i-OBS} \right)$$

$$\frac{2}{N} \left(\sum_{i=1}^{N} y_{i-OBS} \right)^2 > \frac{1}{N} \left(\sum_{i=1}^{N} y_{i-OBS} \right)^2$$

Putz M.V.; Putz A.M. (**2011**) Timisoara Spectral – Structure Activity Relationship (Spectral-SAR) algorithm: from statistical and algebraic fundamentals to quantum consequences. In: Quantum Frontiers of Atoms and Molecules, Ed. Putz M.V., NOVA Science Publishers, Inc.: New York (ISBN: 978-1-61668-158-6), 539-580.

COS5: Chemical Structure-Biological Activity Correlation

OECD-QSAR4: Algebraic Correlation Factor

### Application on *Tetrahymena pyriformis*

ecotoxic activity to *Tetrahymena pyriformis*, determined in a population growth impairment assay with a 40 h static design and population density measured spectrophotometrically as the endpoint A=Log (1/IGC50)

1	methanol
2	ethanol
3	butan-1-ol
4	butanone
5	pentan-3-one
6	phenol
7	aniline
8	3-cresol
9	4-methoxiphenol
10	2-hydroxyaniline
11	Benzaldehyde
12	2-cresol
13	3,4-dimeyhylphenol
14	3-nitrotoluene
15	4-chlorophenol
16	2,4-dinitroaniline
17	2-methyl-1-4-naphtoquinone
18	1,2-dichlorobenzene
19	2,4-dinitrophenol
20	1,4-dinitrobenzene
21	2,4-dinitrotoluene
22	2,6-ditertbutil 4-methyl phenol
23	2,3,5,6-tetrachloroaniline
24	penthaclorophenol
25	phenylazophenol
26	pentabromophenol

A	$|1\rangle$	$Log\,P$	POL	E_{TOT}
$|Y\rangle$	$|X_0\rangle$	$|X_1\rangle$	$|X_2\rangle$	$|X_3\rangle$

	Ia	Ib	Ic	IIa	IIb	IIc	III
$\left\|\|Y\rangle^{PREDICTED}\right\|$	3.86176	6.22803	6.0607	6.24858	6.32297	6.43641	6.44557
$r_{S-SAR}^{STATISTIC}$	0.53905	0.90759	0.88193	0.91074	0.92214	0.9395	0.9409
$r_{S-SAR}^{ALGEBRAIC}$	0.56521	0.91154	0.88705	0.91455	0.92543	0.94204	0.94338

Models	Vectors
Ia	$|X_0\rangle, |X_1\rangle$
Ib	$|X_0\rangle, |X_2\rangle$
Ic	$|X_0\rangle, |X_3\rangle$
IIa	$|X_0\rangle, |X_1\rangle, |X_2\rangle$
IIb	$|X_0\rangle, |X_1\rangle, |X_3\rangle$
IIc	$|X_0\rangle, |X_2\rangle, |X_3\rangle$
III	$|X_0\rangle, |X_1\rangle, |X_2\rangle, |X_3\rangle$
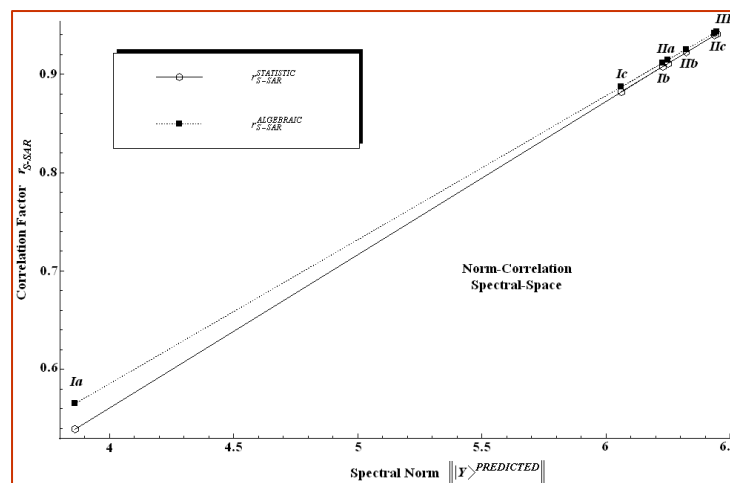
Putz M.V., Lacrămă, A.-M. (**2007**) Introducing Spectral Structure Activity Relationship (S-SAR) analysis. Application to ecotoxicology. *Int. J. Mol. Sci.* 8(5), 363-391.

# COS5: Chemical Structure-Biological Activity Correlation

OECD-QSAR5: Spectral-SAR Map of Mechanistic Interaction

$$\hat{O}_{S-SAR}: \begin{cases} Det(|Y\rangle, |X_0\rangle, |X_1\rangle, ..., |X_M\rangle) = 0, \|Y\|, r_{S-SAR}^{ALGEBRAIC}, \\ \delta\left[A_{(\|\cdot\|, r)}, B_{(\|\cdot\|, r)}\right] = 0, \langle \alpha, \beta, \gamma, ...\rangle, \begin{array}{l} A, B : PREDICTED\ ENDPOINTS \\ \alpha, \beta, \gamma, ... : SPECTRAL\ PATHS \end{array} \end{cases}$$

$$0 = \delta[l, l'] = \delta\sqrt{\left(\|Y_l\rangle\| - \|Y_{l'}\rangle\|\right)^2 + \left(R_l - R_{l'}\right)^2}, \quad l, l' : ENDPOINTS\ MODELS$$

the shortest path the faster biological-chemical interaction is activated,

thus assuring the more effective (toxico-) chemical effect on biological system

Path	Value	
	Statistic	Algebraic
Ia-IIa-III	2.61485	2.61132
Ia-IIb-III	2.61485	2.61132
Ia-IIc-III	2.61485	2.61132
Ib-IIa-III	**0.220072**	**0.219855**
Ib-IIb-III	**0.220072**	**0.219855**
Ib-IIc-III	**0.220072**	**0.219855**
Ic-IIa-III	0.389359	0.388969
Ic-IIb-III	0.389359	0.388969
Ic-IIc-III	0.389359	0.388969
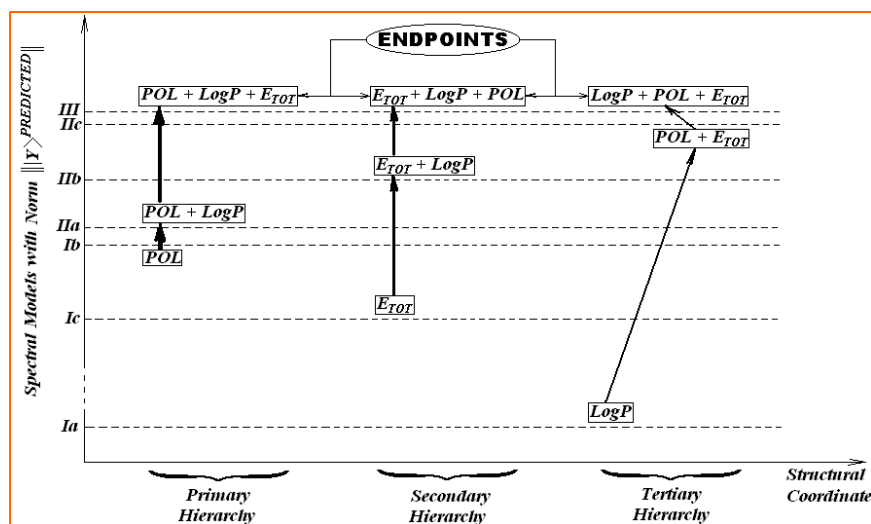
Putz M.V., Lacrămă, A.-M. (**2007**) Introducing Spectral Structure Activity Relationship (S-SAR) analysis. Application to ecotoxicology. *Int. J. Mol. Sci.* 8(5), 363-391; **Lacrămă, A.-M., Putz M.V., Ostafe, V.** (**2008**) Designing a spectral structure-activity ecotoxico-logistical battery. In: Advances in Quantum Chemical Bonding Structures, Ed. Putz M.V., Transworld Research Network: Kerala (ISBN: 978-81-7895-306-9), 389-419; **Chicu S.A.; Putz M.V.** (**2009**) Köln-Timişoara molecular activity combined models toward interspecies toxicity assessment. *Int. J. Mol. Sci.* 10(10), 4474-4497.

COS5: Chemical Structure-Biological Activity Correlation-Perspectives

The Catastrophe-QSAR Approach

Model	QSAR Equation
GROUP I: with one descriptor only, $\lvert X_1\rangle$	
QSAR-(I)	$\lvert Y_I\rangle = a_0\lvert 1\rangle + a_{11}\lvert X_1\rangle$
Fold	$\lvert Y_F\rangle = f_0\lvert 1\rangle + f_{11}\lvert X_1\rangle + f_{13}\lvert X_1^3\rangle$
Cusp	$\lvert Y_C\rangle = c_0\lvert 1\rangle + c_{11}\lvert X_1\rangle + c_{12}\lvert X_1^2\rangle + c_{14}\lvert X_1^4\rangle$
Swallow tail	$\lvert Y_{ST}\rangle = s_0\lvert 1\rangle + s_{11}\lvert X_1\rangle + s_{12}\lvert X_1^2\rangle + s_{13}\lvert X_1^3\rangle + s_{15}\lvert X_1^5\rangle$
Butterfly	$\lvert Y_B\rangle = b_0\lvert 1\rangle + b_{11}\lvert X_1\rangle + b_{12}\lvert X_1^2\rangle + b_{13}\lvert X_1^3\rangle + b_{14}\lvert X_1^4\rangle + b_{16}\lvert X_1^6\rangle$
GROUP II: with two descriptors, $\lvert X_1\rangle$, $\lvert X_2\rangle$	
QSAR-(II)	$\lvert Y_{II}\rangle = q_0\lvert 1\rangle + q_{11}\lvert X_1\rangle + q_{21}\lvert X_2\rangle$
Hyperbolic umbilic	$\lvert Y_{HU}\rangle = h_0\lvert 1\rangle + h_{11}\lvert X_1\rangle + h_{21}\lvert X_2\rangle + h_{1121}\lvert X_1 X_2\rangle + h_{13}\lvert X_1^3\rangle + h_{23}\lvert X_2^3\rangle$
Elliptic umbilic	$\lvert Y_{EU}\rangle = e_0\lvert 1\rangle + e_{11}\lvert X_1\rangle + e_{21}\lvert X_2\rangle + e_{12}\lvert X_1^2\rangle + e_{22}\lvert X_2^2\rangle + e_{1122}\lvert X_1 X_2^2\rangle + e_{13}\lvert X_1^3\rangle$
Parabolic umbilic	$\lvert Y_{PU}\rangle = p_0\lvert 1\rangle + p_{11}\lvert X_1\rangle + p_{21}\lvert X_2\rangle + p_{12}\lvert X_1^2\rangle + p_{22}\lvert X_2^2\rangle + p_{1221}\lvert X_1^2 X_2\rangle + p_{24}\lvert X_2^4\rangle$

Gaussian mapping (Putz et al., 2011)

$$Y_{i=1,N}^{\Gamma/QSAR}(X_1,...X_M) = Y_{i=1,N}^{QSAR}(X_1,...X_M) \pm Y_{i=1,N}^{M/\Gamma/QSAR}(X_2,...X_M)$$

$$Y_{i=1,\overline{N}}^{M/\Gamma/QSAR}(X_2,...X_M) = \sum_{j=2}^{M}\frac{1}{\sqrt{\pi}}\exp\left(-\frac{X_j^2}{4\sigma_{i=1,\overline{N}}}\right)$$

$$Y_{i=1,\overline{N}}^{\Gamma/QSAR}(X_1,...X_M) \xrightarrow{\sigma_{i=1,\overline{N}}\to 0} Y_{i=1,\overline{N}}^{QSAR}(X_1,...X_M)$$

$$Y_{i=1,\overline{N}}^{\Gamma/QSAR}(X_1,..X_M) \xrightarrow{\sigma_{i=1,\overline{N}}\to\infty} Y_{i=1,\overline{N}}^{QSAR}(X_1,..X_M) \pm \widetilde{X}_2^2 \pm ... \pm \widetilde{X}_M^2$$

Putz M.V.; Lazea M.; Putz A.M.; Duda-Seiman C. (2011) Introducing Catastrophe-QSAR. Application on modeling molecular mechanisms of pyridinone derivative-type HIV non-nucleoside reverse transcriptase inhibitors. *Int. J. Mol. Sci.* 12(12), 9533-9569.

catastrophe transformation

$$Y^{\infty/\Gamma/QSAR} = \int_0^\infty \frac{1}{\sqrt{\pi}}\exp\left(-\frac{X^2}{4\sigma}\right)dX = \sqrt{\sigma}$$

$$R_\Gamma = \sqrt{1 - \frac{1}{\sigma_A}\sum_{i=1}^{N}\left(A_i - Y_i^{\Gamma/QSAR}\right)^2}$$

$$= \sqrt{R_0^2 - \frac{1}{\sigma_A}\sum_{i=1}^{N}\left(Y_i^{M/\Gamma/QSAR}\right)^2 + \frac{2}{\sigma_A}\sum_{i=1}^{N}\left(A_i - Y_i^{QSAR}\right)\left(Y_i^{M/\Gamma/QSAR}\right)}$$

$$\leq \sqrt{R_0^2 - \frac{1}{\sigma_A}\sum_{i=1}^{N}\left(Y_i^{M/\Gamma/QSAR}\right)^2 + 2\sqrt{\frac{1}{\sigma_A}\sum_{i=1}^{N}\left(A_i - Y_i^{QSAR}\right)^2}\sqrt{\frac{1}{\sigma_A}\sum_{i=1}^{N}\left(Y_i^{M/\Gamma/QSAR}\right)^2}}$$

$$R_0 = \sqrt{1 - \frac{1}{\sigma_A}\sum_{i=1}^{N}\left(A_i - Y_i^{QSAR}\right)^2}$$

$$\sigma = \sigma_A = \sigma_i, \forall i = \overline{1,N}$$

$$\sigma_A = \sum_{i=1}^{N}\left(A_i - \overline{A}\right)^2$$

$$M \to \infty$$

$$R_{\infty/\Gamma}^2 \leq R_0^2 - N + 2\sqrt{N\left(1 - R_0^2\right)}$$

$$-N + 2\sqrt{\left(1 - R_0^2\right)}\sqrt{N} + \left(R_0^2 - R_{\infty/\Gamma}^2\right) \geq 0$$

$$R_{\infty/\Gamma} \geq 1$$

$$R_{M/\Gamma} \to 1 \geq \forall R_0$$

Conclusions COS5:
Orthogonal Space of Chemical Structure-Biological Activity Correlation

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SPECTRAL VS. STATISTIC APPROACH OF
STRUCTURE–ACTIVITY RELATIONSHIP. APPLICATION
ON ECOTOXICITY OF ALIPHATIC AMINES

MIHAI V. PUTZ*,‡, ANA-MARIA PUTZ*,†, MARIUS LAZEA*
and ADRIAN CHIRIAC*

Full Research Paper

A Spectral-SAR Model for the Anionic-Cationic Interaction in
Ionic Liquids: Application to *Vibrio fischeri* Ecotoxicity

Ana-Maria Lacrămă [1,2], Mihai V. Putz [3,]* and Vasile Ostafe [2]

Full Research Paper

Introducing Spectral Structure Activity Relationship (S-SAR)
Analysis. Application to Ecotoxicology

Mihai V. Putz* and Ana-Maria Lacrămă

Chemistry Department, West University of Timişoara, Pestalozzi Street No.16, Timişoara, RO-300115, Romania.

ORIGINAL RESEARCH

Variational principles for mechanistic quantitative structure–
activity relationship (QSAR) studies: application on uracil
derivatives' anti-HIV action

Mihai V. Putz · Nicoleta A. Dudaş

$$RA \equiv \frac{\left\| \left| Y_{PRED} \right\rangle \right\|}{\left\| \left| Y_{OBS} \right\rangle \right\|}$$

$$\begin{vmatrix} \left\| Y_{PRED} \right\rangle & \omega_0 & \omega_1 & \cdots & \omega_k & \cdots & \omega_M \\ \left| X_0 \right\rangle & 1 & 0 & \cdots & 0 & \cdots & 0 \\ \left| X_1 \right\rangle & r_0^1 & 1 & \cdots & 0 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & & \vdots & \\ \left| X_k \right\rangle & r_0^k & r_1^k & \cdots & 1 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots & & \vdots & \\ \left| X_M \right\rangle & r_0^M & r_1^M & \cdots & r_k^M & \cdots & 1 \end{vmatrix} = 0$$

$$0 = \delta[l,l'] = \delta\sqrt{\left(\left\| \left| Y_l \right\rangle \right\| - \left\| \left| Y_{l'} \right\rangle \right\| \right)^2 + (R_l - R_{l'})^2}, \; l,l': ENDPOINTS \; MODELS$$

$$\left\langle Y_{PRED} \middle| prediction \; error \right\rangle = 0$$

Chemistry Central Journal

RESEARCH ARTICLE   Open Access

Residual-QSAR. Implications for genotoxic
carcinogenesis

Mihai V Putz

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International Journal of
Molecular Sciences
ISSN 1422-0067
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Article

Introducing Catastrophe-QSAR. Application on Modeling
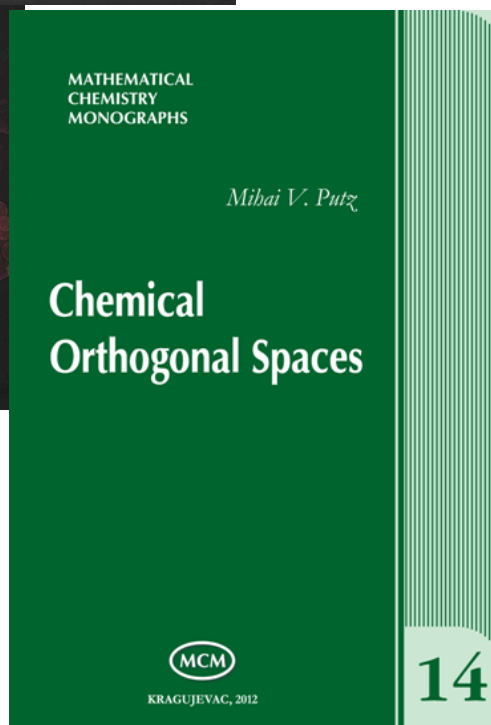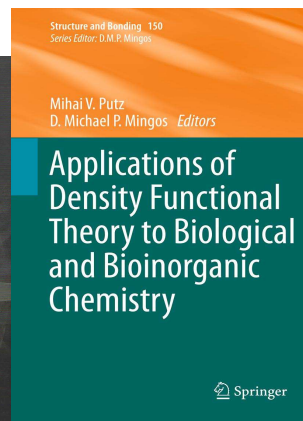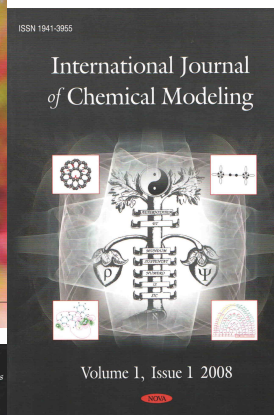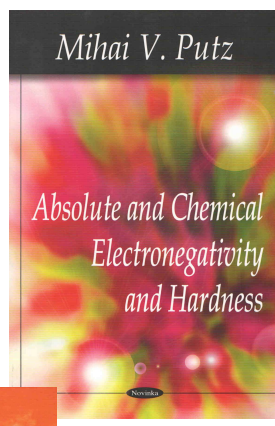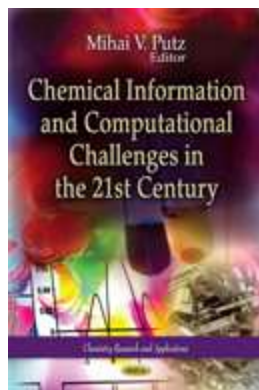Molecular Mechanisms of Pyridinone Derivative-Type HIV
Non-Nucleoside Reverse Transcriptase Inhibitors

Mihai V. Putz [1,]*, Marius Lazea [1], Ana-Maria Putz [1,2,]* and Corina Duda-Seiman [1]

GRAND CONCLUSION…
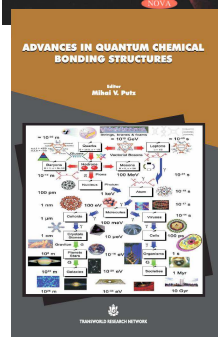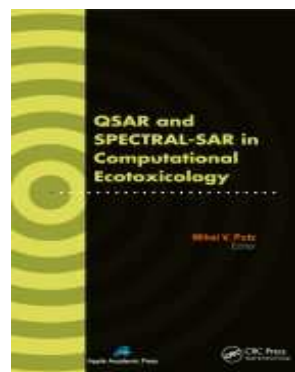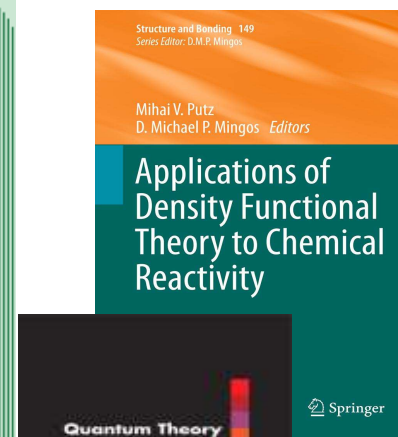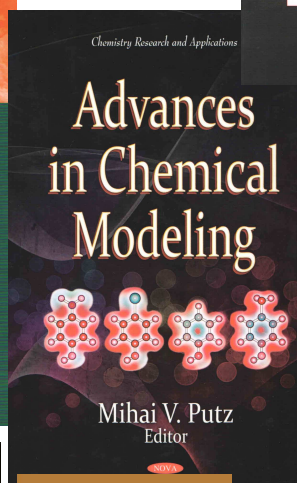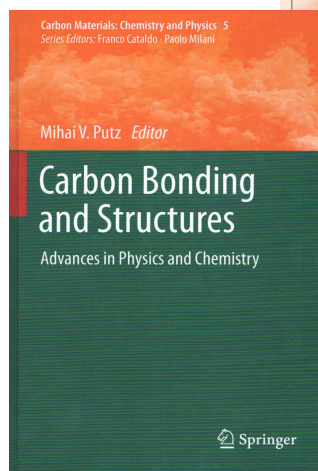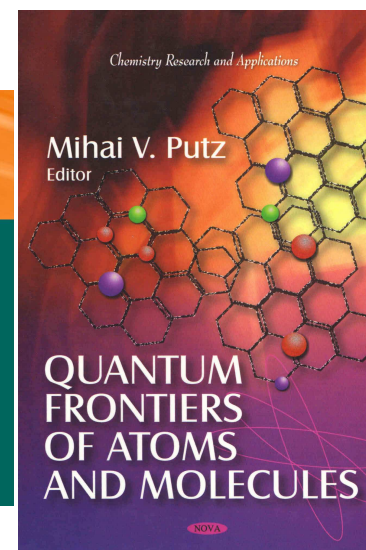
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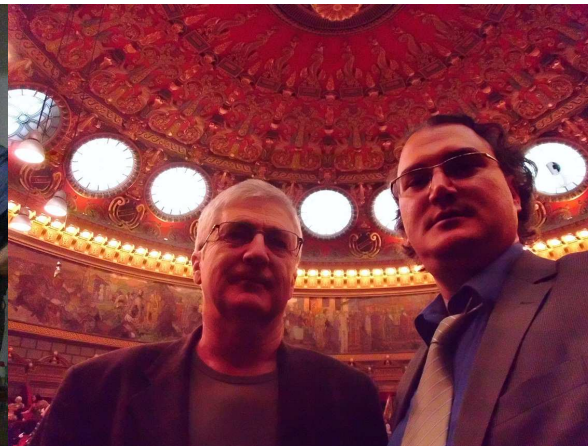
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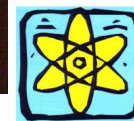(Rudjer Boskovic Institute, Zagreb)

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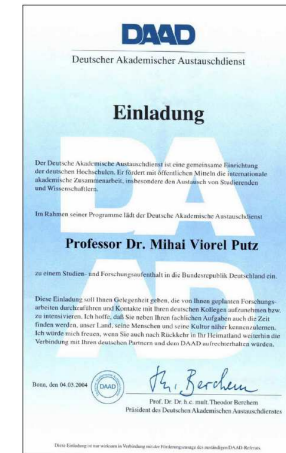
CNCSIS, CNCS, UEFISCDI, ANCS (Romanian National Council for Scientific Research in Higher Education)
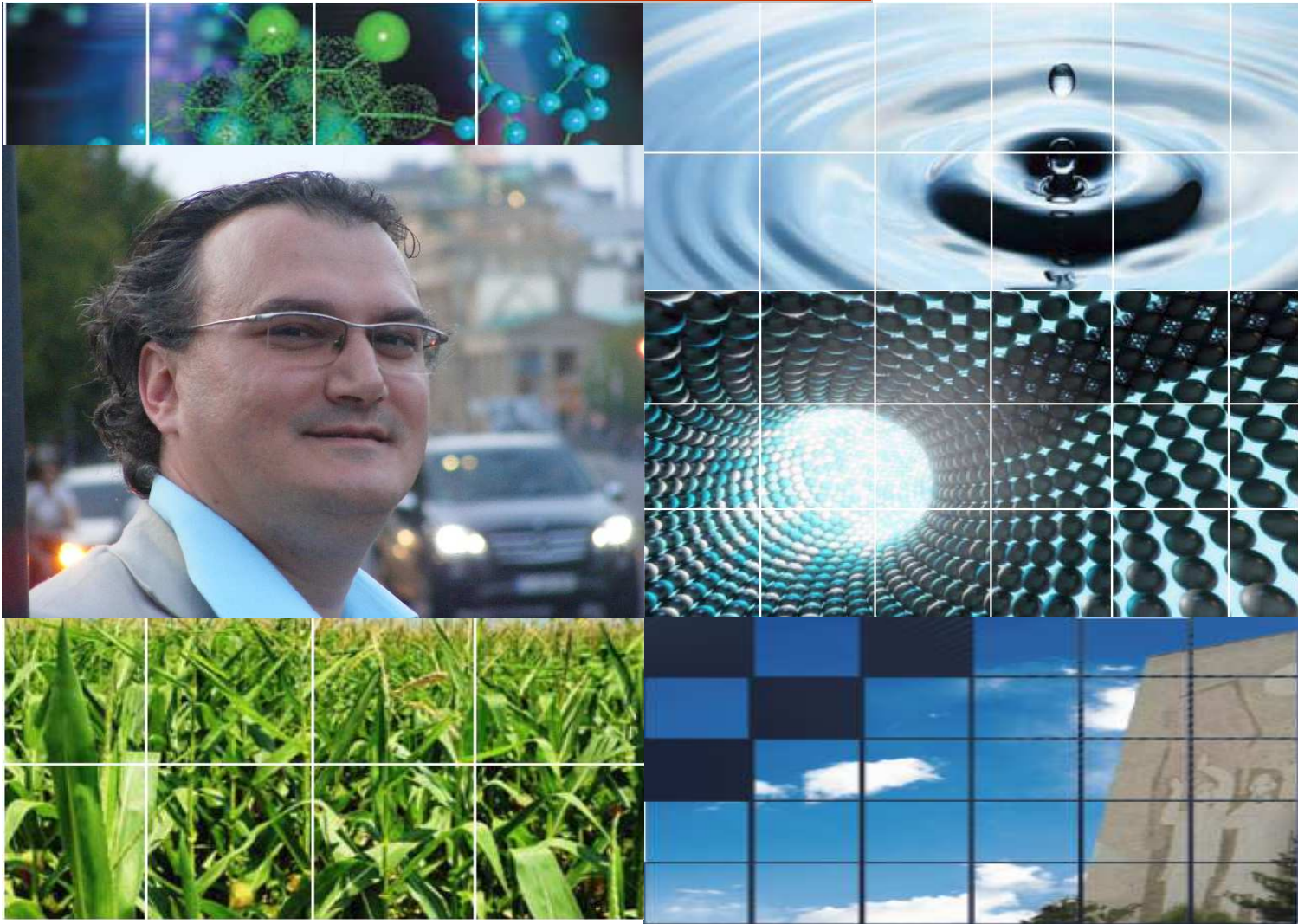
Dinu Patriciu Foundation

Huge Thanks & Dedications:

My Daughters Katy & Ela

& to My Family

THANK YOU ALL!

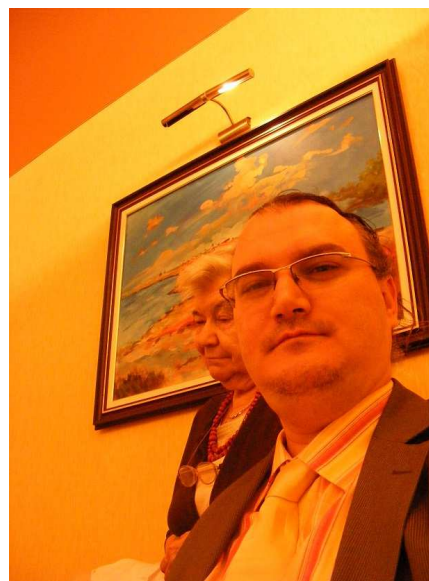**THE STARING SKY ABOVE US
AND THE MORAL LAW INSIDE US!**

…Kant

Habilitation After-Session: 20 March 2013/UBB/Chemistry

**CONSILIUL NAȚIONAL DE ATESTARE A TITLURILOR,
DIPLOMELOR ȘI CERTIFICATELOR UNIVERSITARE**
NATIONAL COUNCIL FOR ATTESTATION OF
ACADEMIC TITLES, DIPLOMAS AND CERTIFICATES
(CNATDCU)

RAPORTUL COMISIEI DE ABILITARE
REPORT OF THE HABILITATION COMMISSION

din data de (date) 20 martie 2013 (March 20th 2013)

NUMELE și Prenumele candidatului (**SURNAME and Forename** of the candidate):

…......................PUTZ MIHAI VIOREL…...
Titlul tezei de abilitare / direcțiile principale de cercetare (Title of habilitation thesis / main research areas):
.................Spatii chimice ortogonale pentru atomi si molecule (Chemical Orthogonal Spaces of Atoms and Molecules)...
....

Domeniul de studii universitare de doctorat (Field of doctoral studies):

....CHIMIE (CHEMISTRY)...
în care urmează să se confere calitatea de conducător de doctorat (future field of doctoral supervision)

Denumirea **Instituției Organizatoare de Studii Universitare de Doctorat** (IOSUD) / **Instituției Organizatoare de Doctorat** (IOD) unde are loc susținerea publică a tezei de abilitare
(Name of the **institution organizing doctoral studies** (IOSUD), (IOD), where the public defense of the habilitation thesis takes place)
.....................Universitatea „Babeș-Bolyai" (Babeș-Bolyai University) Cluj-Napoca.............
....

Punctele tari ale tezei de abilitare (**Strong points** of the habilitation thesis):
1. Originalitatea ridicata a cercetarii efectuate si introducerea de noi concepte (The high level of originality of the research work and the introducing of new concepts)
2. Numarul mare de publicatii de foarte buna calitate. (The high number of publications of very good quality)
3. Capacitatea ridicata de a transmite continuturi stiintifice (The high capacity to convey scientific contents)
4. O cultura stiintifica foarte bogata (Broad scientific culture)
5. Conecsiuni inovative intre structura electronica si teoria grafurilor. (Innovative connections between the electronic structure and the graph theory)
Punctele slabe ale tezei de abilitare (**Weak points** of the habilitation thesis):
1. Nu sunt mentionate puncte slabe (no weak points were mentioned)
Rezultatul votului / observații / concluziile *comisiei de abilitare* se motivează în continuare
(**Voting result / observations / premises for the conclusions** of the *habilitation commission* are as follows)
Membrii juriului accepta teza de abilitare si recomanda acordarea certicatului de abilitare. (The members of the habilitation jury agree to accept the habilitation thesis and recomment to be conffered the habilitation certificate to the candidate).
(a se continua pe verso – dacă este necesar) (continue overleaf if necessary)

COMISIA DE ABILITARE
HABILITATION COMMISSION

NUMELE și Prenumele   *Semnătura*
SURNAME and Forename   *Signature*
1. Prof. dr. BENEDEK Giorgio
2. Prof. dr. HILLEBRAND Mihaela
3. Prof. dr. BEU Titus