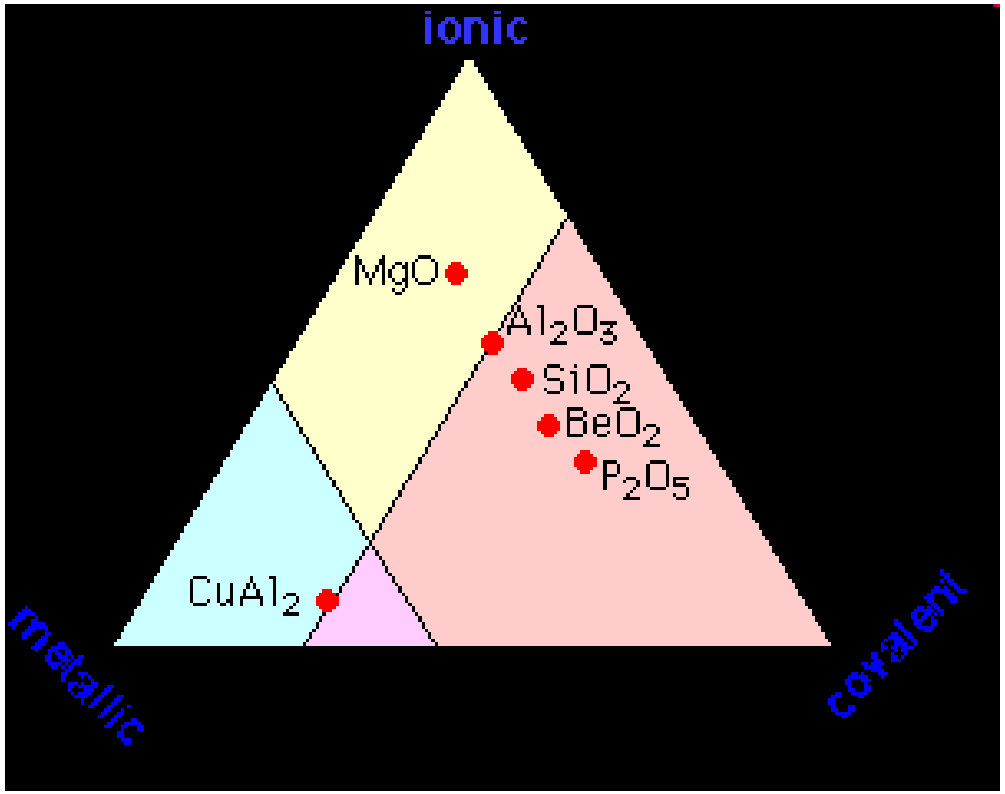
CAPVT II

VEZA

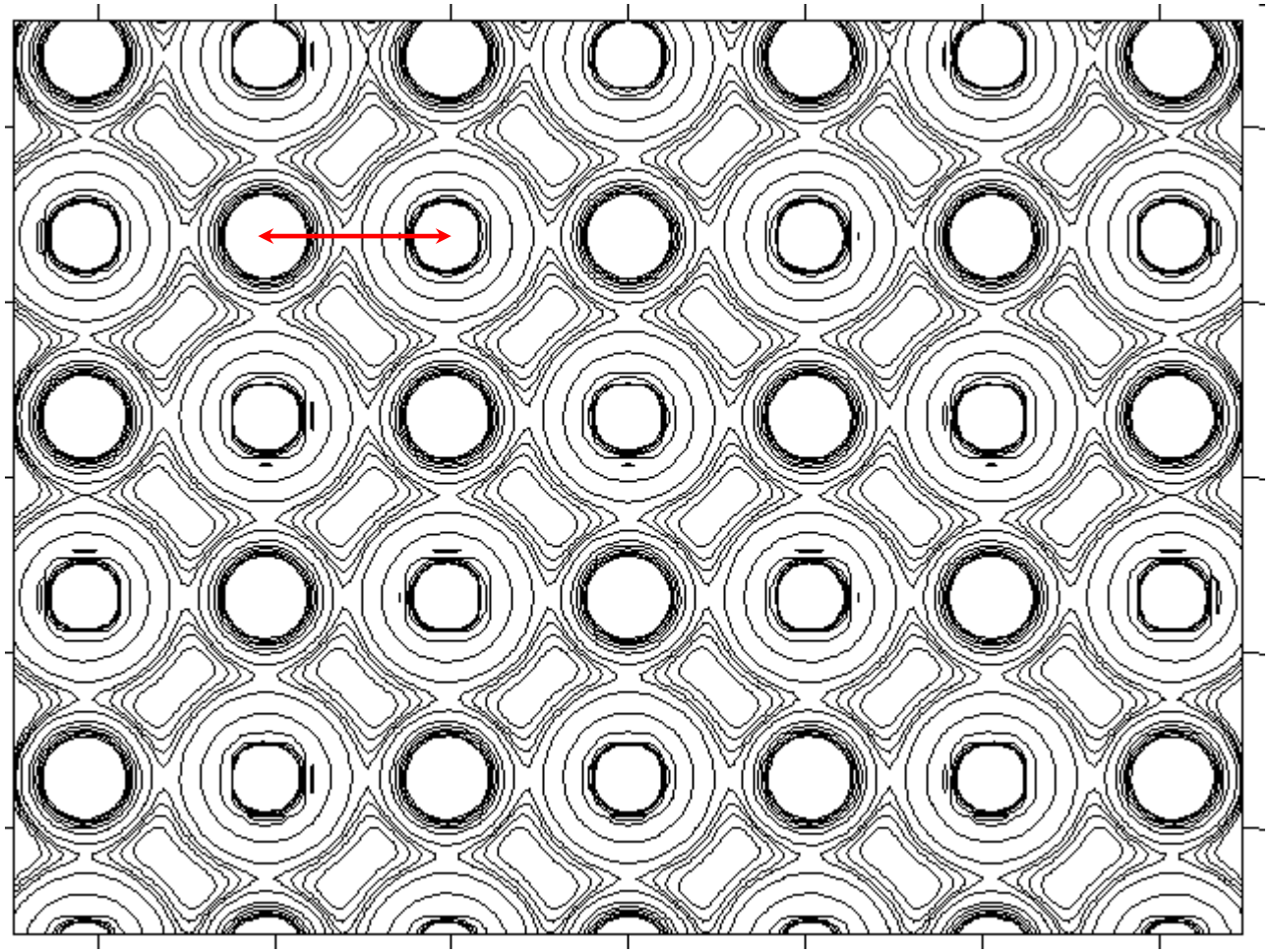
- Kakve kemijske veze mogu biti
  - Kovalentne, ionske, metalne
  - Jednostruke, dvostruke, trostruke...



Svojstva veze

- Duljina
- Energija disocijacije
- Konstanta sile
- Dipolni moment

Duljina veze



1. Udaljenost između jezgara
2. Udaljenost između maksimumâ elektronske gustoće
3. Ravnotežna duljina veze

Duljina veze i kovalentni radijus

$$r_K(S) = \frac{1}{2} d(S-S) = 104\ \text{pm}$$

$$r_K(C) = \frac{1}{2} d(C-C) = 77\ \text{pm}$$

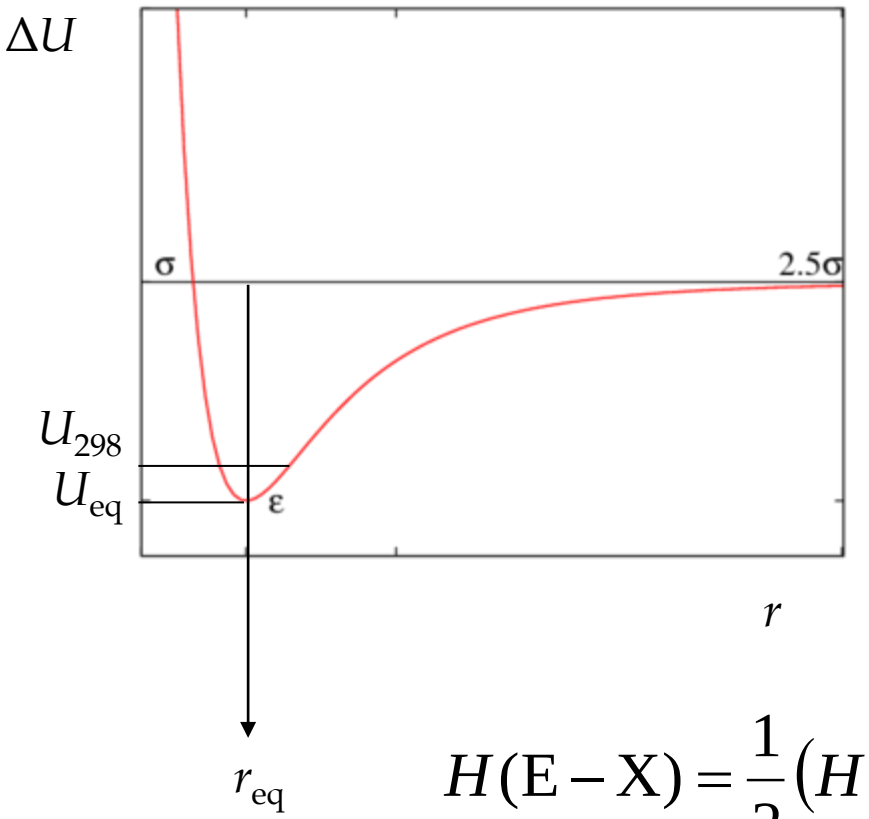
$$d(C-C) = r_K(S) + r_K(C) = 181\ \text{pm}$$

[181,4 pm u H_3CSH i 180,7 u $(H_3C)_2S$]

$$d(A-B) = r_K(A) + r_K(B) - k[\chi(A) - \chi(B)]$$

$(k \approx 9\ \text{pm})$

Energija veze



$$H(\mathrm{E-X}) = \frac{1}{2}\big(H(\mathrm{E-E}) + H(\mathrm{X-X})\big) + k[\chi(\mathrm{X}) - \chi(\mathrm{E})]^2$$

$$k = 96{,}5\ \mathrm{kJ\ mol^{-1}}$$

Konstnta sile

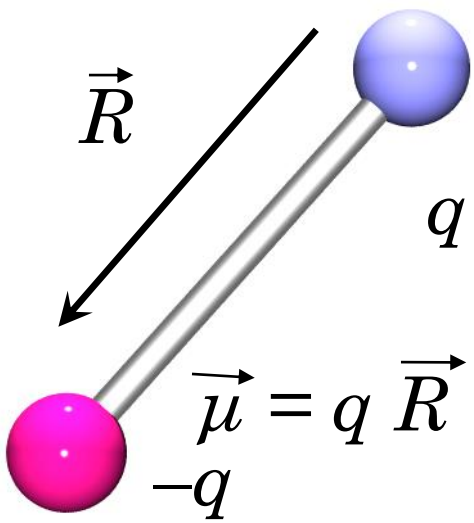
- Mjera za krutost veze (nagib Lennard-Jonesove krivulje)

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

$$k = \frac{(2\pi\nu)^2}{\mu}$$

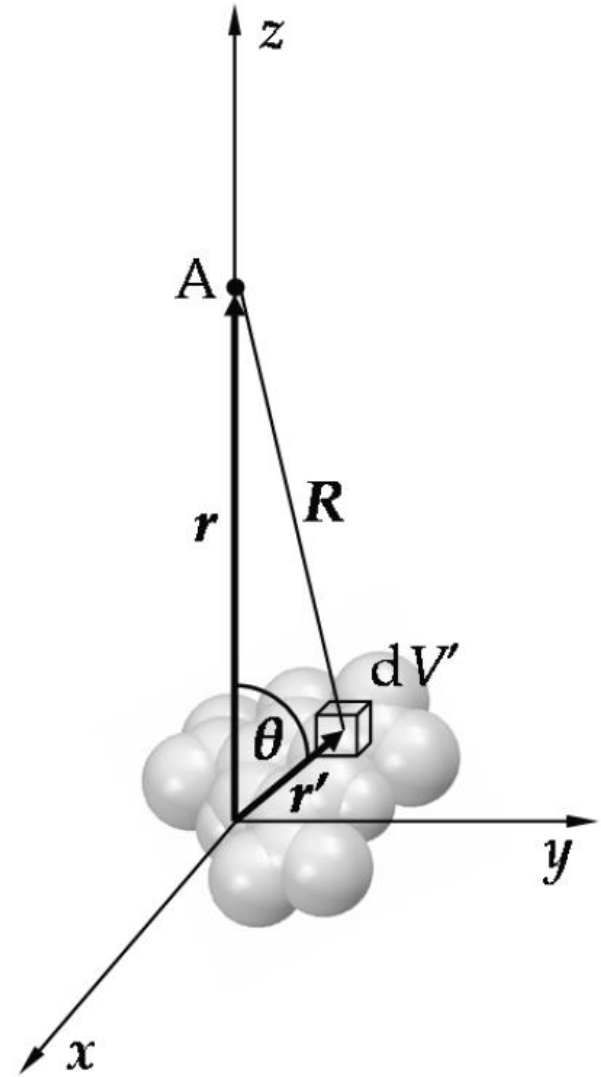
Dipolni moment

- Dipolni moment



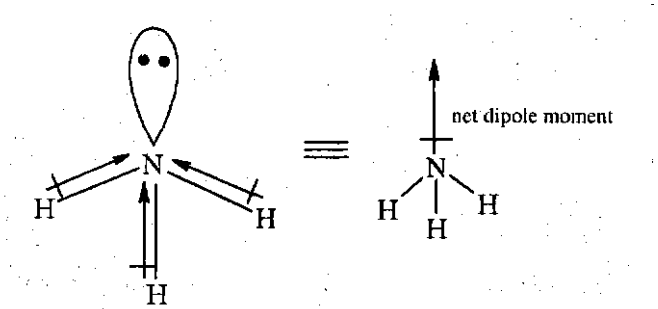
- Molekulski dipolni moment

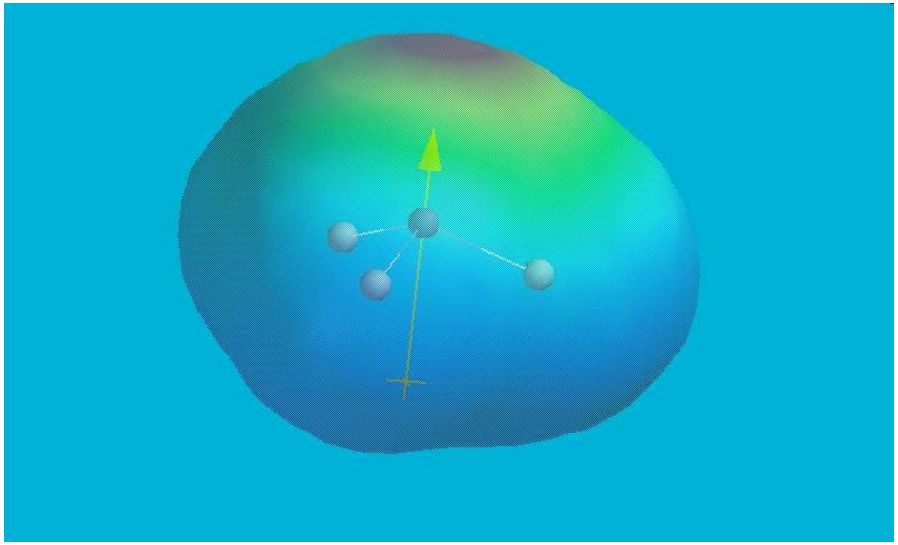
$$\vec{\mu} = \int_V \vec{r'}\rho(V')dV'$$



- Ukupni dipolni moment molekule kao suma dipolnih momenata veza.
- Dipolni moment veze sadrži:
  - Atomske dipolne momente
  - Moment prijenosa

A k tomu i dipol neveznog para





NH_3 – dipolni moment od $4{,}76 \cdot 10^{-3}$ C m

(1,846 D)

CO – dipolni moment od 0,122 D

Geometrija molekule

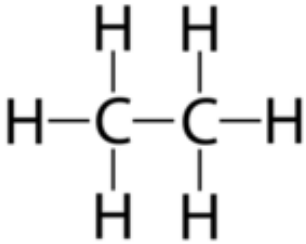
- Određena razmještajem elektrona u molekuli
- Elektroni se odbijaju, a po potrebi i sparuju.

Eliptičnost veze

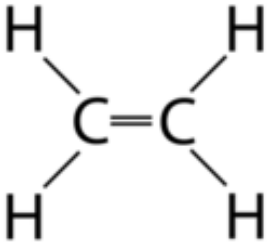
Eliptičnost (ϵ)

$\epsilon = \lambda_1/\lambda_2 - 1$

λ_1 i λ_2 vlastite vrijednosti Hessove matrice pri čemu se uvijek uzima $|\lambda_1| \geq |\lambda_2|$



$\epsilon = 0$



$\epsilon \approx 0{,}45$

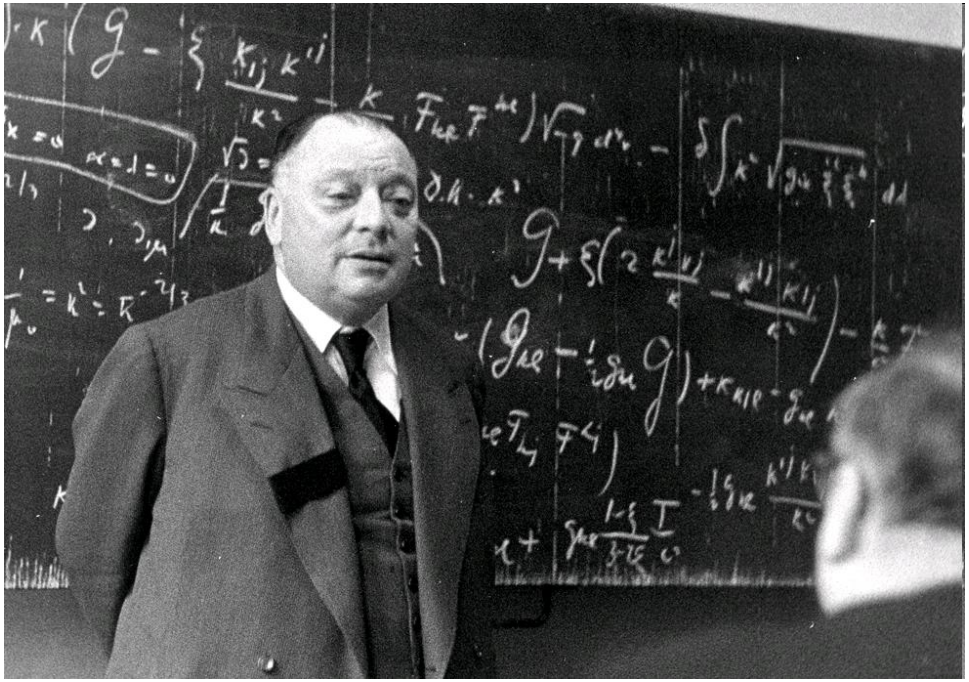
$\epsilon = 0$

Paulijev princip

Elektronska valna funkcija mora biti antisimetrična s obzirom na izmjenu elektrona

Iliti dva elektrona ne mogu biti u istom stanju (na istom mjestu u isto vrijeme)

Ponašaju se kao da se odbijaju uslijed *"Paulijeve sile"*

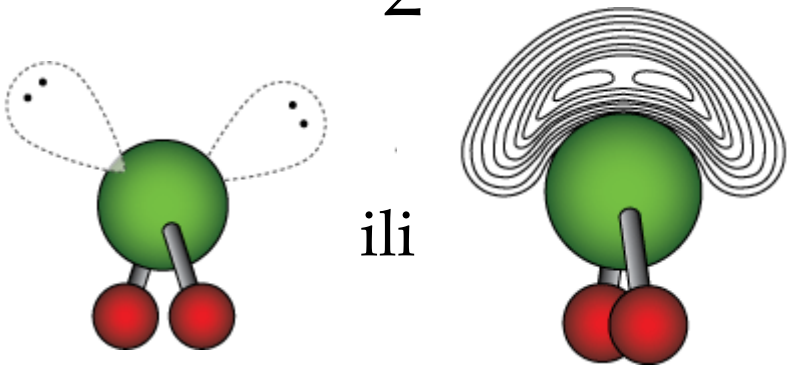


O sparivanju elektrona

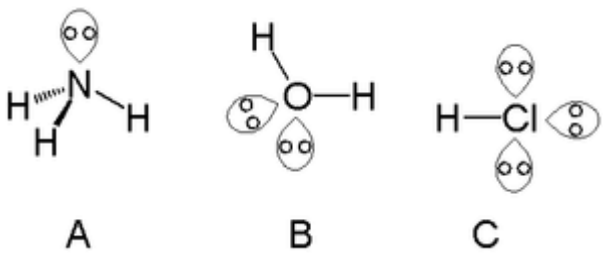
Kažu da zbog Paulija elektroni se sparuju.

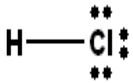
Zašto i koliko to elektroni čine?

H_2O



Monovalentni halogeni





Central atom: Cl

Cl contributes: 7 e^-

H contibutes: 1 e^-

Total VSE: 8

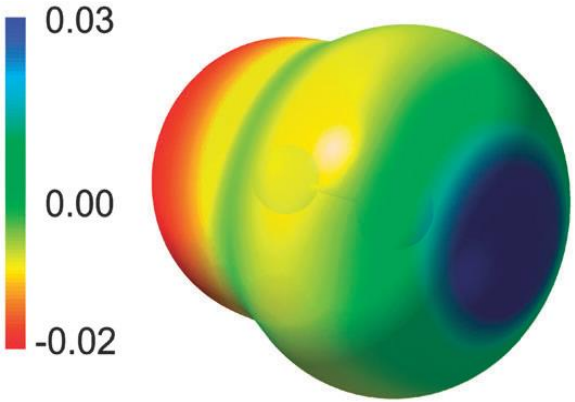
Total VSEP: 4

Geometry: Linear (based on tetrahedral)

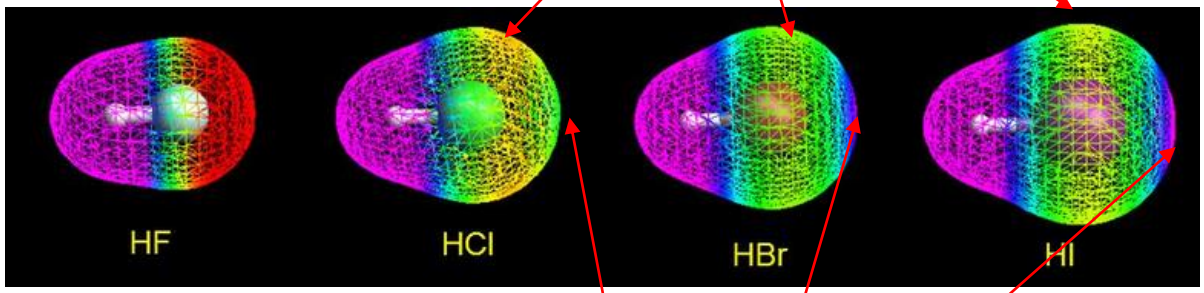
Što ne valja na ovoj slici?

Preuzeto od Univerity of Bristol, School of Chemistry, Bristol ChemLabs;
http://www.inchm.bris.ac.uk/schools/vsepr/examples/hcl.htm

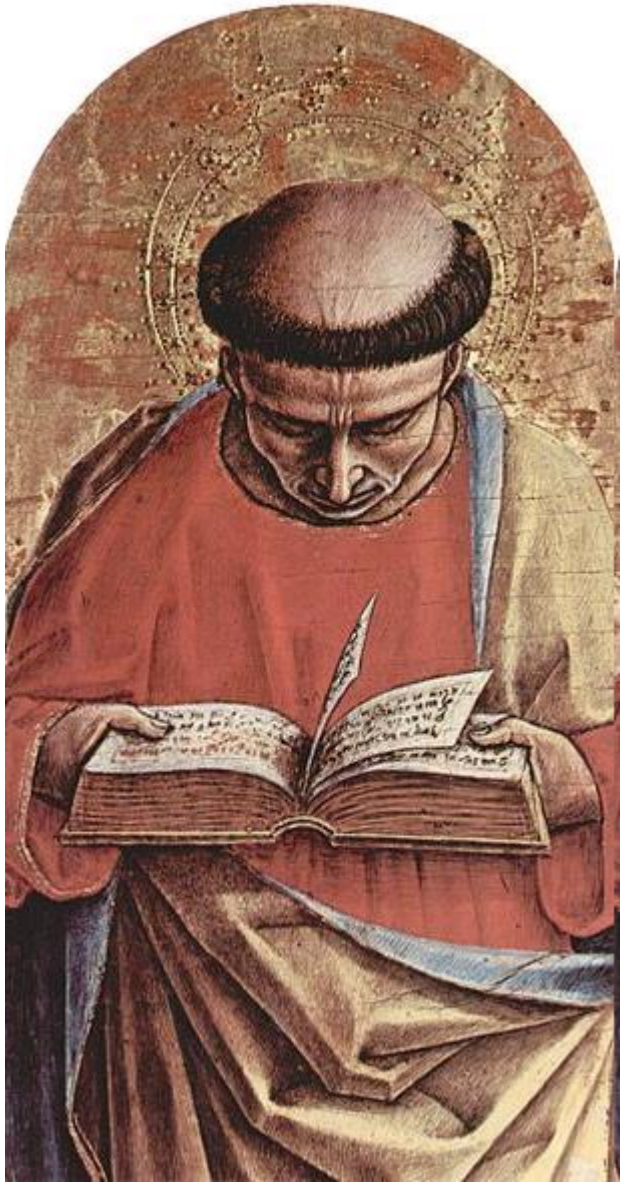
Monovalentni halogeni



povećana elektronska gustoća

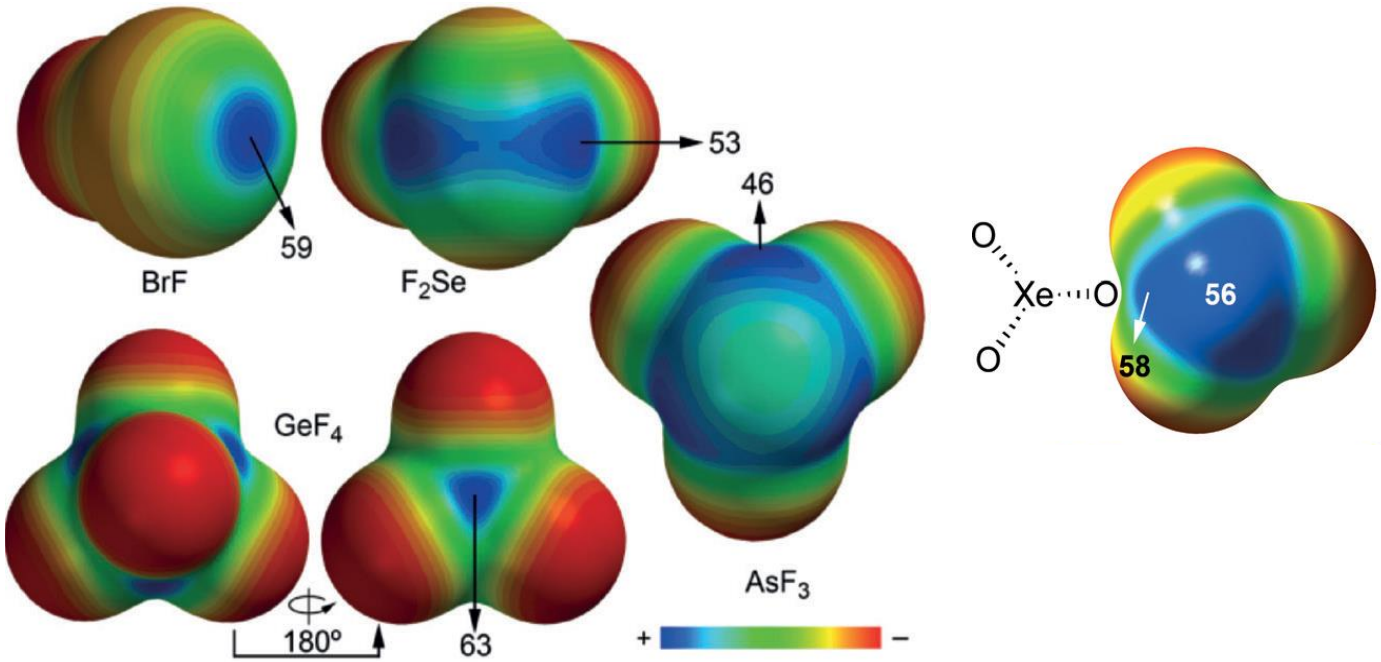


smanjena elektronska gustoća
σ-šupljina (*σ-hole*)

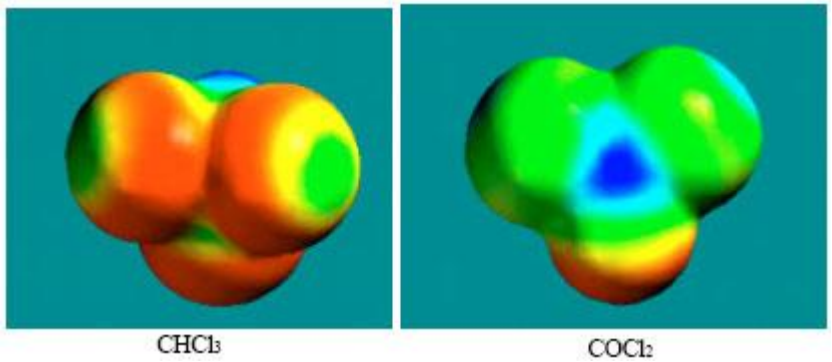


σ-, π- i ostale molekulske rupe

Nedostatak elektronske gustoće javlja se u nastavku **svake** kovalentne veze



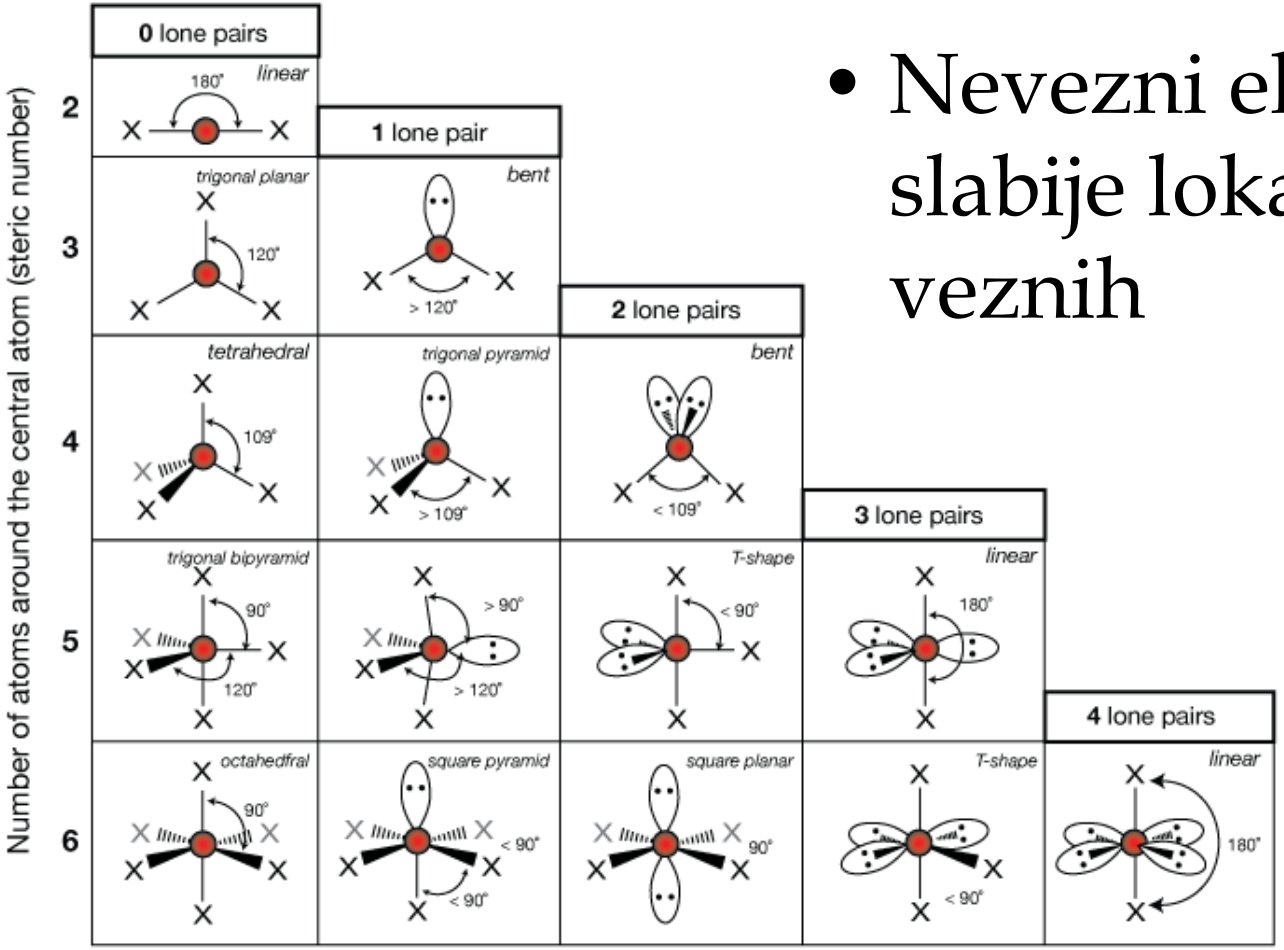
Nedostatak elektronske gustoće kadkad se javlja okomito na (višestruke) kovalentne veze – **π-šupljina**



VSEPR

- **Valence shell electron pair repulsion**
- Vezni i nevezni elektronski parovi razmještaju se tako da budu što dalje jedni od drugih
- Jače lokalizirani parovi se manje odbijaju
- Ne funkcionira za Na_2O i njemu slične
- Ne fukcionira baš ni za preteške atome

VSEPR - binarni spojevi

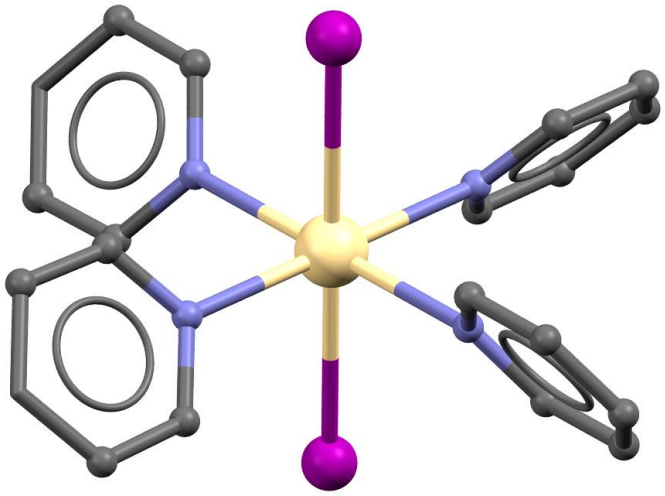


- Nevezni elektroni su slabije lokalizirani od veznih

VSEPR - ternarni spojevi

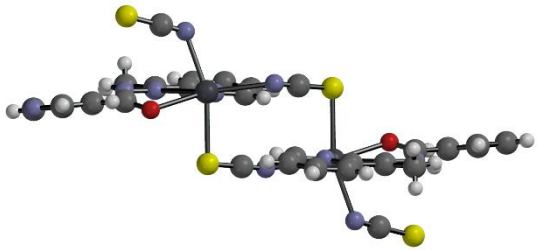
Bentovo pravilo – elektronegativniji supstituenti preferiraju aksijalni položaj (pripadni elektronski parovi su **jače** lokalizirani)

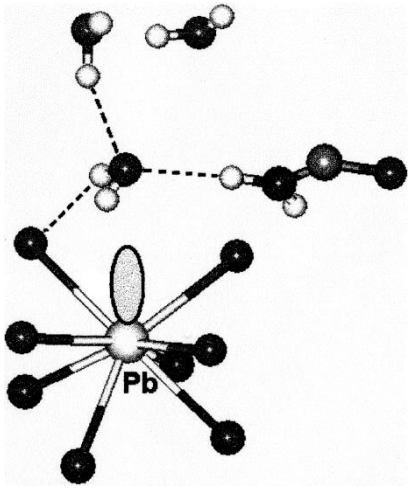
Vrijedi čak i za slučajeve s višeatomnim ligandima (npr. $CdI_2(pyr)_4$)



Olovo(II) i ‘sterički aktivni elektronski par’

- Hemidirekcionalna koordinacija (‘sterički aktivan elektronski par’)





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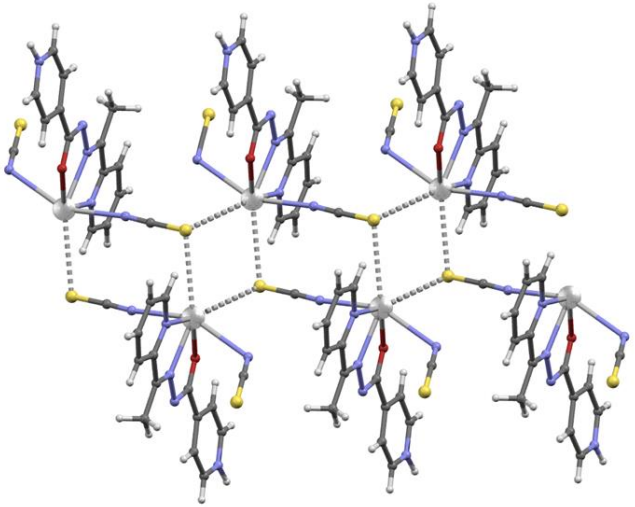
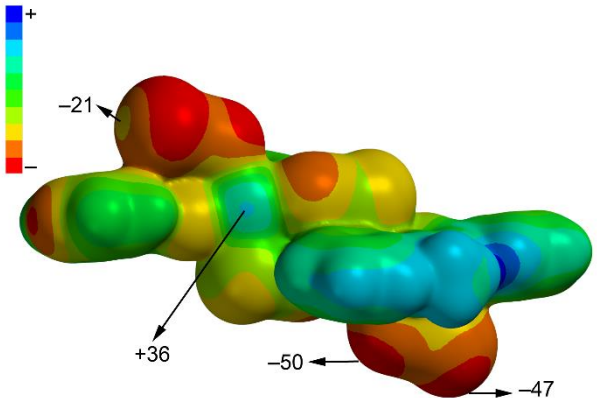
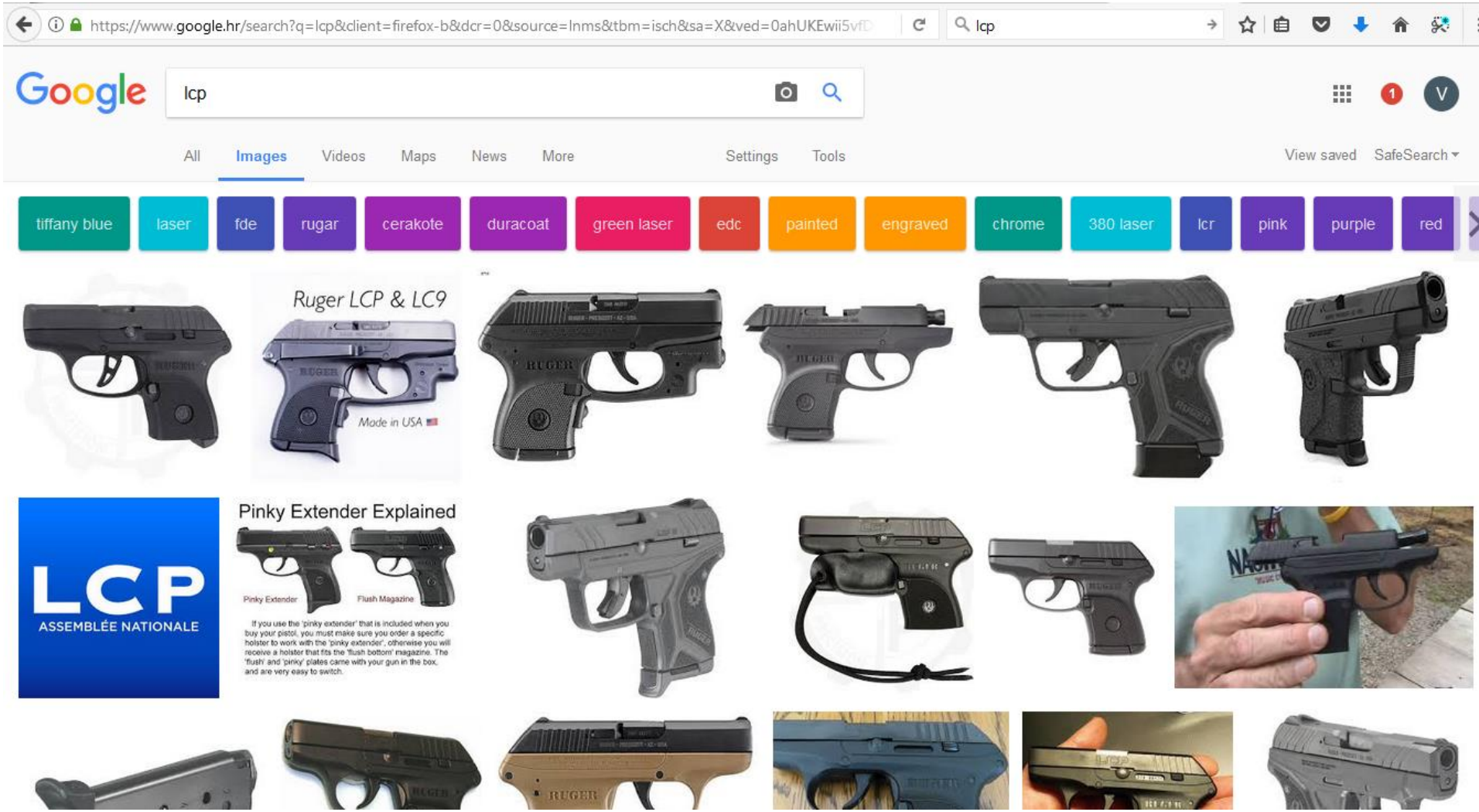




Kad VSEPR ne radi - LCP



LCP

- Gusto pakiranje liganada (Ligand Close Packing) oko centralnog atoma
- Alternativa VSRPR-u (1997./8. Gillespie i Robinson)
- Sterički model

- Nevezna udaljenost se ne mijenja od molekule do molekule
- Intramolekulski nevezni ligandni radius je konstantan za danu kombinaciju središnjeg atoma i liganda
- Ligandi se gusto pakiraju oko centralnog atoma

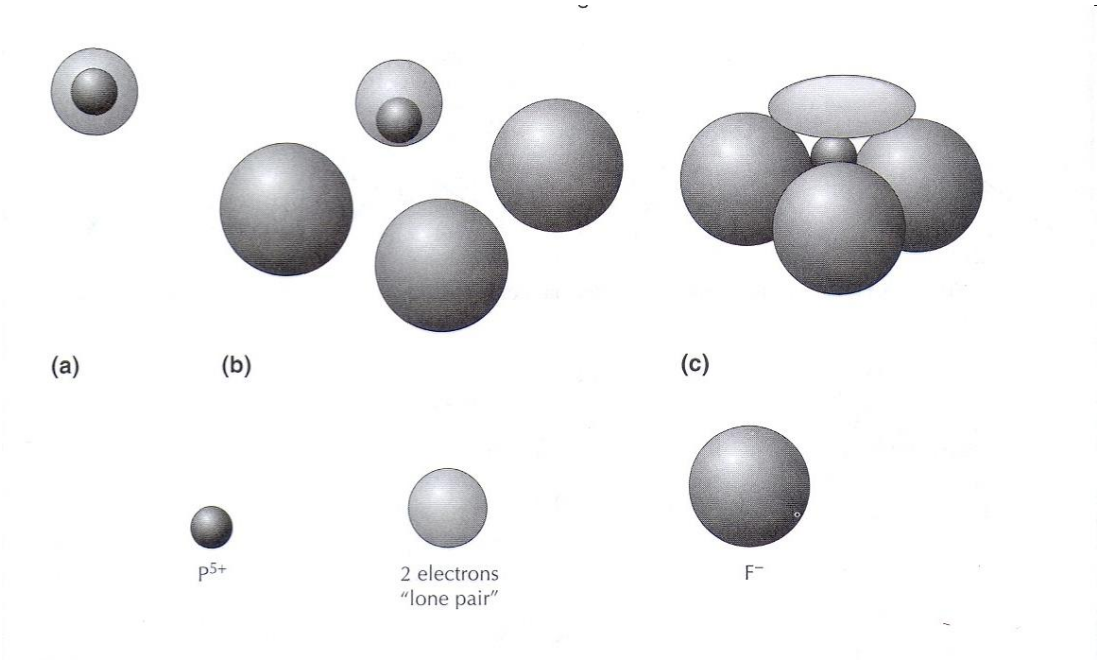
molekula	koordinacijski broj	d(A-F)/pm	$\angle$(F-A-F)/°		d(F...F)/pm
BeF_3^-	3	149	120		258
BeF_4^{2-}	4	155.4	109.5		254
				prosjek	**256**
F_3B	3	130.7	120.0		226
$F_2B—OH$		132.3	118.0		227
$F_2B—NH_2$		132.5	117.9		227
$F_2B—Cl$		131.5	118.1		226
$F_2B—H$		131.1	118.3		225
F_4B^-	4	138.2	109.5		226
$F_3B—CH_3^-$		142.4	105 .4		227
$F_3B—CF_3^-$		139.1	109 .9		228
$F_3B—PH_3$		137.2	112.1		228
				prosjek	**226**
CF_3^{+a}	3	124.4	120		216
$F_2C=CF_2$		131.9	112.4		219
$F_2C=CCl_2$		131.5	112.1		218
$F_2C=CH_2$		132.4	109.4		216
$F_2C=CHF$		133.6	109.2		218
F_4C	4	131.9	109.5		215
$F_3C—CF_3$		132.6	109.8		217
$F_3C—OF$		131.9	109.4		215
F_3CO^-		139.2	101.3		215
				prosjek	**216**

Pravilnosti

- U molekuli AX_n duljina veze A-X raste s porastom *n*
- Nevezne udaljenosti između različitih liganada približne su sumi njihovih neveznih radijusa
- Temeljem kovalentnih i ligandnih radijusa, mogu se procijeniti vezni kutevi

Nevezni parovi

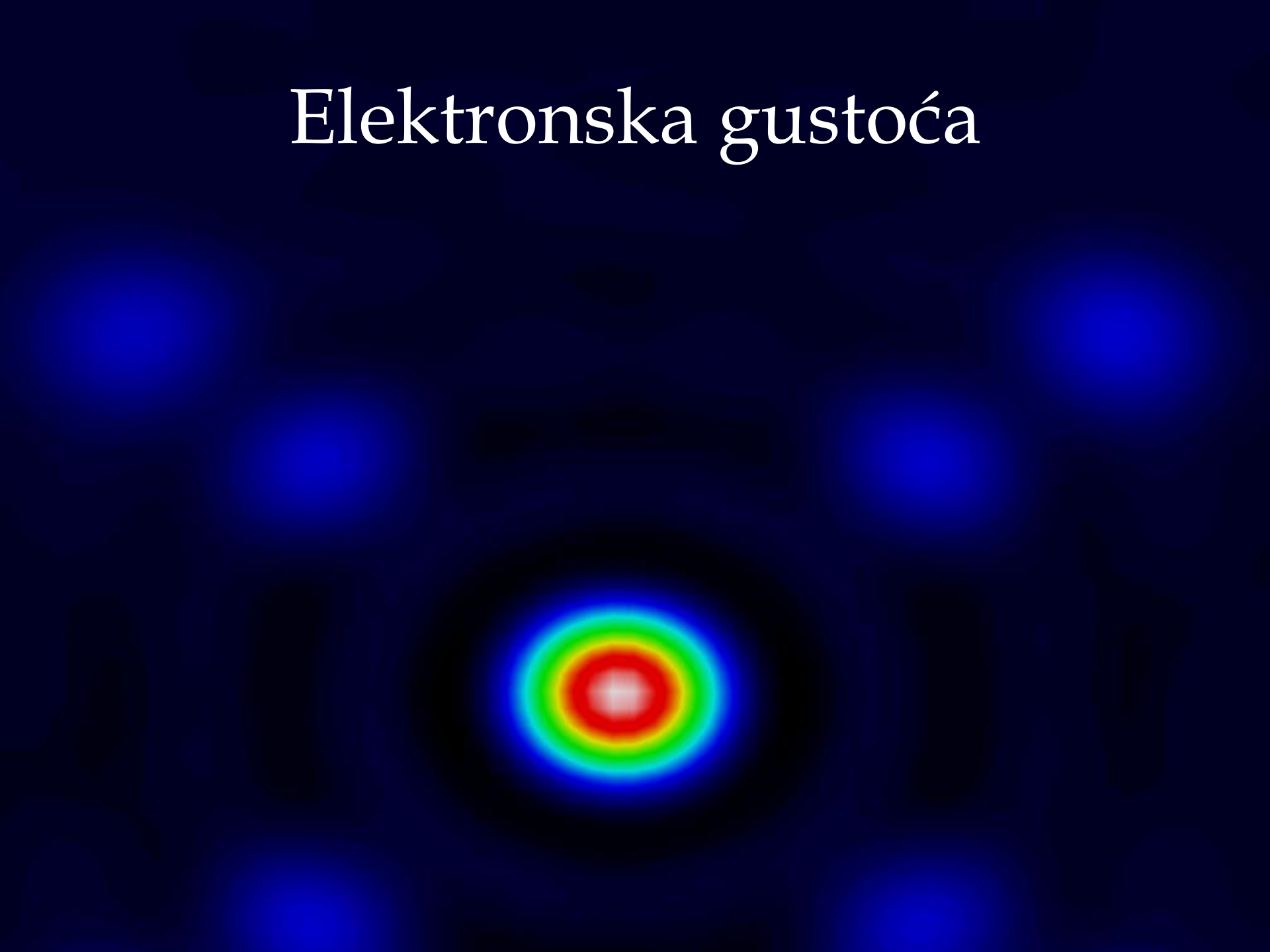
- Središnji se atom ima tretirati kao nesferičan ukoliko ima sparenih neveznih elektrona



Ligandi niske elektronegativnosti

	d(A-O)/pm	$\angle$(O-A-O)/°	$\angle$(A-O-H)/°
LiOH	158.2	—	180.0
$Be(OH)_2$	142.3	180.0	134.5
$B(OH)_3$	136.8	120.0	112.8
$C(OH)_4$	139.3	103.6, 112.5	106.9
$N(OH)_3$	141.3	103.8	102.6
$O(OH)_2$	144.4	100.3	98.7
FOH	143.2	—	98.6

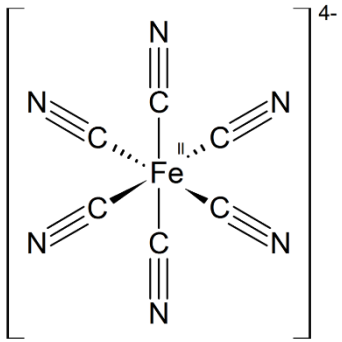
Elektronska gustoća



Kako do gustoće?

Računski: *ab initio,* semiempirijski

Mjerenjem: rentgenska i elektronska difrakcija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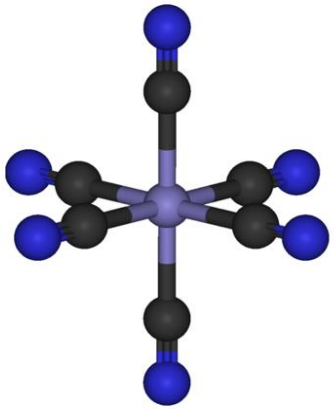

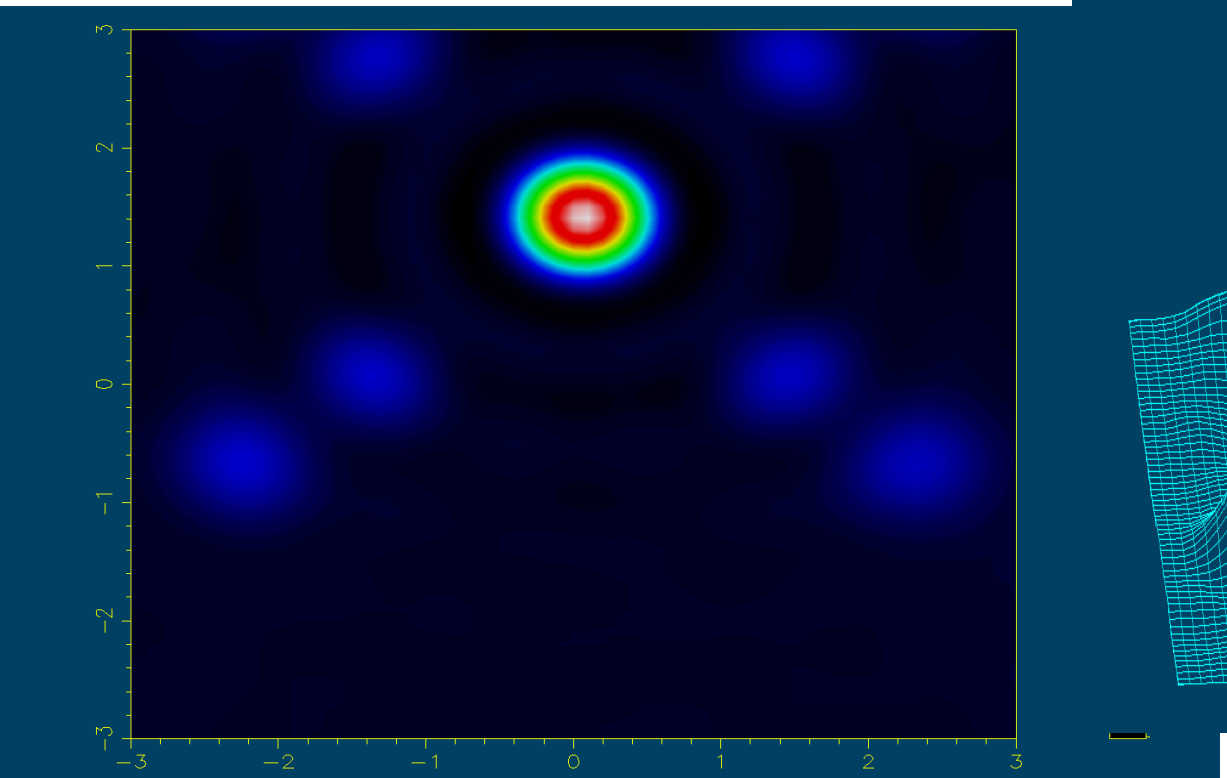
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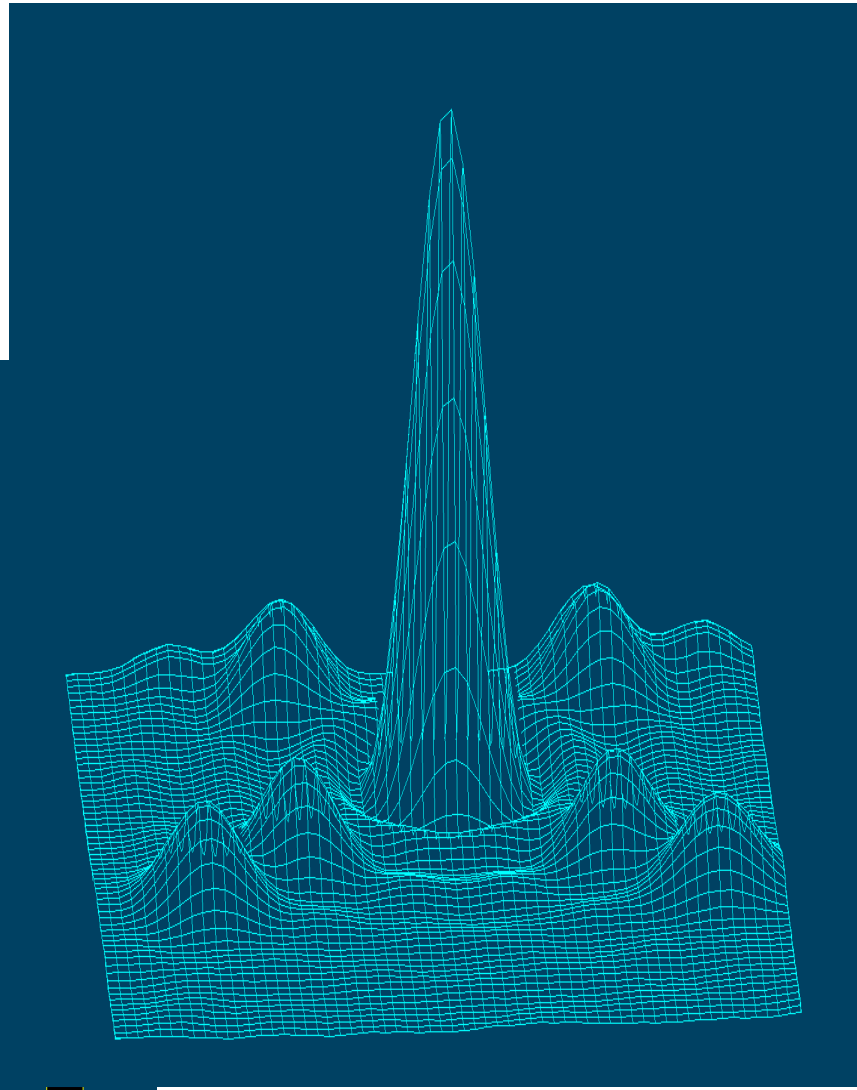
3



Problemi

Nepotpuni podatci (‘*musavi Fourier*’)

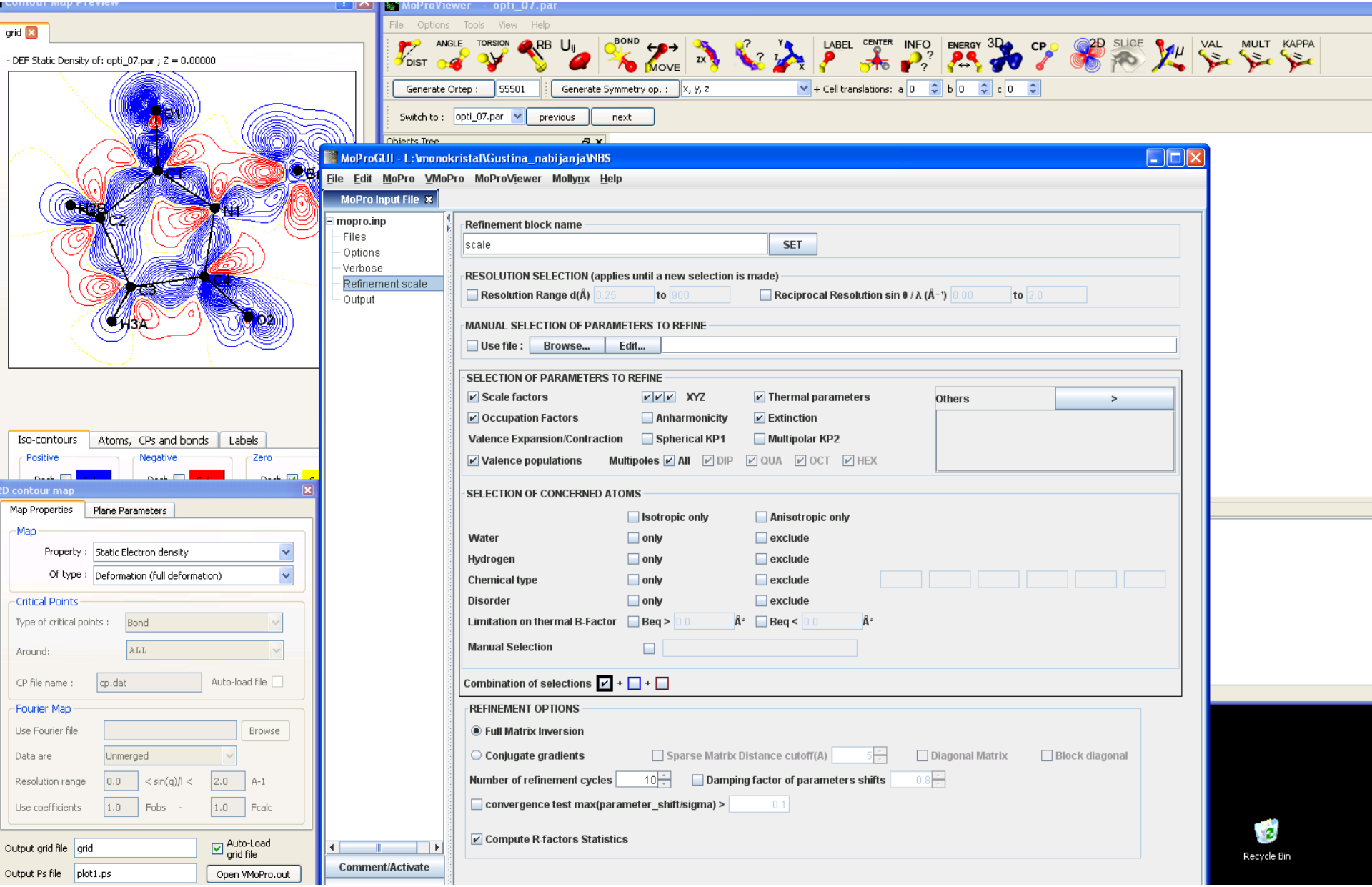
Termičko gibanje (dekonvolucija)

Nesavršenost kristala (artefakti)

Absorpcija i ekstinkcija

Cu – premala rezolucija; Mo,Ag – premali intenzitet

...


MoProViewer - opti_07.par
File Options Tools View Help
DIST ANGLE TORSION RB Uij BOND MOVE LABEL CENTER INFO ENERGY 3D CP 2D SLICE VAL MULT KAPPA
Generate Ortep : 55501
Generate Symmetry op. : x, y, z
+ Cell translations: a 0 b 0 c 0
Switch to : opti_07.par previous next
Objects Tree
grid
- DEF Static Density of: opti_07.par ; Z = 0.00000
O1
C1
B1
H2B
C2
N1
C3
C4
H3A
O2
Iso-contours
Atoms, CPs and bonds
Labels
Positive
Negative
Zero
2D contour map
Map Properties
Plane Parameters
Map
Property : Static Electron density
Of type : Deformation (full deformation)
Critical Points
Type of critical points : Bond
Around: ALL
CP file name : cp.dat
Auto-load file
Fourier Map
Use Fourier file
Browse
Data are Unmerged
Resolution range 0.0 < sin(q)/l < 2.0 A-1
Use coefficients 1.0 Fobs - 1.0 Fcalc
Output grid file grid
Auto-Load grid file
Output Ps file plot1.ps
Open VMoPro.out
MoProGUI - L:\monokristal\Gustina_nabijanja\NBS
File Edit MoPro VMoPro MoProViewer Mollynx Help
MoPro Input File
mopro.inp
Files
Options
Verbose
Refinement scale
Output
Comment/Activate
Refinement block name
scale
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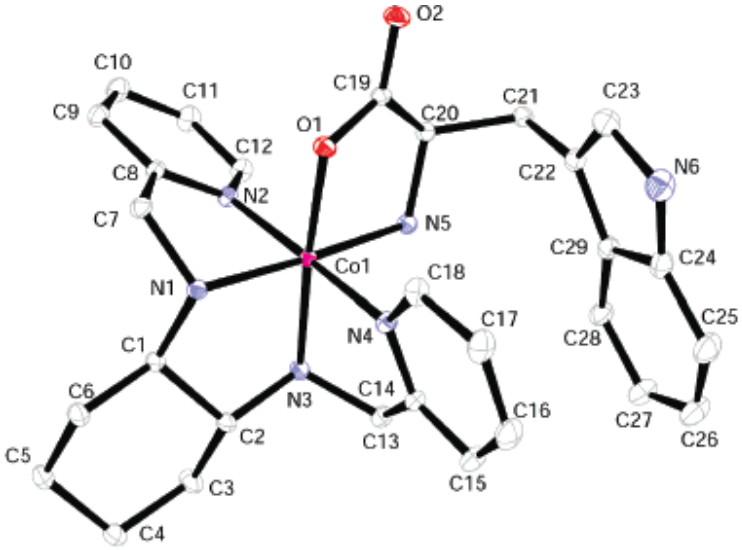
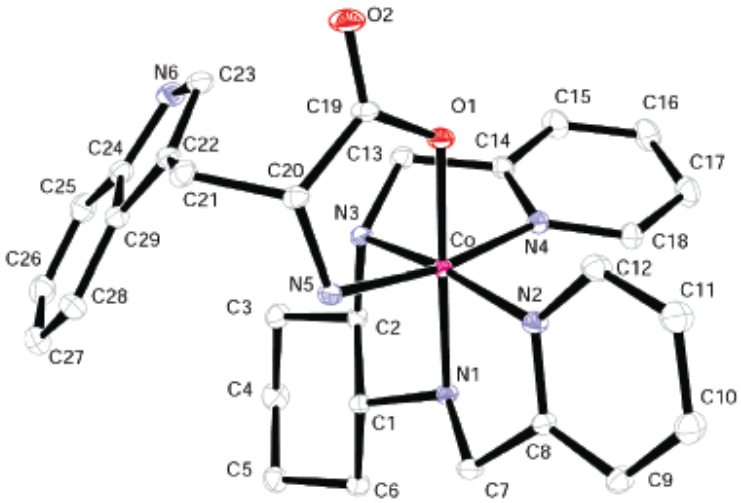
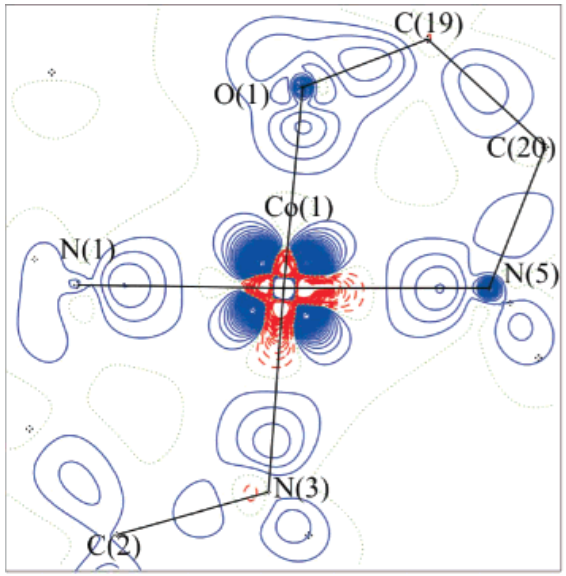
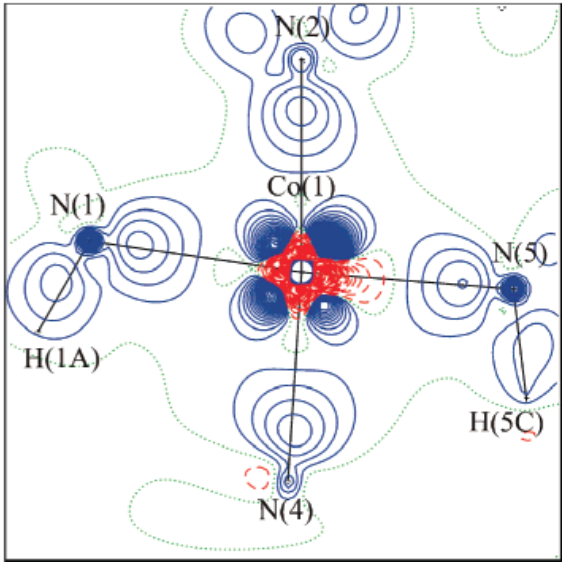
RESOLUTION SELECTION (applies until a new selection is made)
Resolution Range d(Å) 0.25 to 900
Reciprocal Resolution sin θ / λ (Å⁻¹) 0.00 to 2.0
MANUAL SELECTION OF PARAMETERS TO REFINE
Use file : Browse... Edit...
SELECTION OF PARAMETERS TO REFINE
Scale factors
XYZ
Thermal parameters
Occupation Factors
Anharmonicity
Extinction
Valence Expansion/Contraction
Spherical KP1
Multipolar KP2
Valence populations
Multipoles All DIP QUA OCT HEX
Others
SELECTION OF CONCERNED ATOMS
Isotropic only
Anisotropic only
Water only exclude
Hydrogen only exclude
Chemical type only exclude
Disorder only exclude
Limitation on thermal B-Factor Beq > 0.0 Å² Beq < 0.0 Å²
Manual Selection
Combination of selections
REFINEMENT OPTIONS
Full Matrix Inversion
Conjugate gradients
Sparse Matrix Distance cutoff(A) 5
Diagonal Matrix
Block diagonal
Number of refinement cycles 10
Damping factor of parameters shifts 0.8
convergence test max(parameter_shift/sigma) > 0.1
Compute R-factors Statistics
Recycle Bin

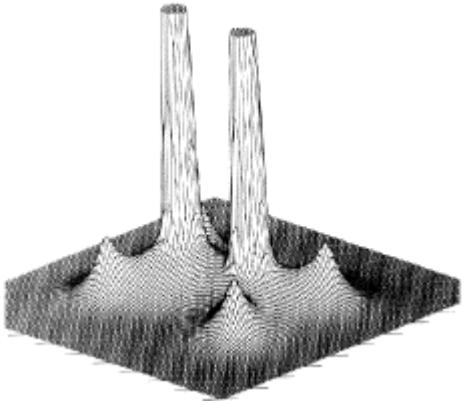

O2
C10
C11
C9
C19
C20
C21
C23
O1
C12
C22
N6
C8
N2
N5
C7
C29
C24
Co1
C18
N1
N4
C17
C25
C28
C1
C6
N3
C14
C16
C27
C26
C2
C13
C5
C3
C15
C4

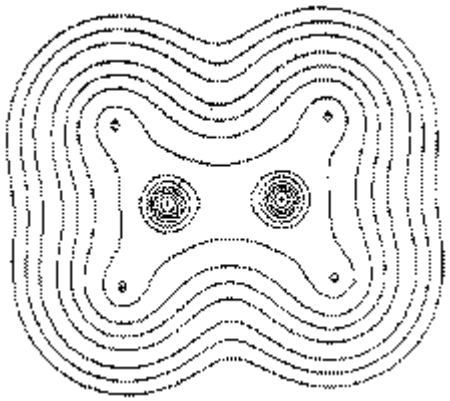

O2
N6
C23
C19
O1
C15
C16
C24
C22
C14
C13
C17
C25
C20
C21
N3
C29
Co
N4
C18
C26
N5
C12
C28
N2
C11
C3
C2
C27
N1
C4
C10
C1
C8
C5
C6
C7
C9

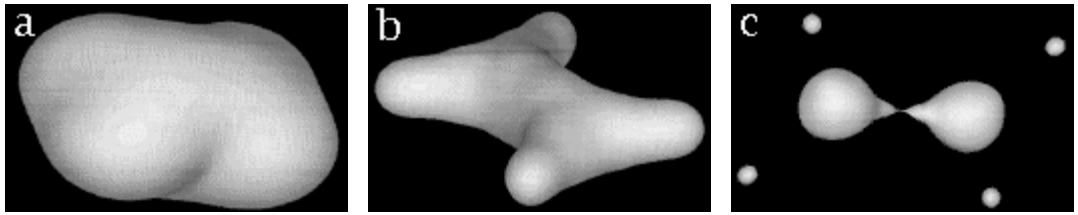

C(19)
O(1)
C(20)
Co(1)
N(1)
N(5)
N(3)
C(2)


N(2)
Co(1)
N(1)
N(5)
H(1A)
H(5C)
N(4)

Prikazi elektronske gustoće





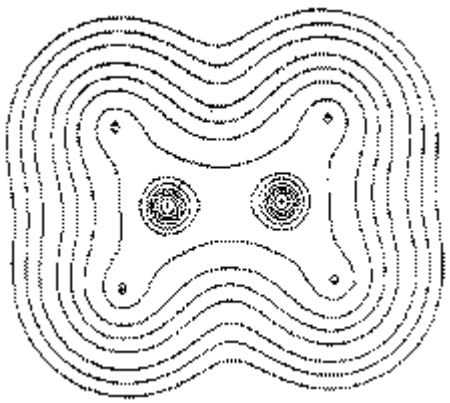


AIM

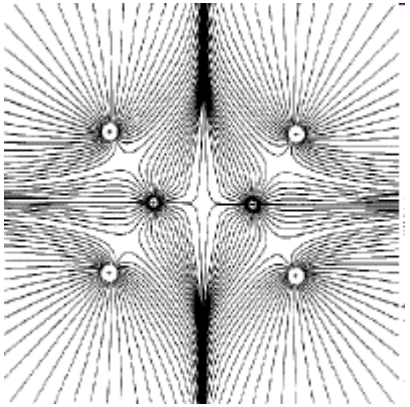
- Atoms In Molecules
- Raspodjela elektronske gustoće u prostoru definira strukturu molekule
- Kako definirati atome, veze itd. u oblaku molekulske elektronske gustoće?

Topologija funkcije gustoće

- Gradijenti, polja, kritične točke i atraktori



envelopa



gradijent

Gradijent – $\nabla\rho$

Vektorsko polje gradijenta – skup svih gradijenatnih putanja

Kritična točka

Atraktor – točka u kojoj se spajaju putanje gradijenata – razdjeljuju molekulu na područja pod utjecajem pojedinih atraktora

Kritične točke

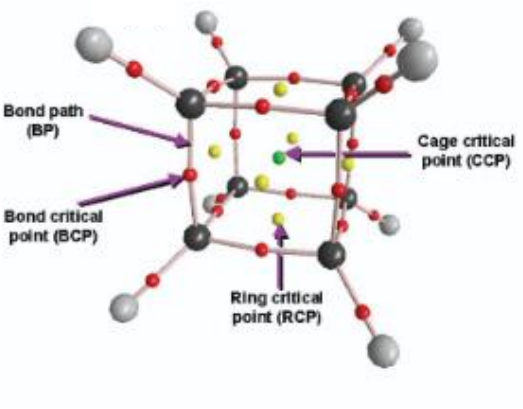
Atraktori (nuklearne kritične točke, NCP) – maksimumi (položaji atoma)

Kritične točke veze (BCP) – sedlaste točke (u 2 smjera maksimum)

Kritične točke prstena (RCP) – sedlaste točke (u 2 smjera minimum)

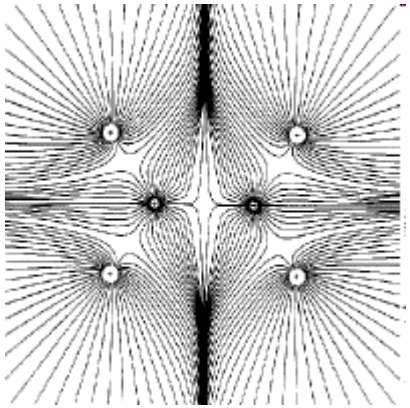
Kritične točke kaveza (CCP) – minimumi

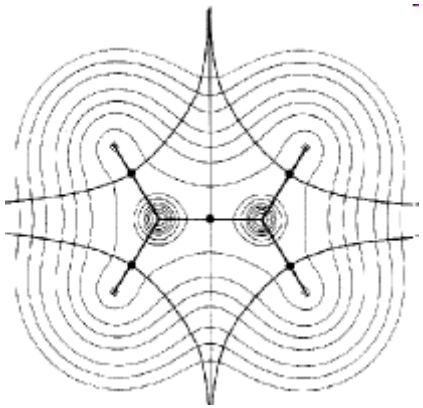
n(NCP) – n(BCP) + n(RCP) – n(CCP) = 1 za izolirane molekule / 0 za (beskonačne) kristalne strukture

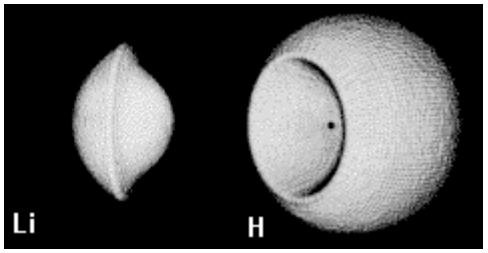


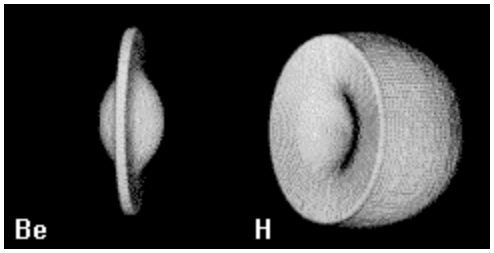
Atom

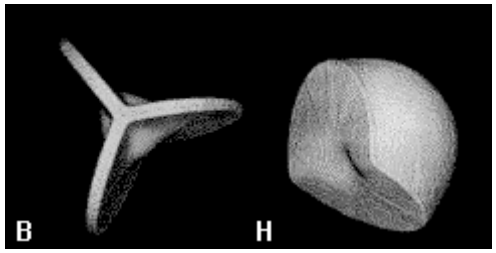
- Jezgra je atraktor
- Pripadni atom je dio prostora u kojemu sve putanje gradijenata imaju isti atraktor
- Postoji skup putanja gradijenata bez atraktora – granice među atomima

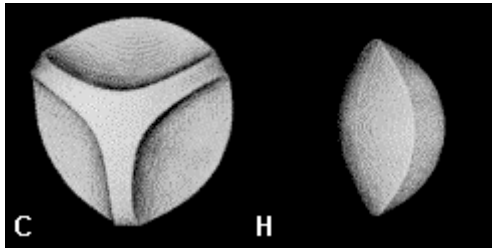


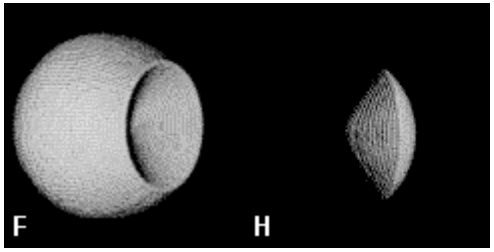


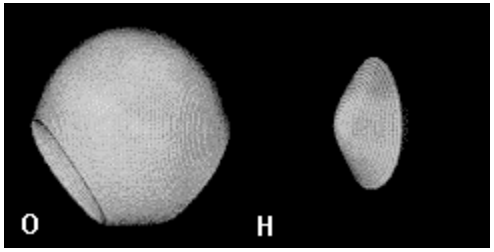

Li
H

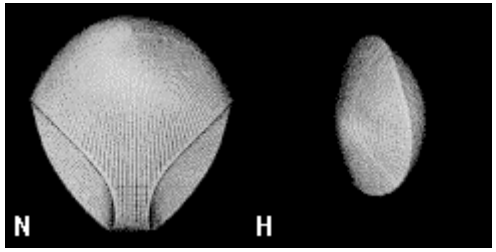

Be
H


B
H


C
H

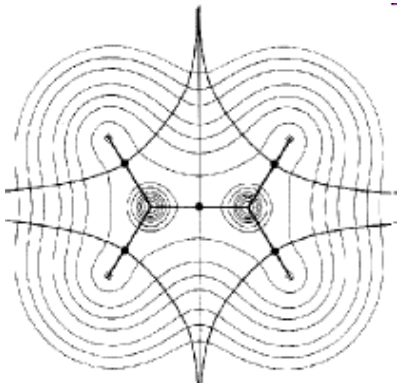

F
H

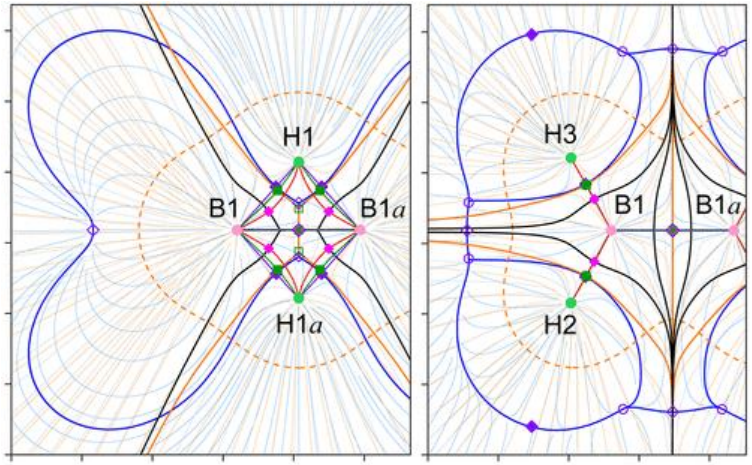

O
H


N
H

Veza

Za svaki par atraktora postoji jedna putanja gradijenta koja ih povezuje – veza



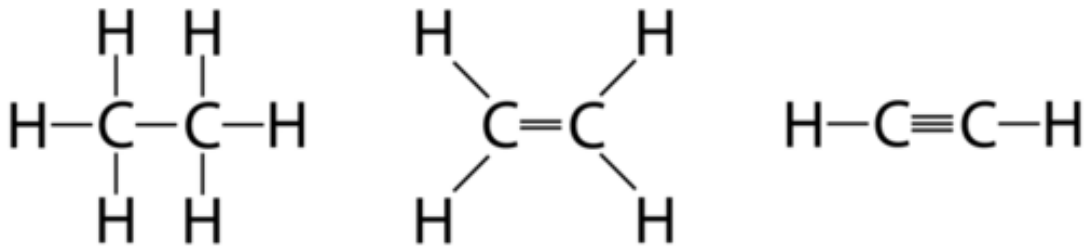


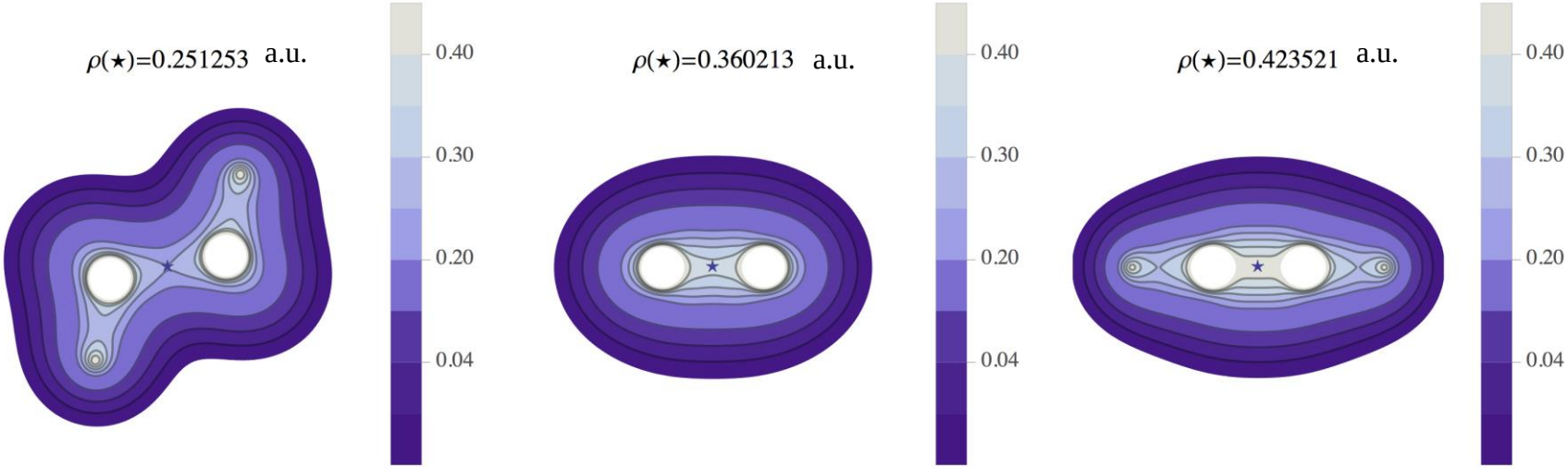
J. Phys. Chem. A 2024, 128, 34, 7284–7297

Svojstva veze

- Vezna udaljenost
- Gustoća naboja u kritičnoj točki
- Eliptičnost

Gustoća naboja u kritičnoj točki



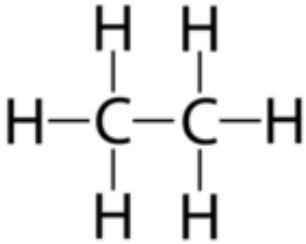


Eliptičnost veze

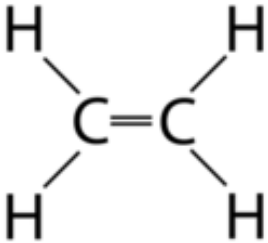
Eliptičnost (ϵ)

$\epsilon = \lambda_1/\lambda_2 - 1$

λ_1 i λ_2 vlastite vrijednosti Hessove matrice pri čemu se uvijek uzima $|\lambda_1| \geq |\lambda_2|$



$\epsilon = 0$



$\epsilon \approx 0{,}45$

$\epsilon = 0$

Kovalentnost i ionskost veze

- Što znači da je veza kovalentna?
- Je li kovalentnija C-O ili C=O?

‘Udio ionske veze’

- Pauling:

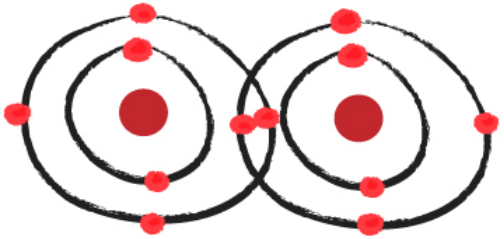
$$\left(1 - e^{-\left(\frac{\Delta\chi}{2}\right)^2}\right) * 100\%$$

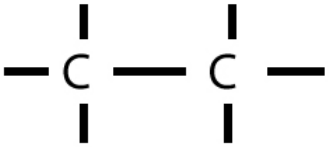
- Preko dipolâ:

$$\left(\frac{\mu_{\mathrm{obs}}}{\mu_{\mathrm{calc}}}\right) * 100\%$$

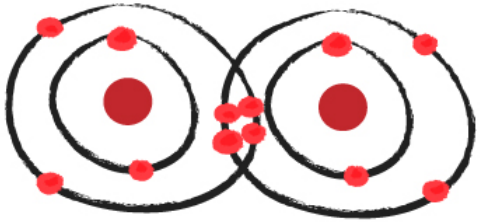
$(\mu_{\mathrm{calc}}) =$ molekulski dipol za slučaj da je veza potpuno ionska (q = Z)

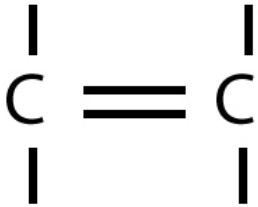
Red veze



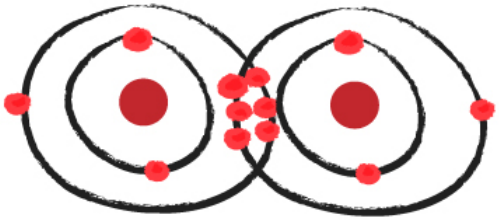


JEDNOSTRUKA



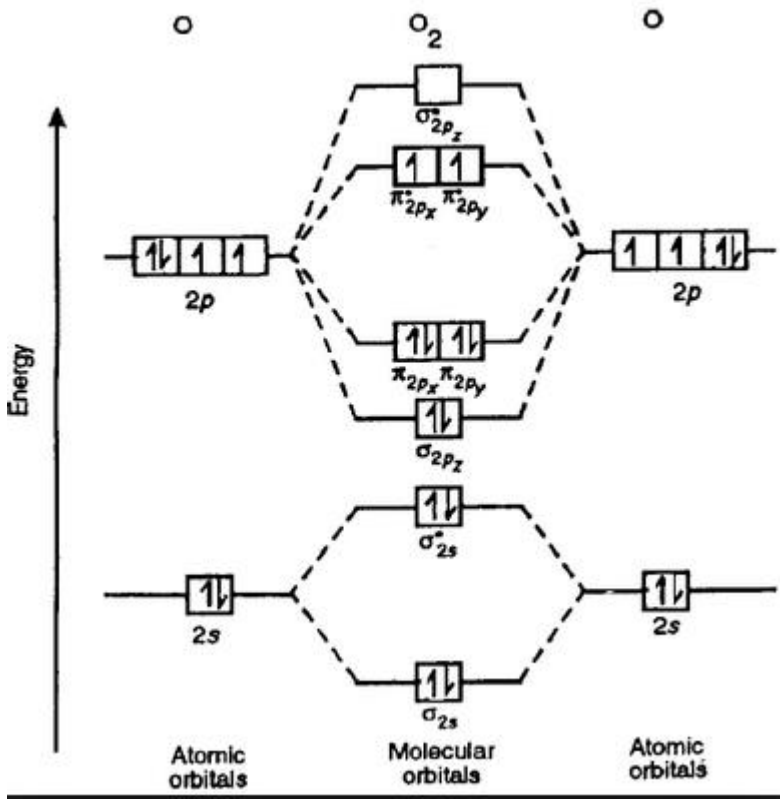


DVOSTRUKA



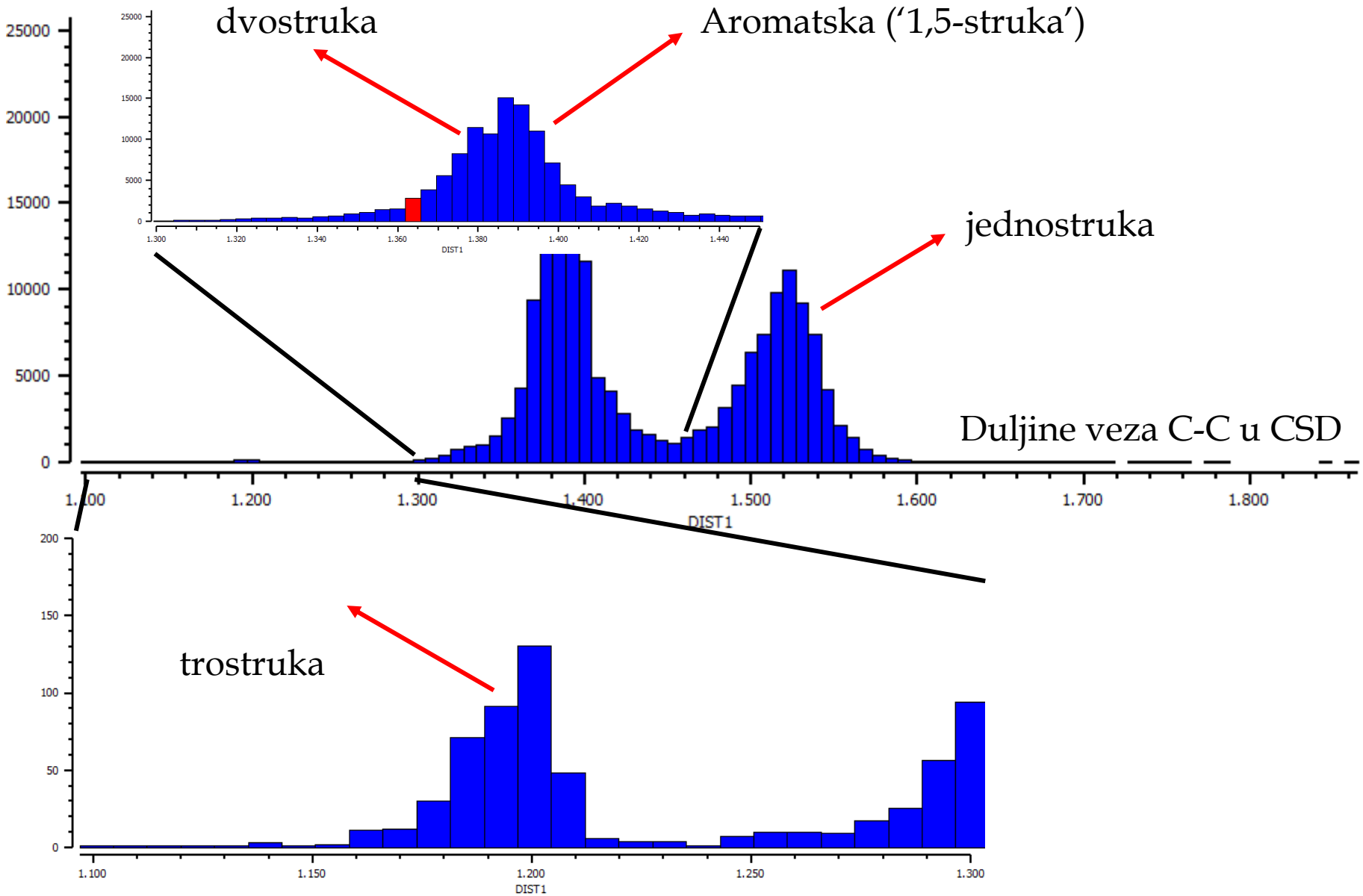
TROSTRUKA

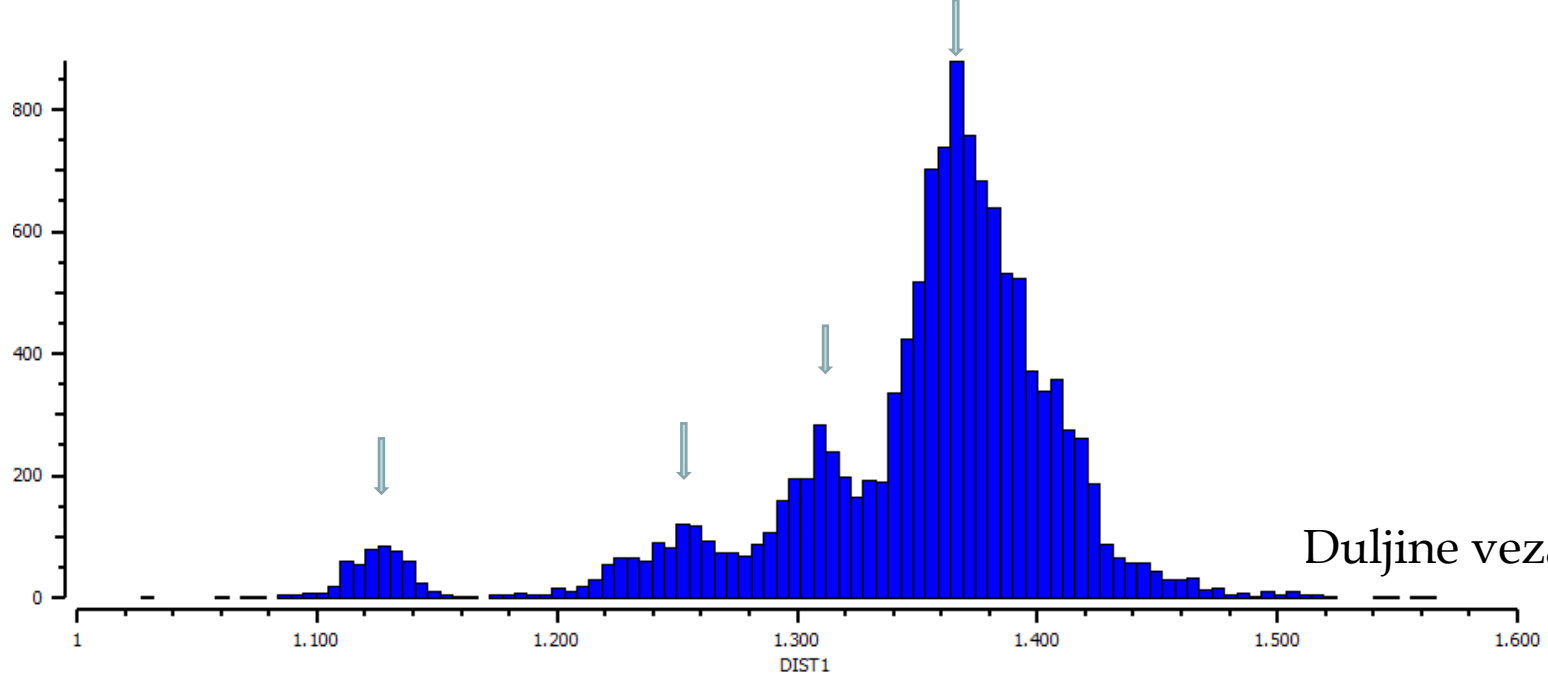
Molekulske orbitale



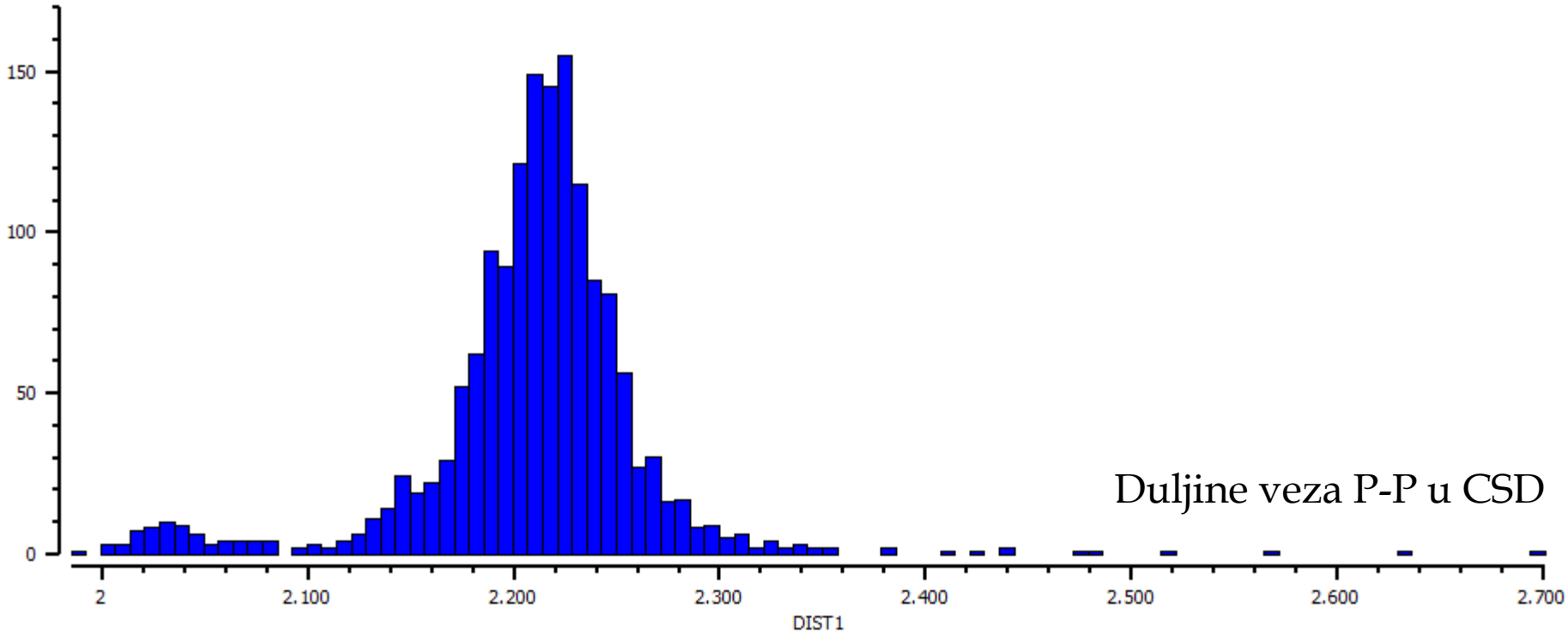
Red veze = $(N(e_{vezni}) - N(e_{protuvezni}))/2$

Red veze i duljina veze

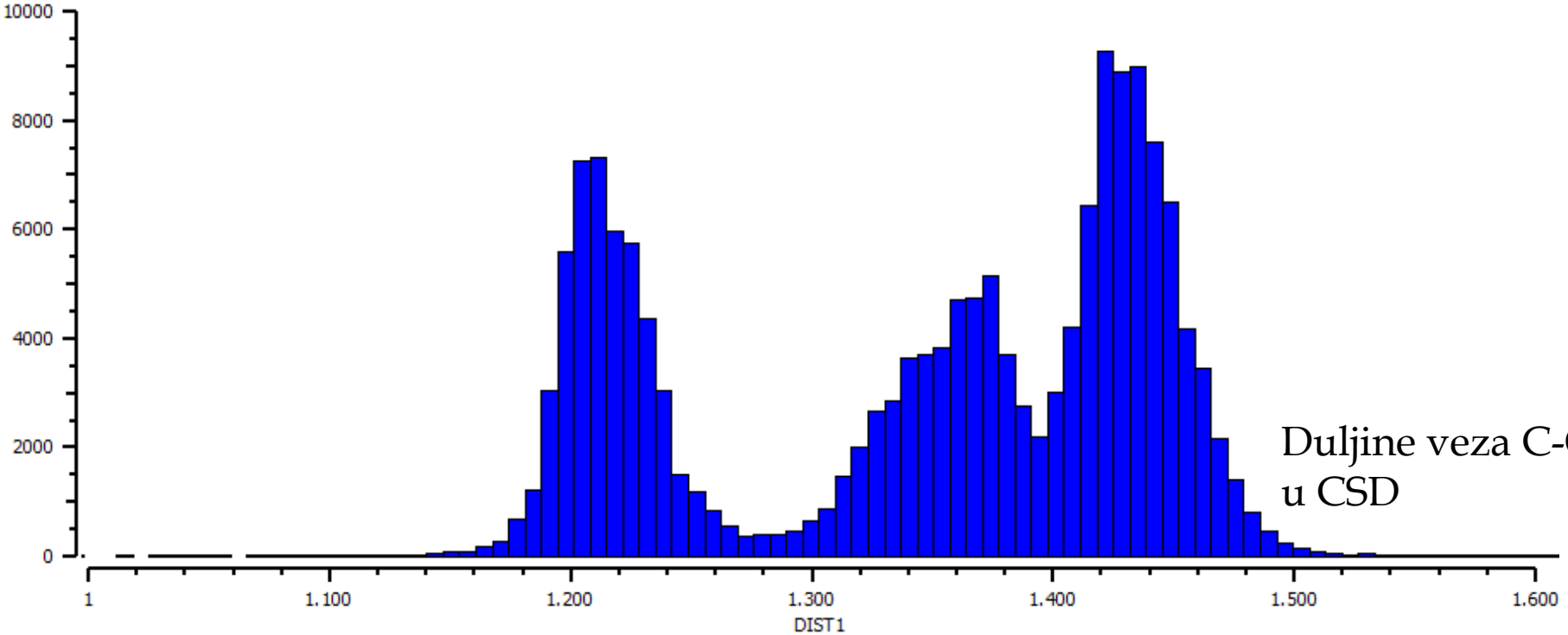




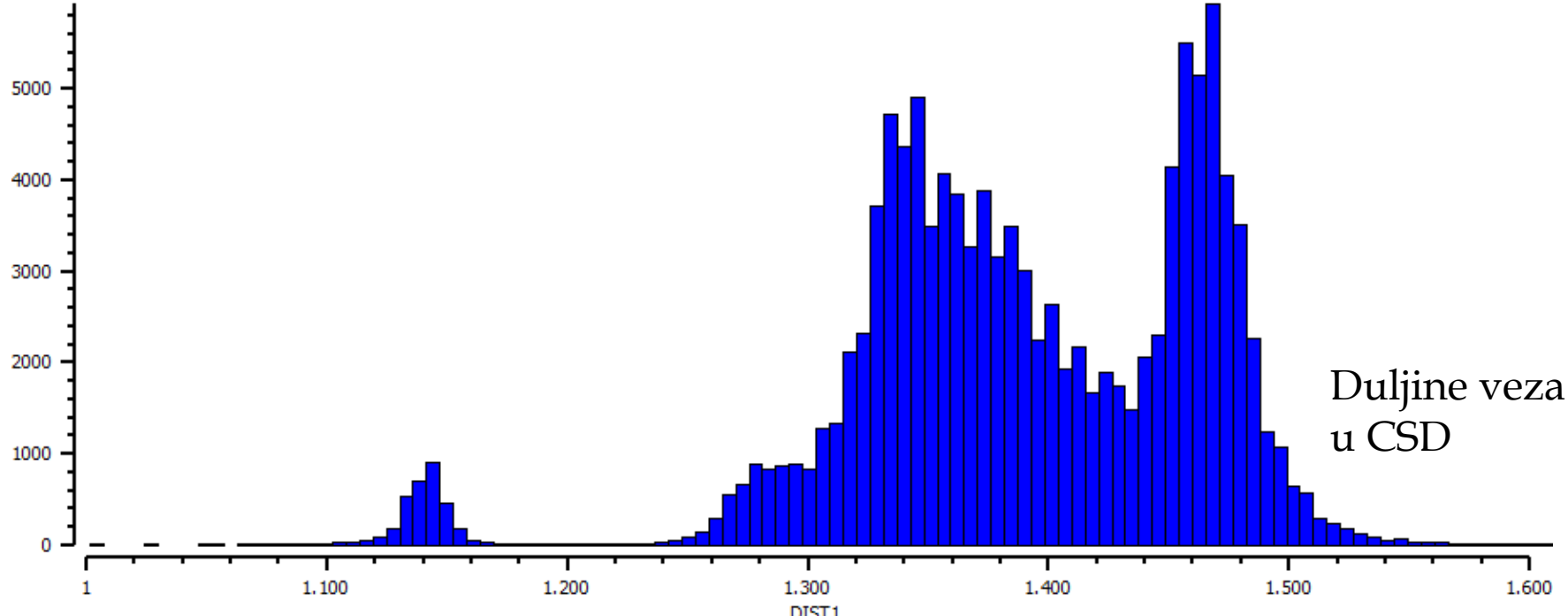
Duljine veza N-N u CSD



Duljine veza P-P u CSD



Duljine veza C-O u CSD



Duljine veza C-N u CSD

Duljina veze i red veze

duljina idealne jednostruke veze

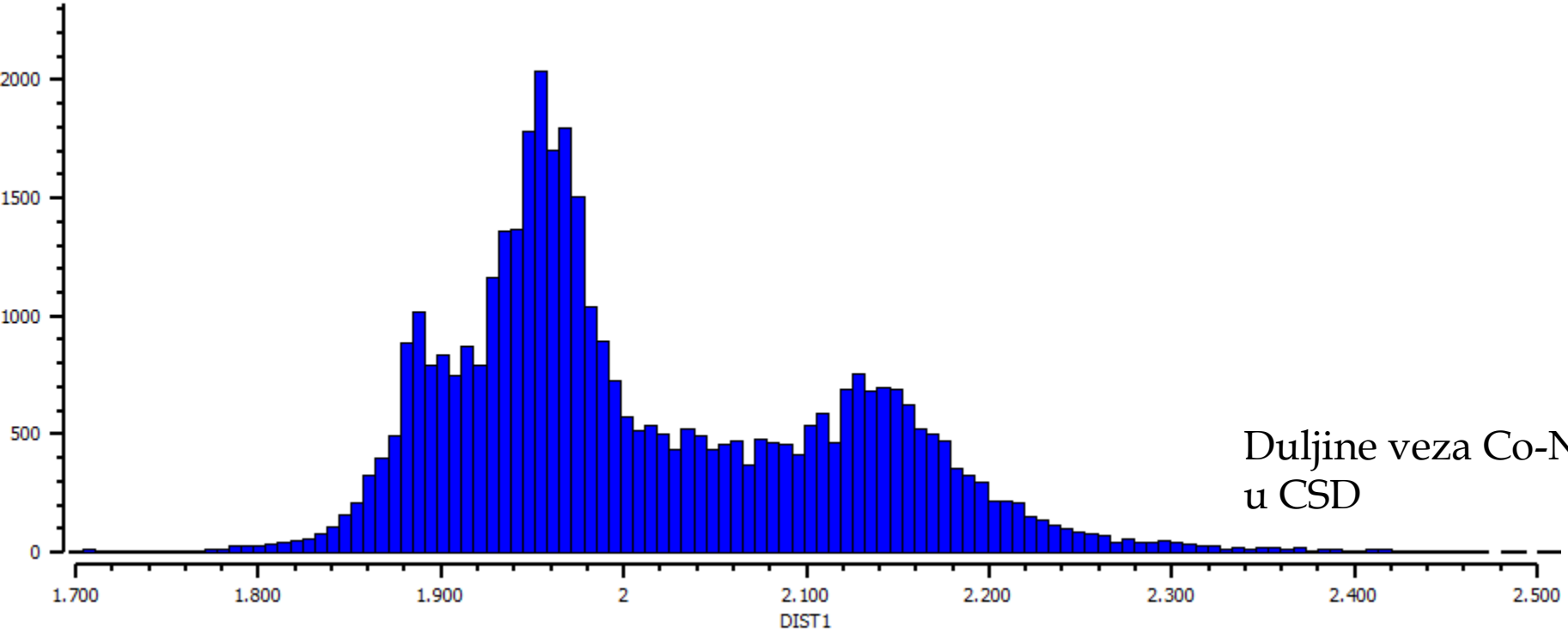
duljina veze

$$S = \exp\left(\frac{d_0 - d}{b}\right)$$

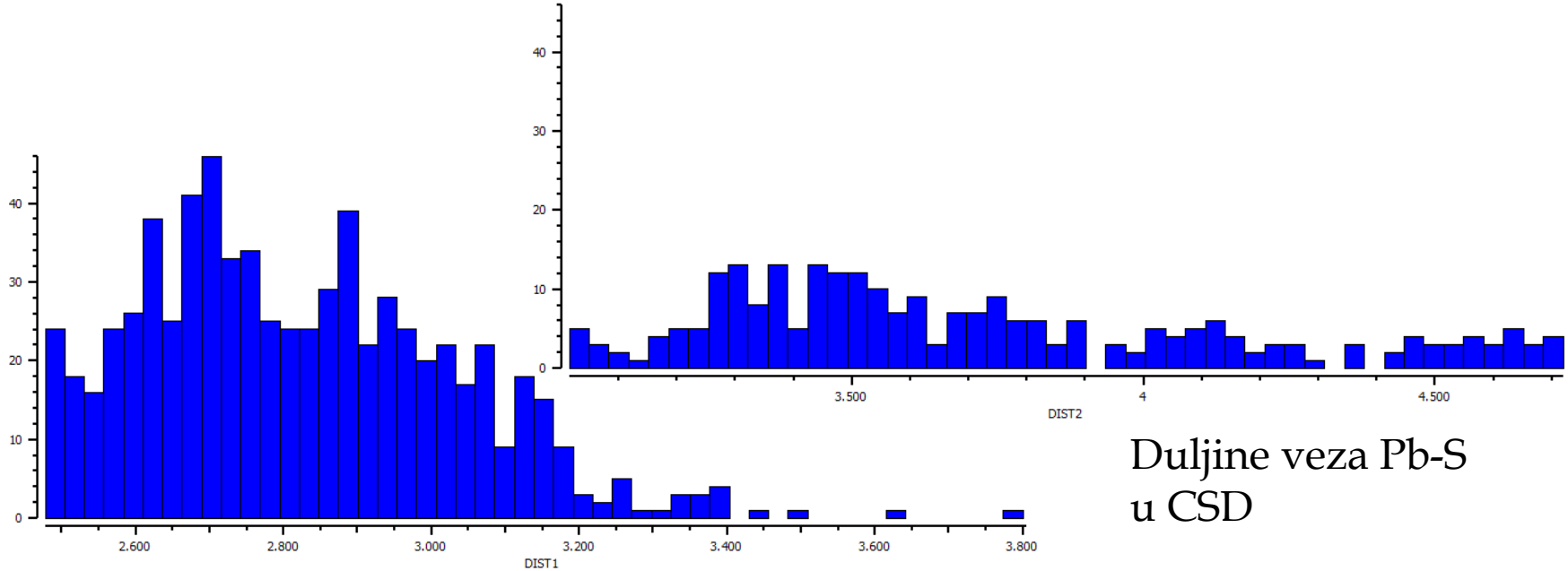
Ugodivi parametar (obično oko 0,37 Å, npr za C 0,352 Å)

Alternativno:

$$S' = \left(\frac{d}{d_0}\right)^{-6}$$



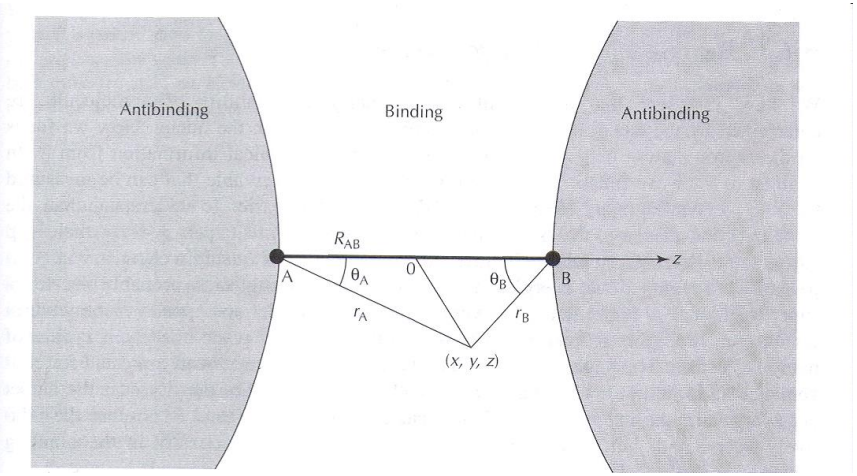
Duljine veza Co-N u CSD



Duljine veza Pb-S u CSD

Ako znamo elektronsku gustoću...

Sila koja djeluje na atomsku jezgru jednaka je zbroju kulonskih sila kojom na nj djeluju ostale jezgre i one kojom na nj djeluje elektronski oblak



$$F_{X_\gamma} = -Z_\gamma \left(\int \mathrm{d}\mathbf{r}\, \rho(\mathbf{r}) \frac{x - X_\gamma}{|\mathbf{r} - \mathbf{R}_\gamma|^3} - \sum_{\alpha \neq \gamma}^{M} Z_\alpha \frac{X_\alpha - X_\gamma}{|\mathbf{R}_\alpha - \mathbf{R}_\gamma|^3} \right).$$

Elektronska gustoća između jezgara je vezna

Elektronska gustoća s vanjske strane jezgara je protuvezna

Razlika integrala vezne i protuvezne = red veze * 2

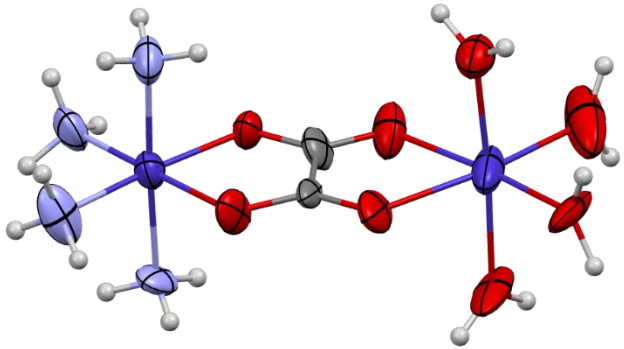
Valencija

Metoda vezne valencije (*bond valency sum*):

Valencija atoma = zbroj redova svih veza koje neki atom čini

- Pogodna metoda za određivanje oksidacijskih stanja temeljem geometrijskih parametara

BVS = 3,49

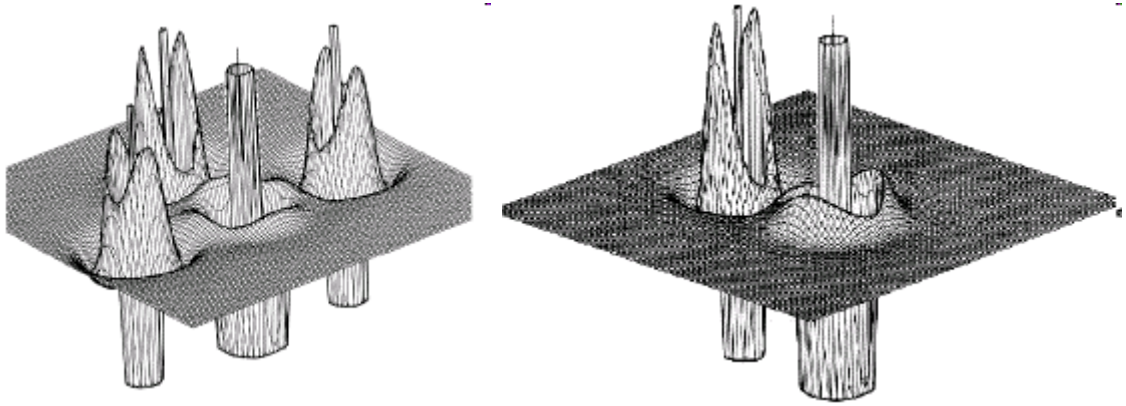


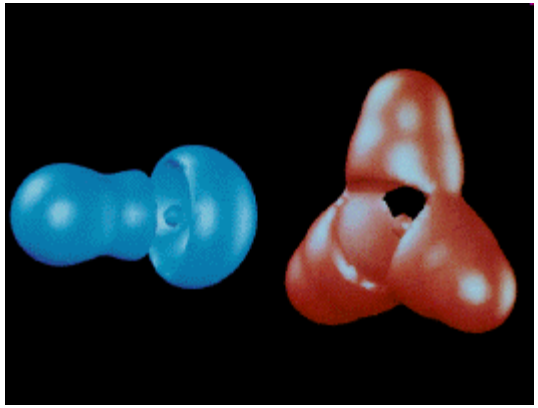
BVS = 2,10

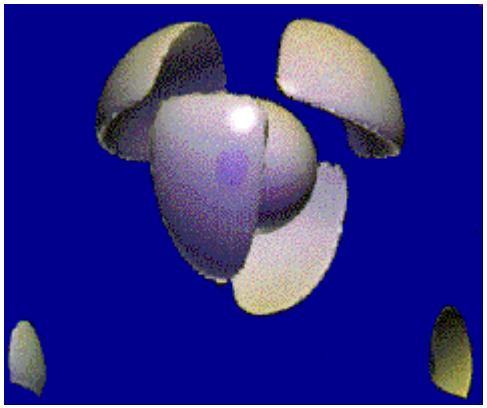
$[(NH_3)_4CoC_2O_4Co(H_2O)_4]^{3+}$.

Nevezni parovi – Laplacian elektronske gustoće

- Suvišak ($\nabla^2\rho < 0$) ili manjak ($\nabla^2\rho > 0$) elektronske gustoće – lociranje neveznih elektrona

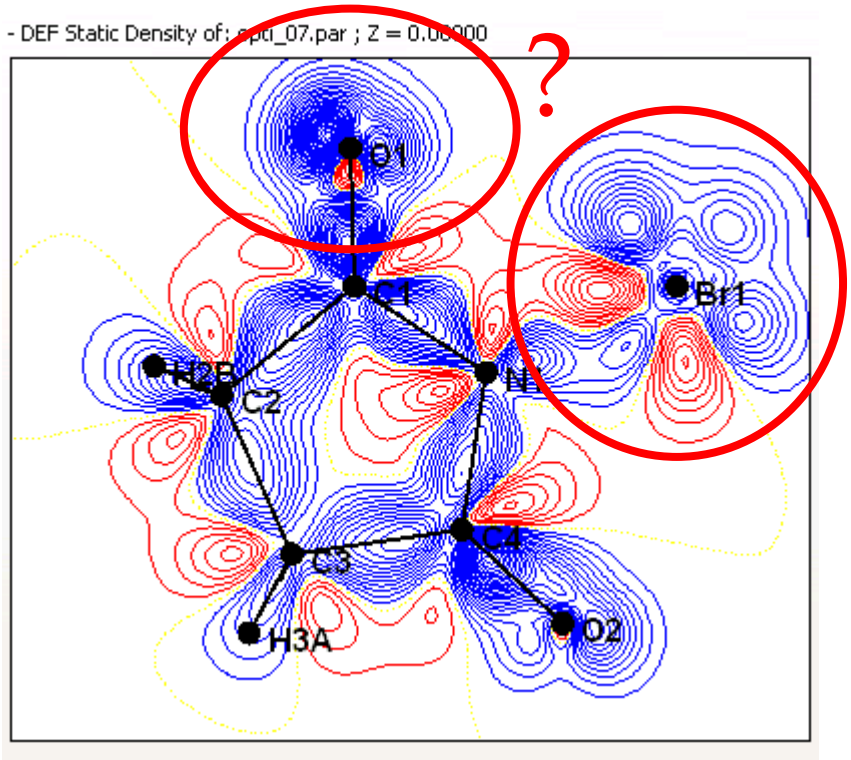


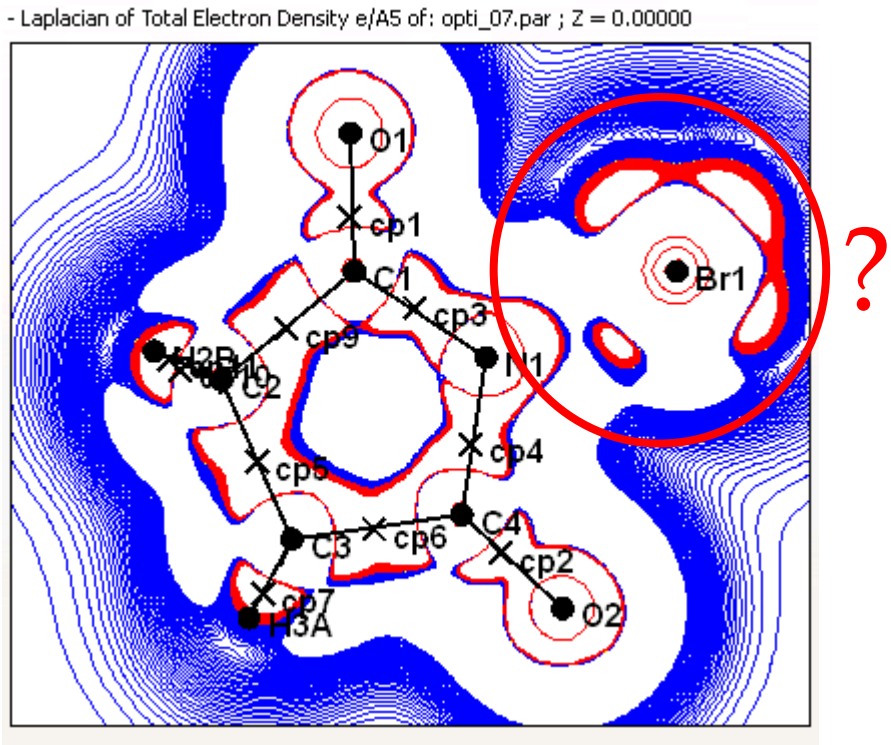




Ali...

- Za gledati fine detalje treba i fina mapa elektronske gustoće...





CAPVT IIa

Vezno, nevezno (ali ne i bezvezno)

Međumolekulske interakcije

- Interakcija permanentnih dipola (Keesomova sila)
- Interakcija permanentnog i induciranog dipola
- Interakcija induciranih dipola (disperzna, Londonova sila)
- Jaka vodikova veza
- Slaba vodikova
- Halogenska veza
- Međuhalogenska veza

- Interakcija π—π
- Interakcija π—kation
- Interakcija π—anion
- Interakcija π—halogen
- Interakcija π—halkogen (O, Te)
- Interakcija π—N
- N–H··· Cl_2–M
- Interakcija halkogen—halkogen
- ...

Najjednostavnije međumolekulske interakcije

- Interakcija permanentnih dipola (Keesomova sila)
- Interakcija permanentnog i induciranog dipola
- Interakcija induciranih dipola (disperzna, Londonova sila)

} van der Waalsove sile (interakcije)

Da bi molekula imala električni dipol

- Mora biti polarne simetrije.
- Mora imati pogodnu raspodjelu naboja – prisuće atomâ velikih razlika u elektronegativnosti.
  - Dipolni momenti obično reda veličine (10^{-30} – 10^{-29}) C m.
  - Pogodna jedinica

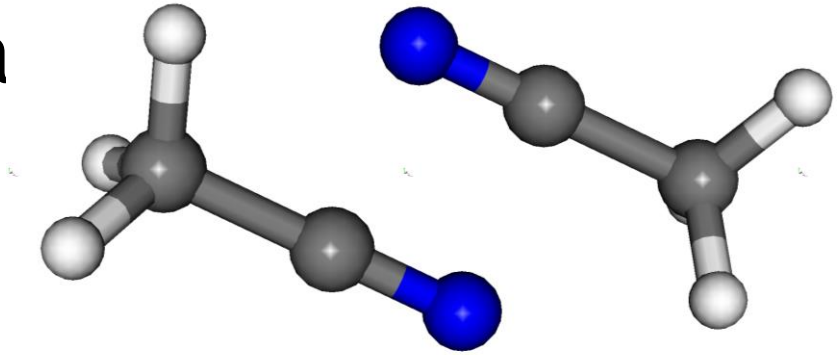
  $D \approx 3.33564 \times 10^{-30}$ C ·m

Molekula	μ/D
H_2O	1,8546(40)
HF	1,82618(6)
HCl	1,1086(3)
NH_3	1,14718
$CHCl_3$	1,04(2)
$(CH_3)_2CO$	2,88(3)
$(CH_3)_2SO$	3,96(4)
C_2H_5OH	1,69(3)
HCN	2,985188

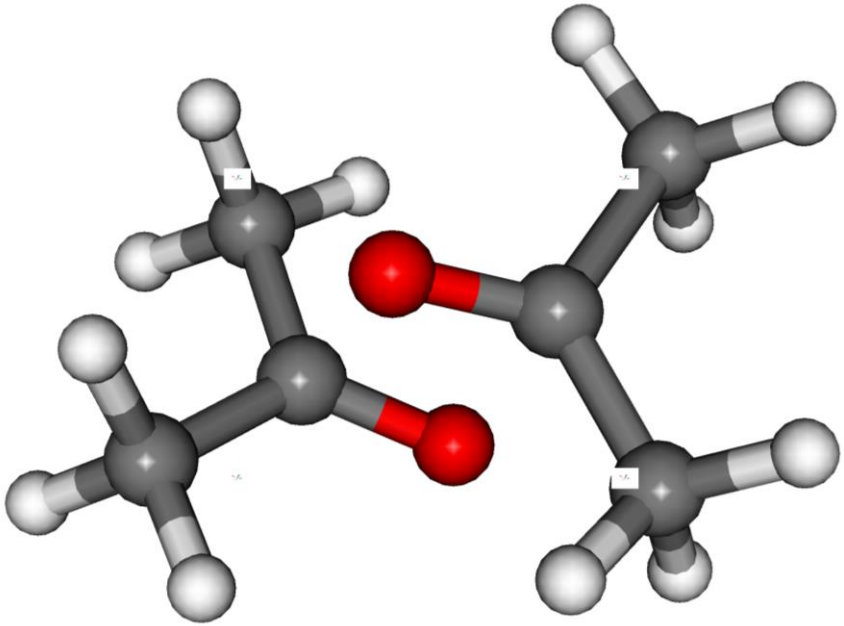
Određivanje dipolnog momenta molekule

- Mjerenjem dielektrične konstante (Clausius-Mosotti-Debyeova jednadžba).
- Iz rotacijskih spektara (Starkov učinak).
- Račun (*ab initio* ili semiempirijski) – nuždno poznavanje razmještaja atomâ u molekuli.

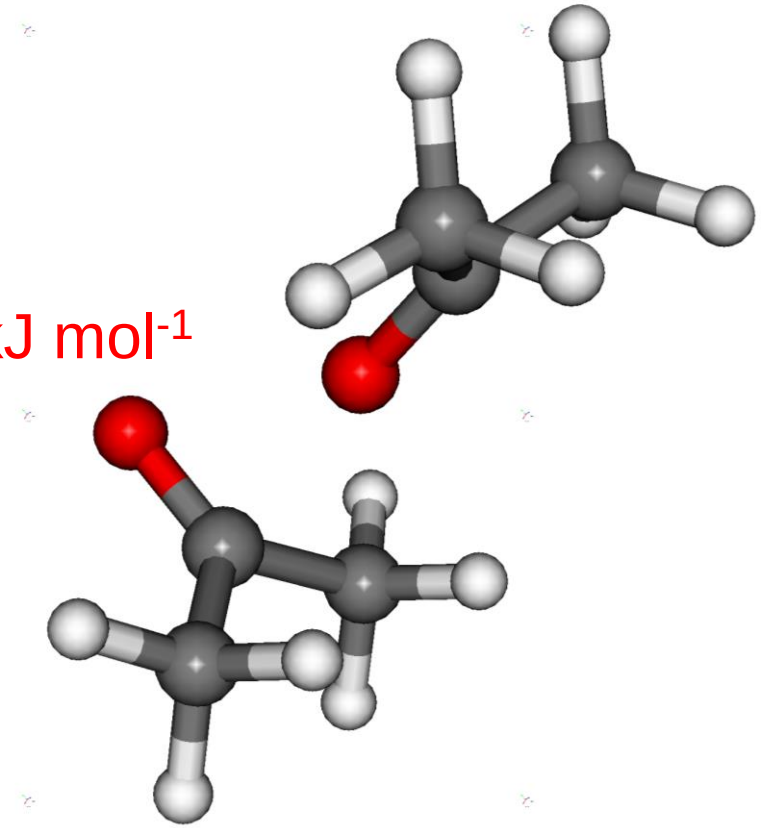
Energije dipolnih interakcija



-16,0 kJ mol^{-1}

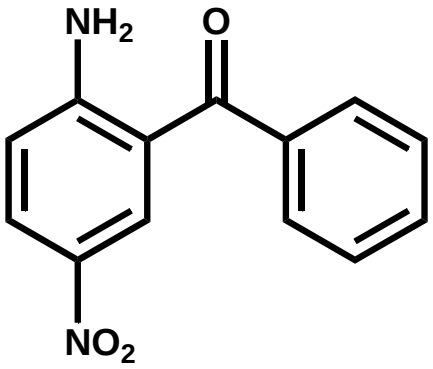


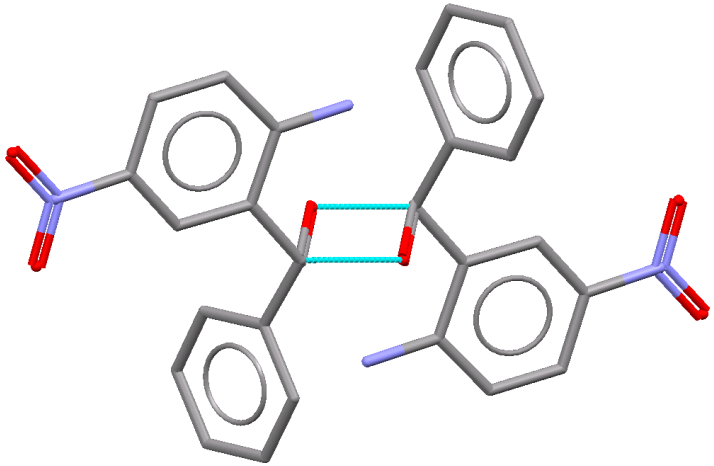
-22,3 kJ mol^{-1}



-7,6 kJ mol^{-1}

Približavanje karbonila – dipolna interakcija ili početak nukleofilne adicije?





Vodikova veza

An *A*–H···*B* interaction is called a hydrogen bond if 1) it constitutes a local bond, and 2) *A*–H acts as a proton donor to *B*.

***Interakcija* A–*H*···B *naziva se vodikovom vezom ako je 1) u pitanju lokalna veza, i 2)* A–*H djeluje kao proton-donor prema* B.**

T. Steiner, *Angew. Chem.*, **41** (2002), 41-76.

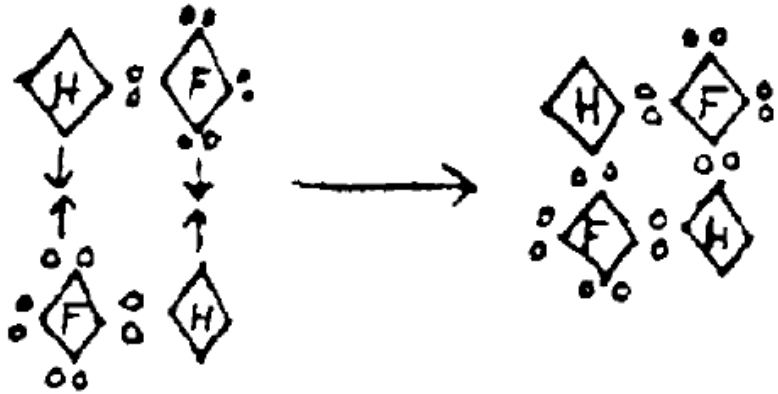
Podjela prema G. A. Jeffreyju (1997.)

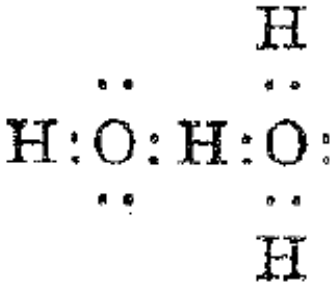
	jaka	srednja	slaba
vrsta interakcije	kovalentna	elektrostatska	elektrostatska / disperzijska
duljina veze H···*A* (Å)	1,2 – 1,5	1,5 – 2,2	> 2,2
produljenje veze *X*–H (Å)	0,08 – 0,25	0,02 – 0,08	< 0,02
omjer *X*–H/H···*A*	*X*–H ≈ H···*A*	*X*–H < H···*A*	*X*–H << H···*A*
X···*A* (Å)	2,2 – 2,5	2,5 – 3,2	> 3,2
usmjerenost	jaka	srednja	slaba
kut (°)	170 – 180	> 130	> 90
energija veze (kcal mol^{-1})	15 – 40	4 – 15	< 4
rel. pomak u IR spektru (cm^{-1})	25 %	10 – 25 %	< 10 %

Kovalentna?

G. N. Lewis, 1916.

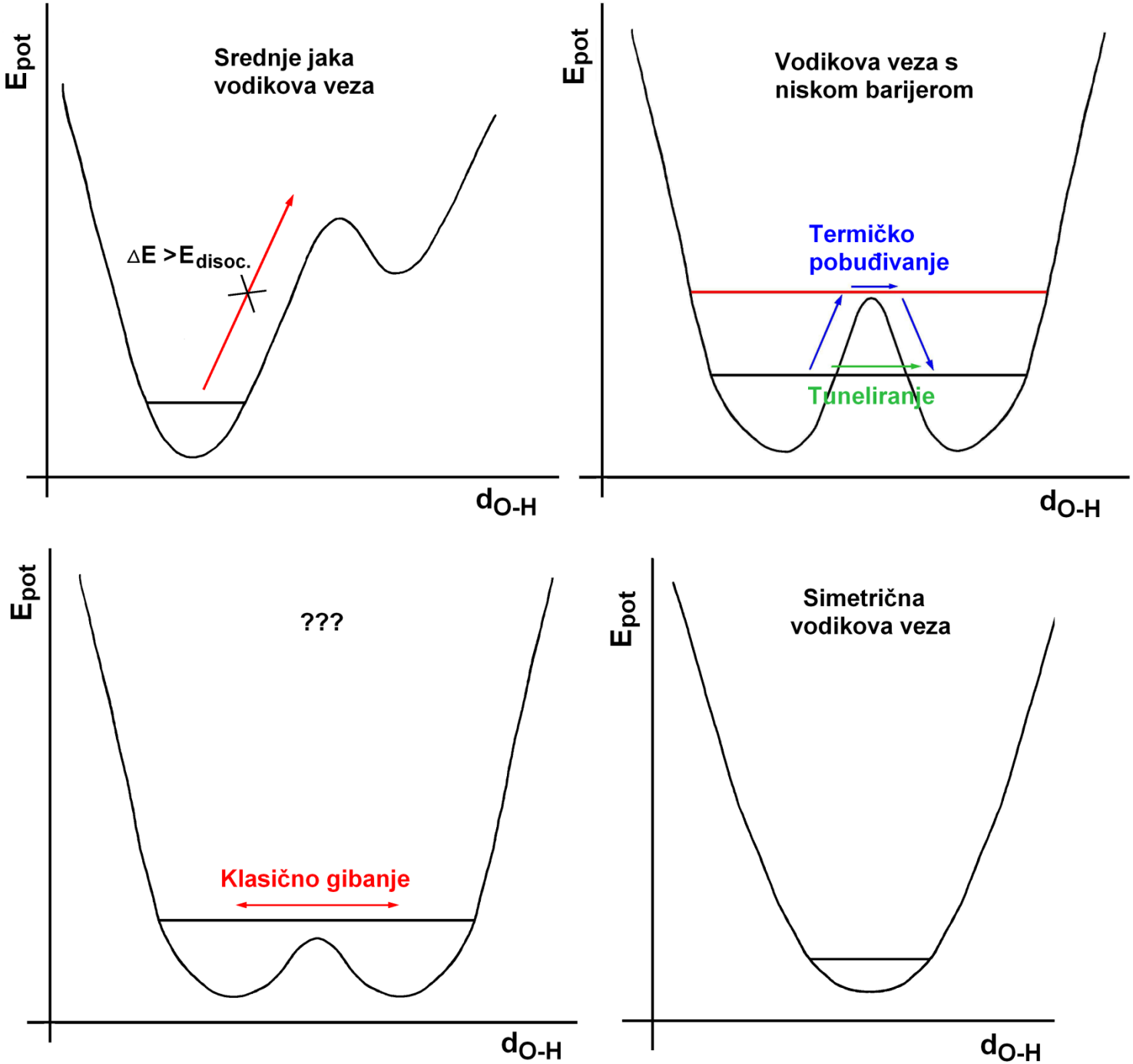
M. L. Huggins, 1919.



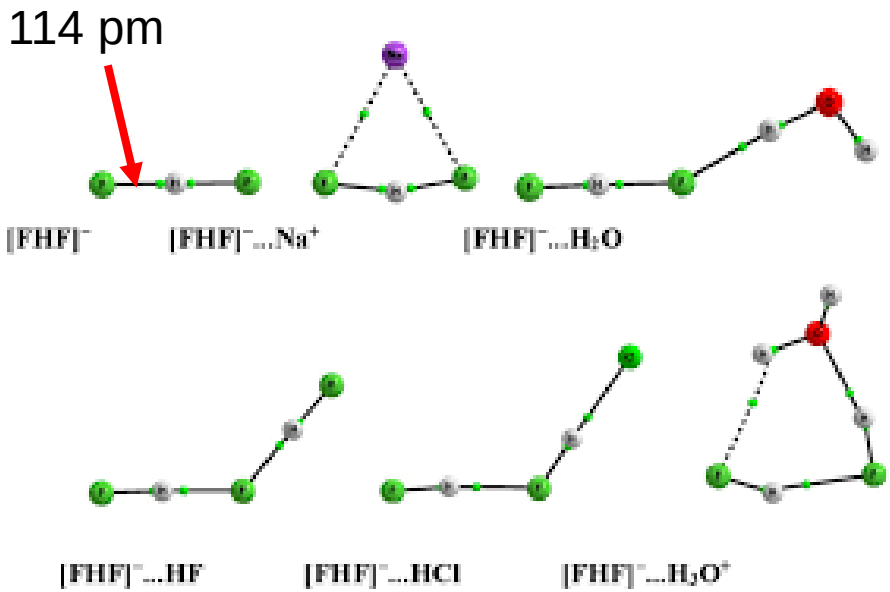


Latimer & Rodebush, 1920.

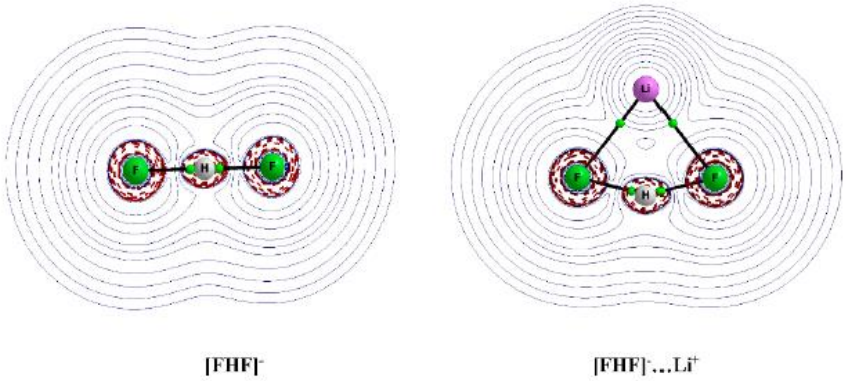
Potencijalne jame



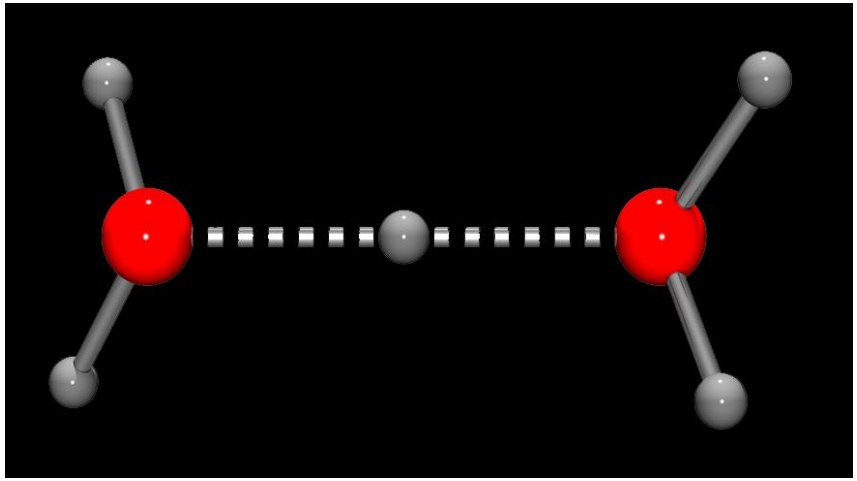
Jaka vodikova veza: hidrogendifluoridni anion (HF_2^-)



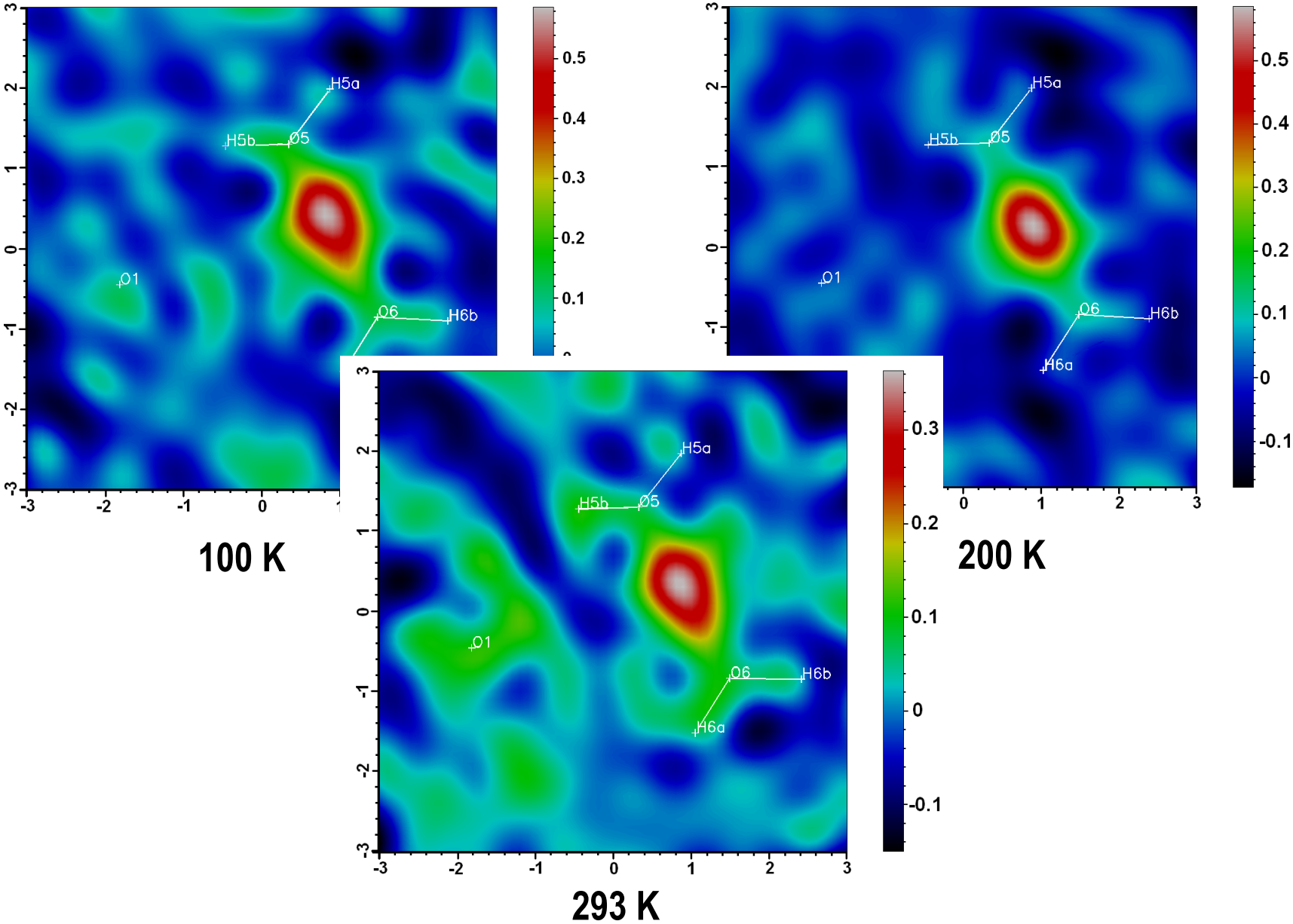
Energija veze > 155 kJ/mol. (energija veze u molekuli HF 565 kJ/mol, a u molekuli F_2 = 155 kJ/mol).



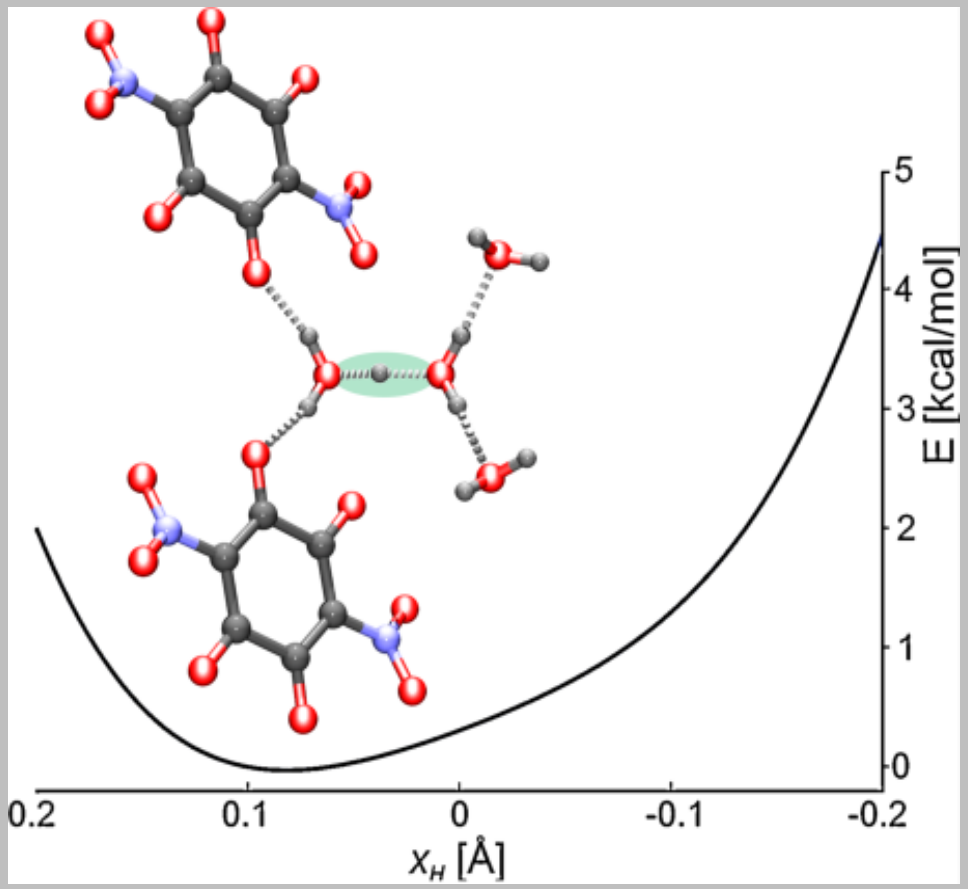
Jaka vodikova veza: Zundelov ion ($H_5O_2^+$)



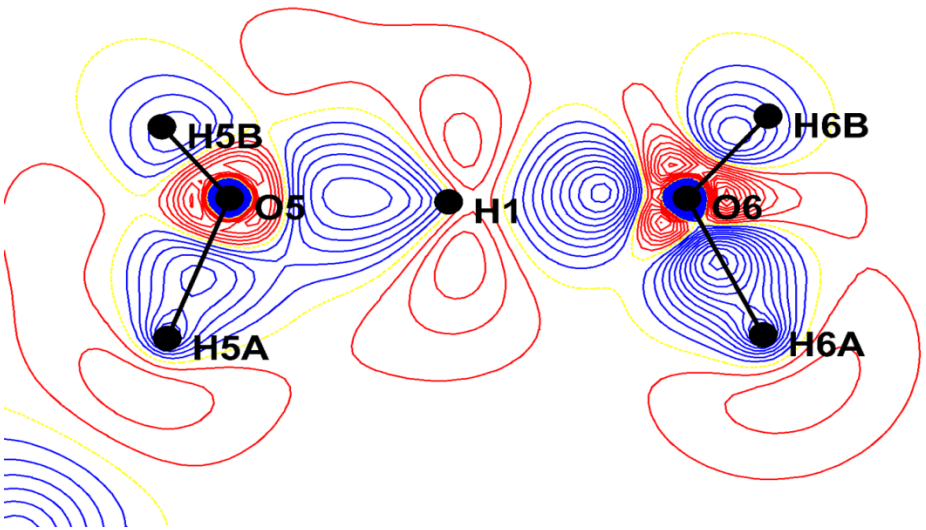
Gdje je proton?



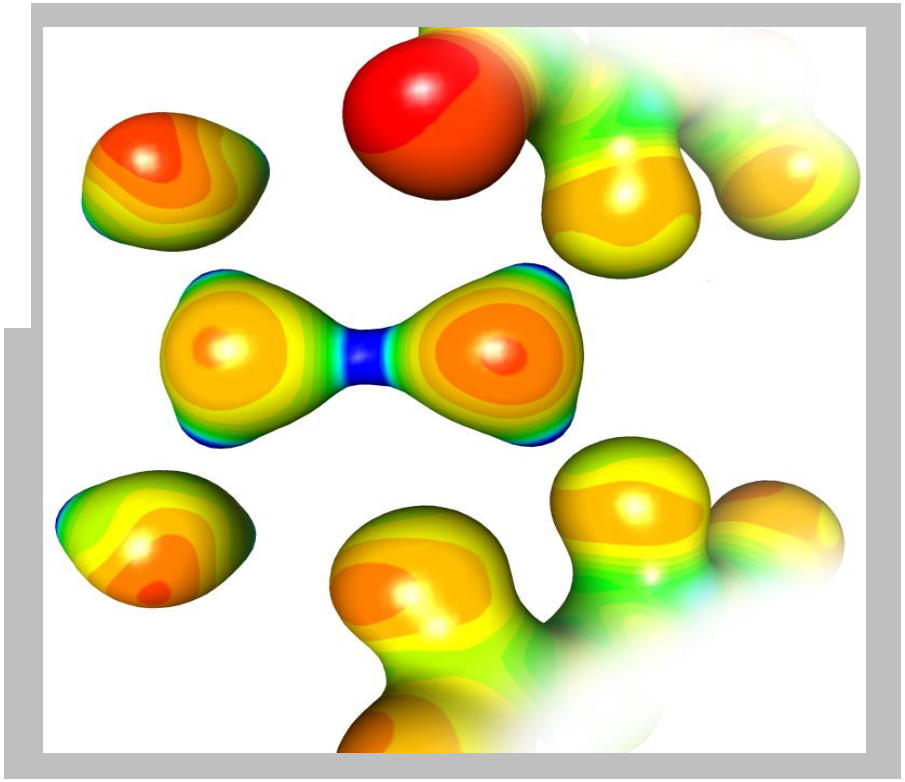
Iz kvantno-kemijskih računa:



Gustća naboja na Zundelovom ionu



Površina: 0,5 e Å-3

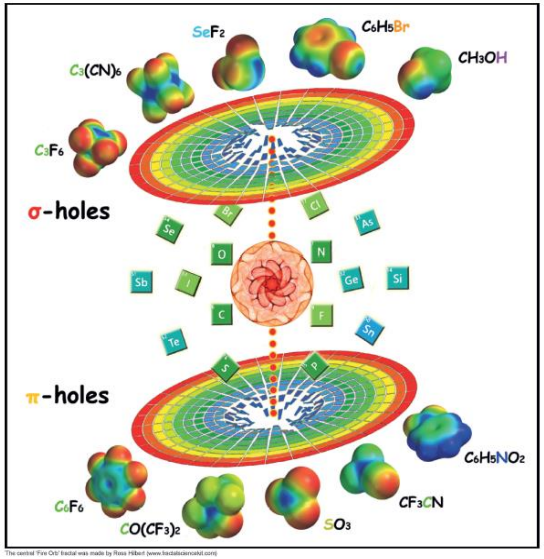


Molčanov, K., Jelsch, C., Wenger, E., Stare, J., Madsen, A.Ø., Kojić-Prodić, B. CrystEngComm, 2017, 19(28), 3898-3901

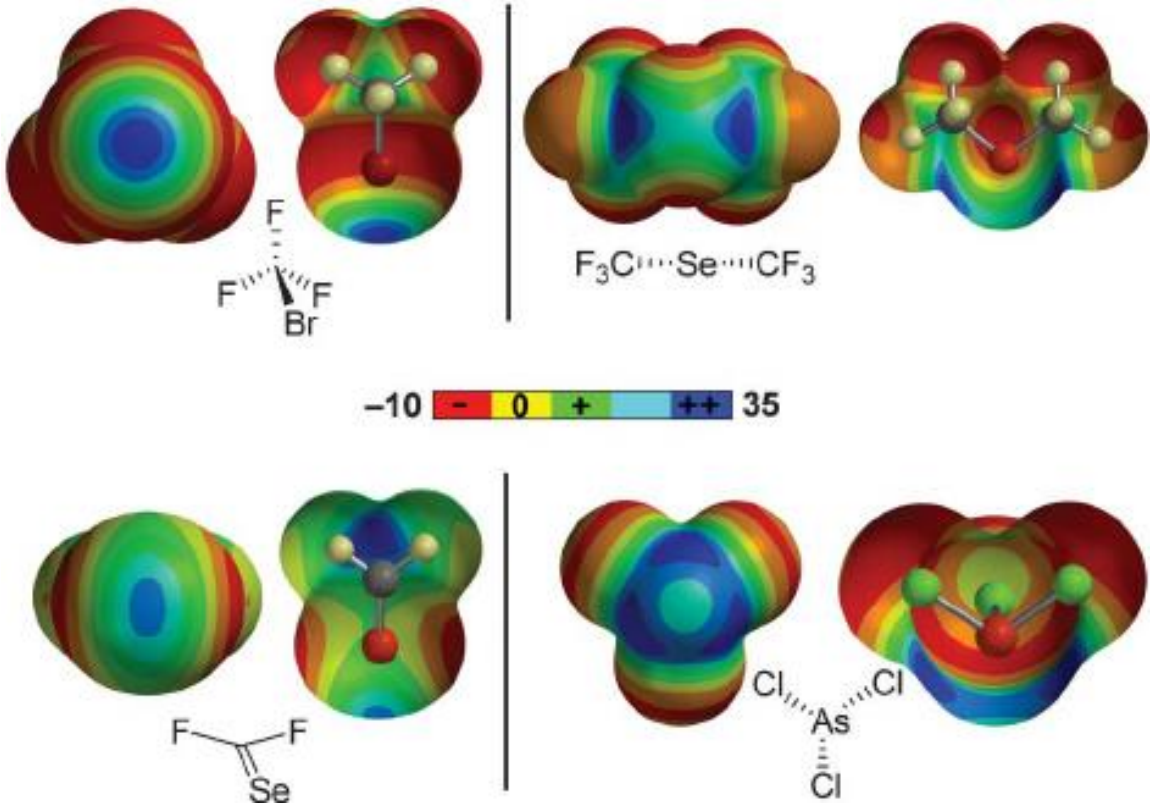
Interakcije σ-šupljine

Svi teški atomi su polarizabilni – nasuprot kovalentne veze imaju manjak elektrionske gustoće – Lewisove kiseline (elektrofili)

Halogenska veza
Halkogenska veza
Pnikogenska veza
Tetrelna veza
Trielna veza
Aerogenska veza



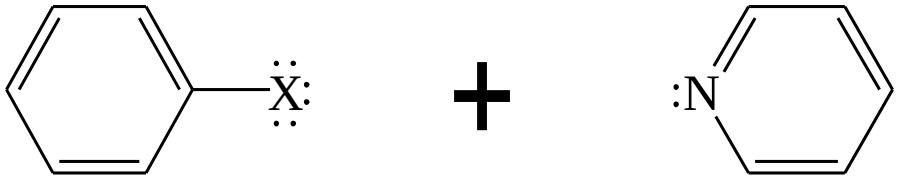
A. Bauza, T.J. Mooibroek, A. Frontera, The Bright Future of Unconventional σ/π-Hole Interactions, *ChemPhysChem.*, 2016, 16, 2496.

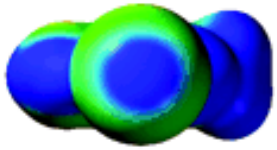


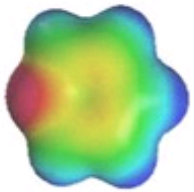
Halogenska veza

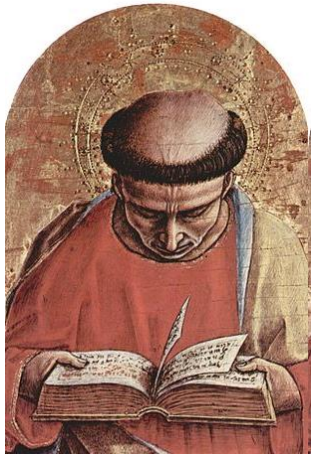
•A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.

Pure Appl. Chem., 2013, 85, 1711.



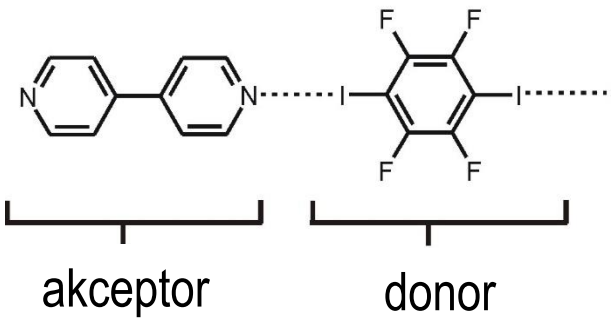






PRIVLAČNOST

Halogenska veza



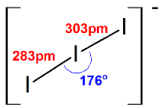
A··· X–Y

•Donor – polarizabilni (& polarizirani) atom halogena (I>Br>Cl>>F)

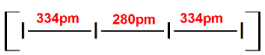
•Akceptor – Lewisove baze (N>O>S)

•Linearne (kut Y-X···A blizu 180°) i jake (neutralne 10–90 kJ mol^{-1} ionske > 150 kJ mol^{-1})

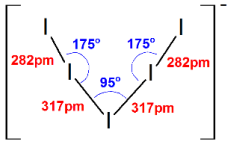
Jaka halogenska veza: polihalogenidni anioni



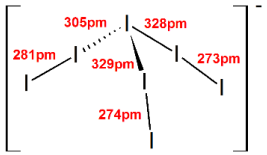
$[I_3]^-$ in $Cs^+[I_3]^-$



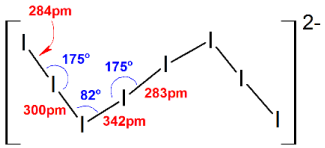
The linear $[I_4]^{2-}$ ion in $[Cu(NH_3)_4]^{2+}[I_4]^{2-}$



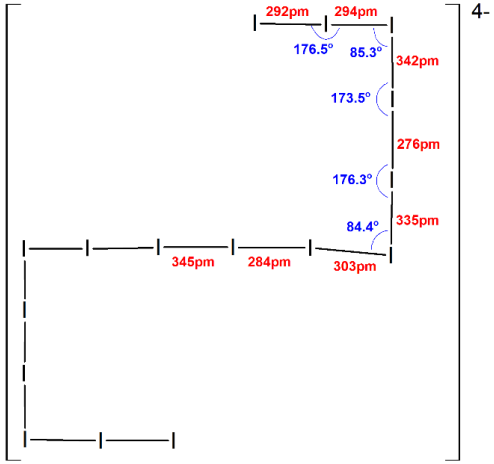
$[I_5]^-$ in $[Me_4N]^+[I_5]^-$



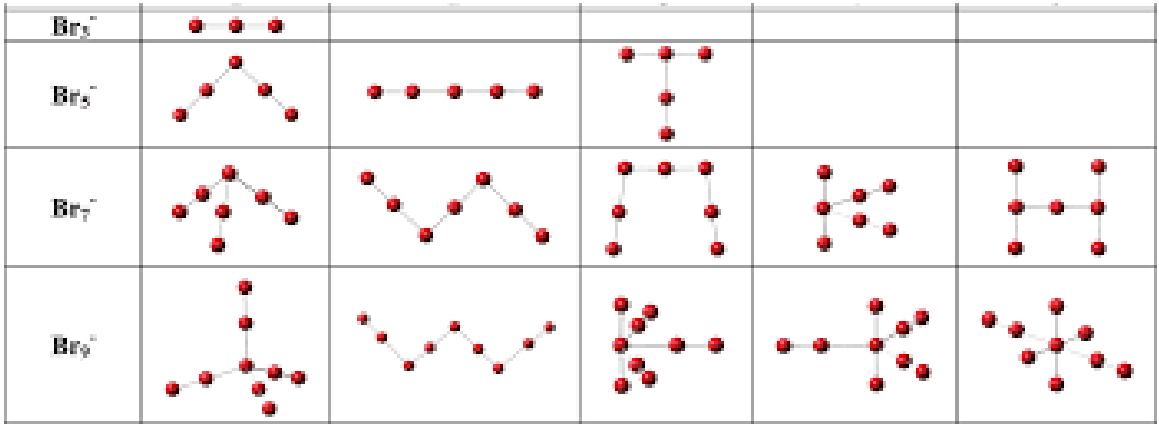
$[I_7]^-$ in $[Ph_4P]^+[I_7]^-$

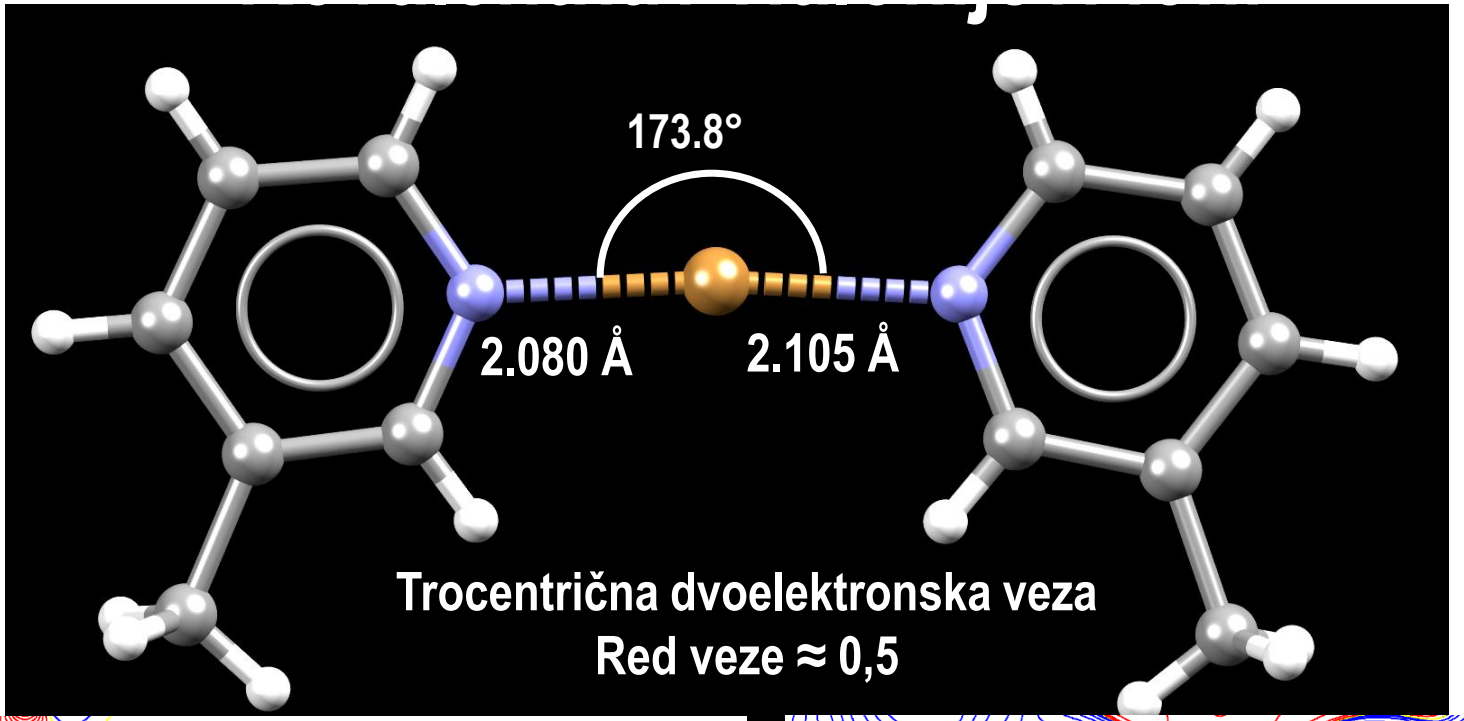


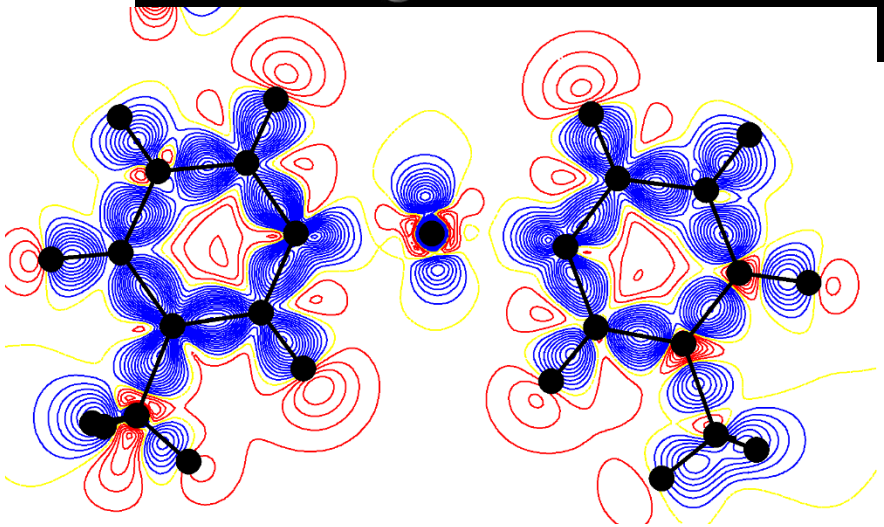
The centrosymmetric $[I_8]^{2-}$ ion in $Cs_2[I_8]$

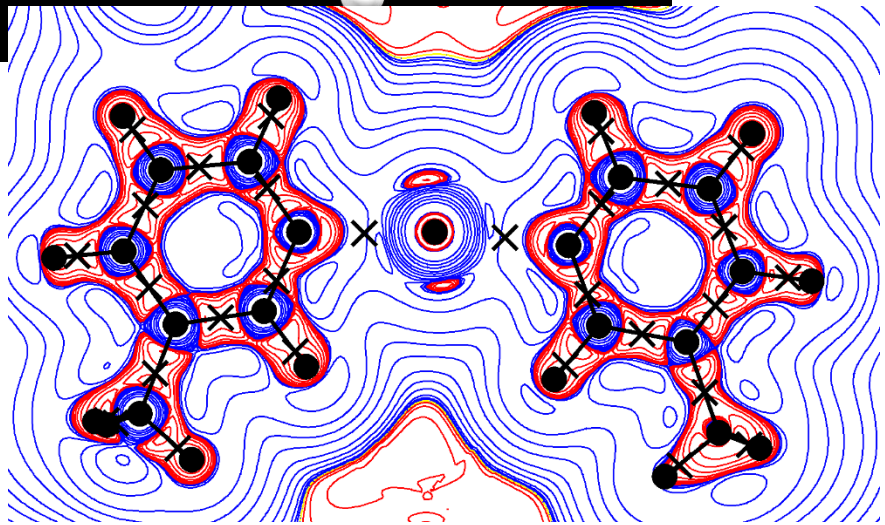


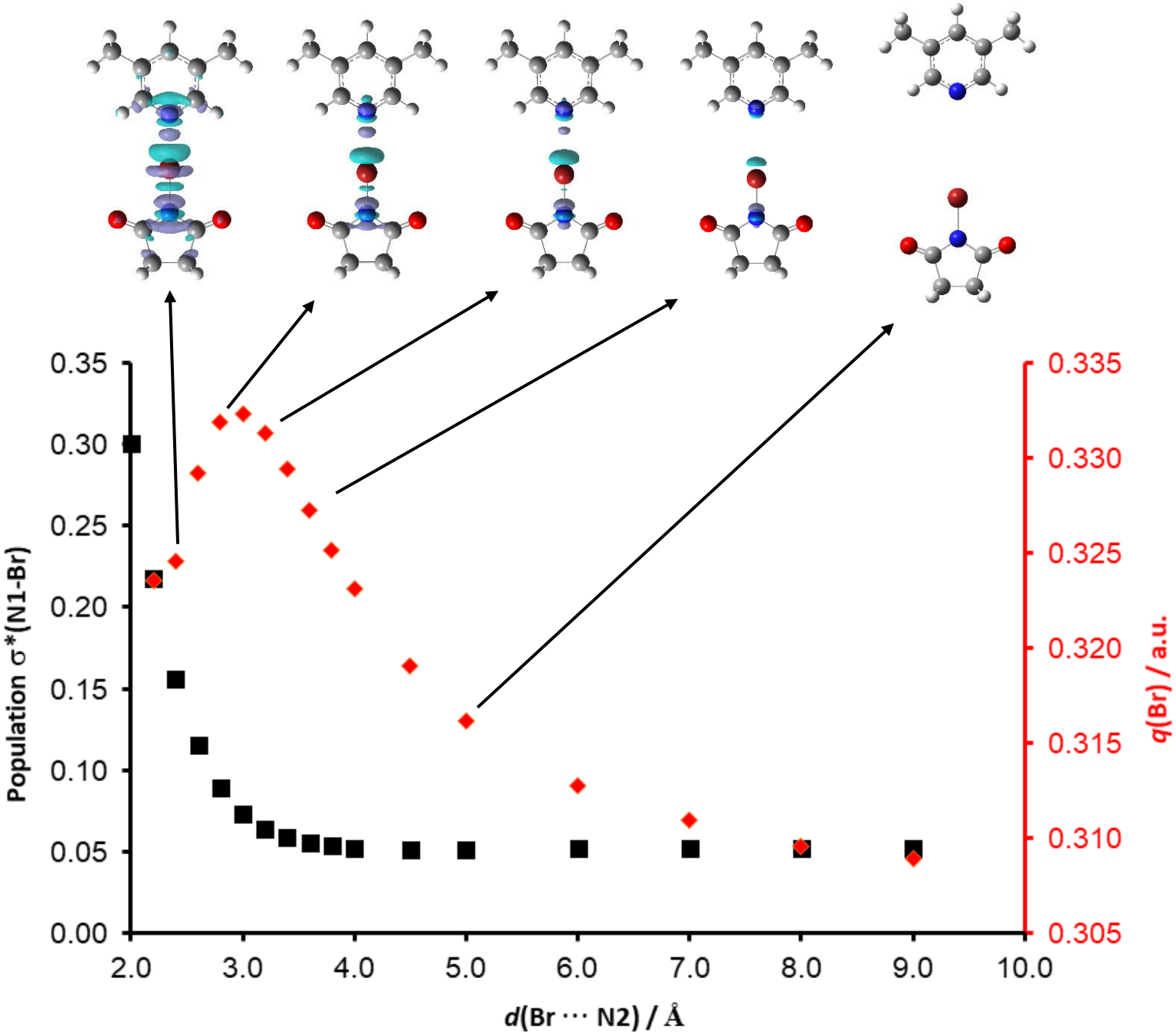
The centrosymmetric $[I_{16}]^{4-}$ ion in $[C_7H_9N_4O_2]_4[I_{16}]$, $[C_7H_9N_4O_2]^+$ is the protonated theobromine ion




173.8°
2.080 Å
2.105 Å
Trocentrična dvoelektronska veza
Red veze ≈ 0,5





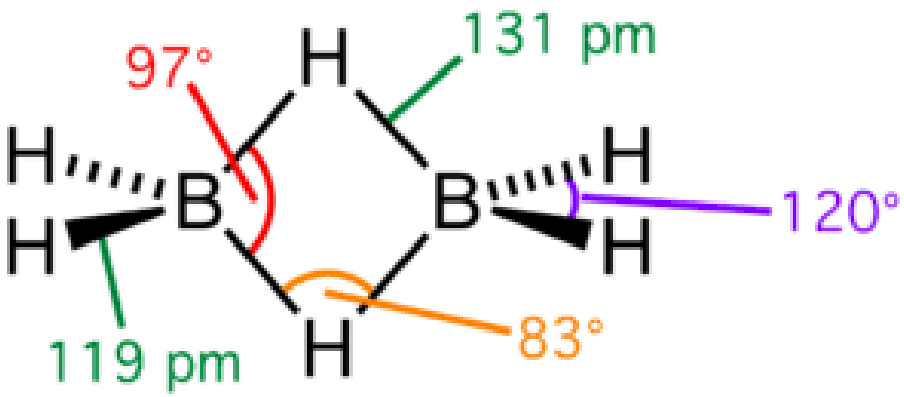


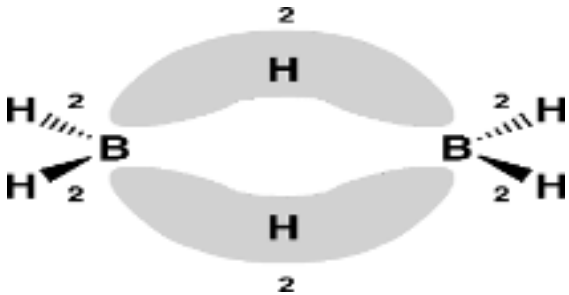
M. Eraković, D. Cinčić, K. Molčanov, V. Stilinović, *Angew. Chem. Int. Ed.* 2019, 58, 15702.

Banane i palačinke

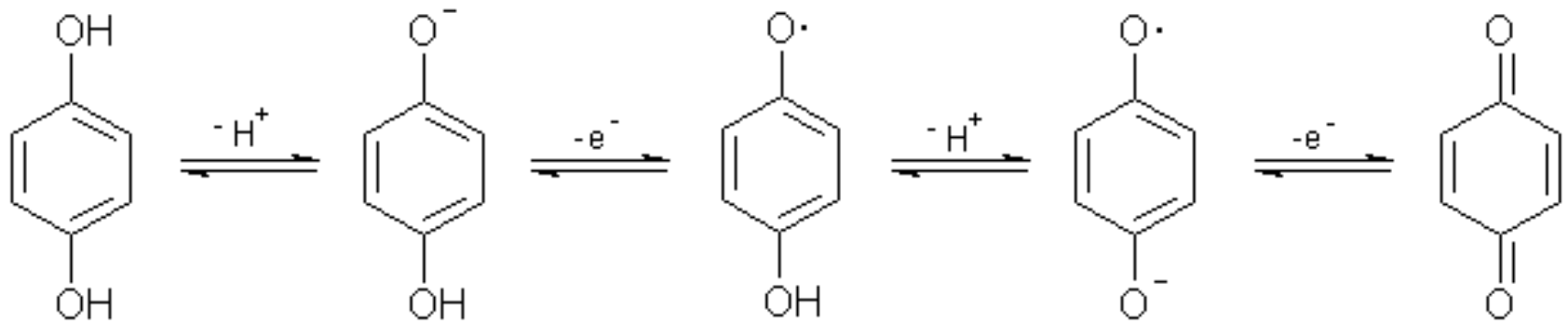
Kratak pogled u svijet policentričnih veza

3c, 2e – '*Banana Bond*'



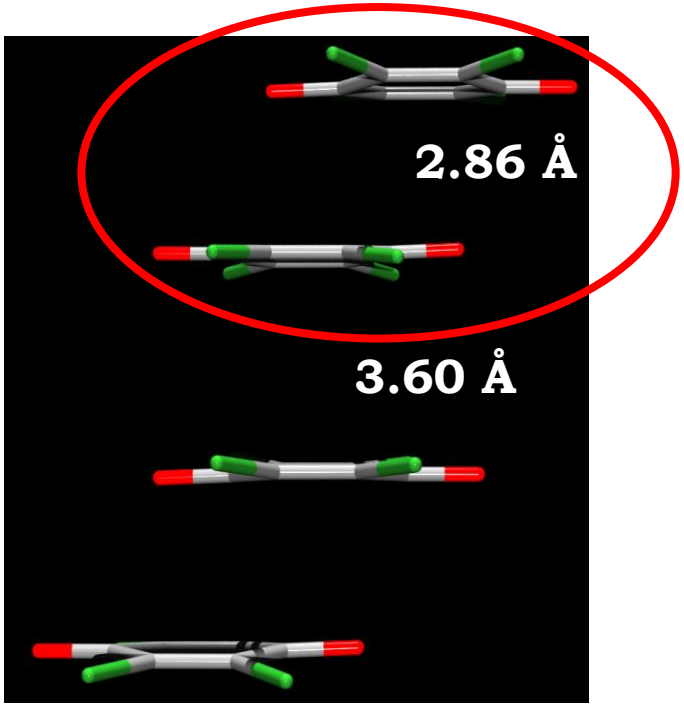


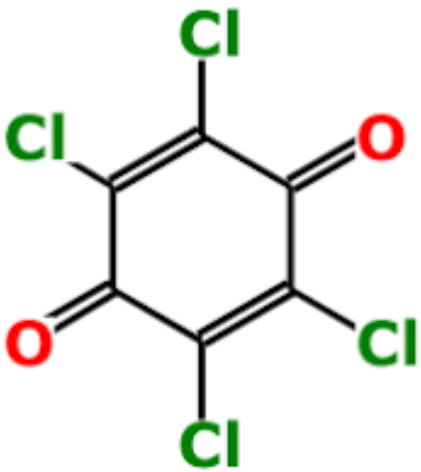
Višecentrične veze? semikinonski radikal-anioni



hidrokinon | fenoksidni anion | fenoksilni radikal | semikinonski radikal-anion | kinon

24c, 2e – '*Pancake Bond*'





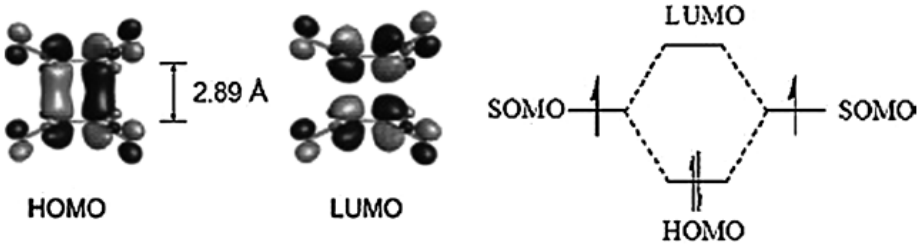
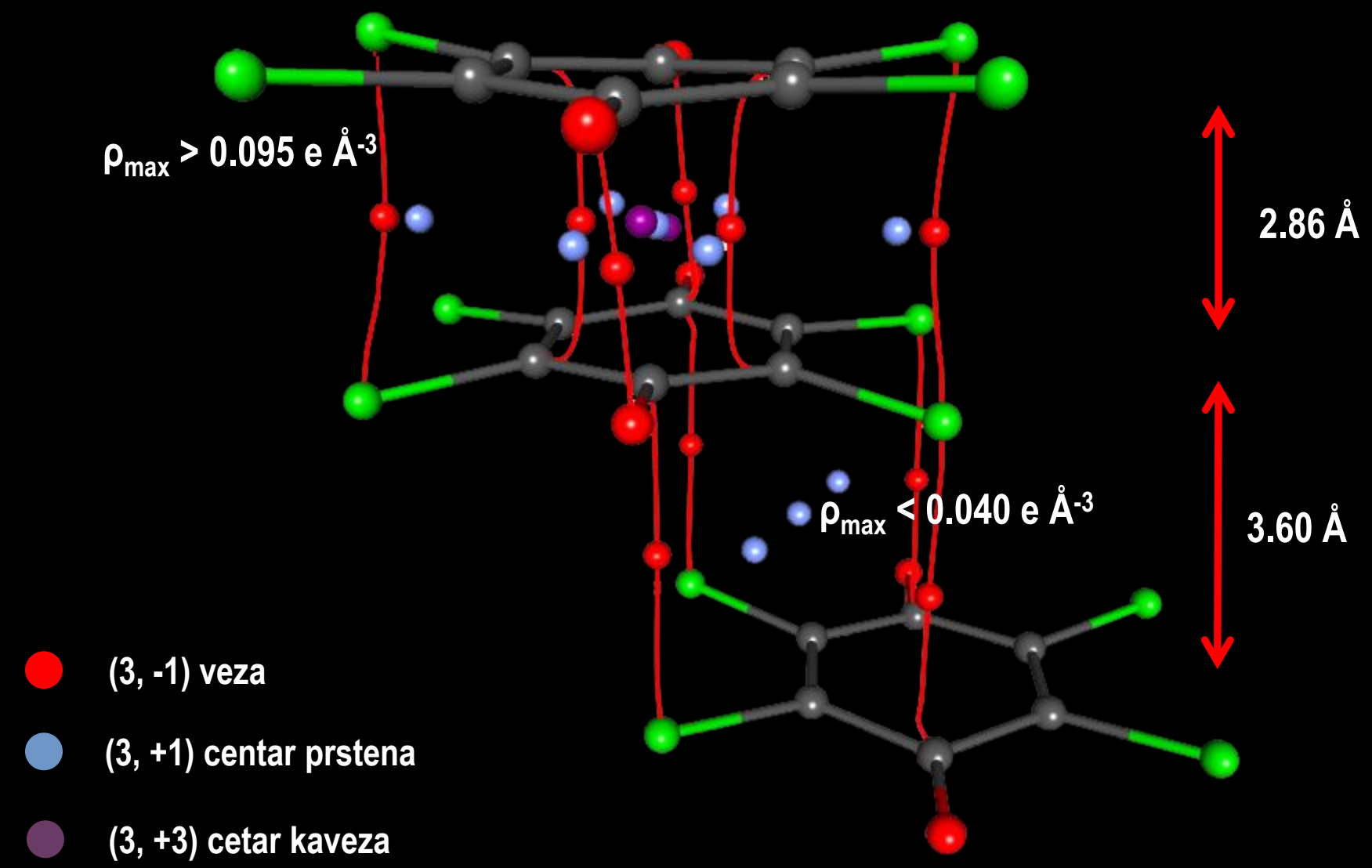
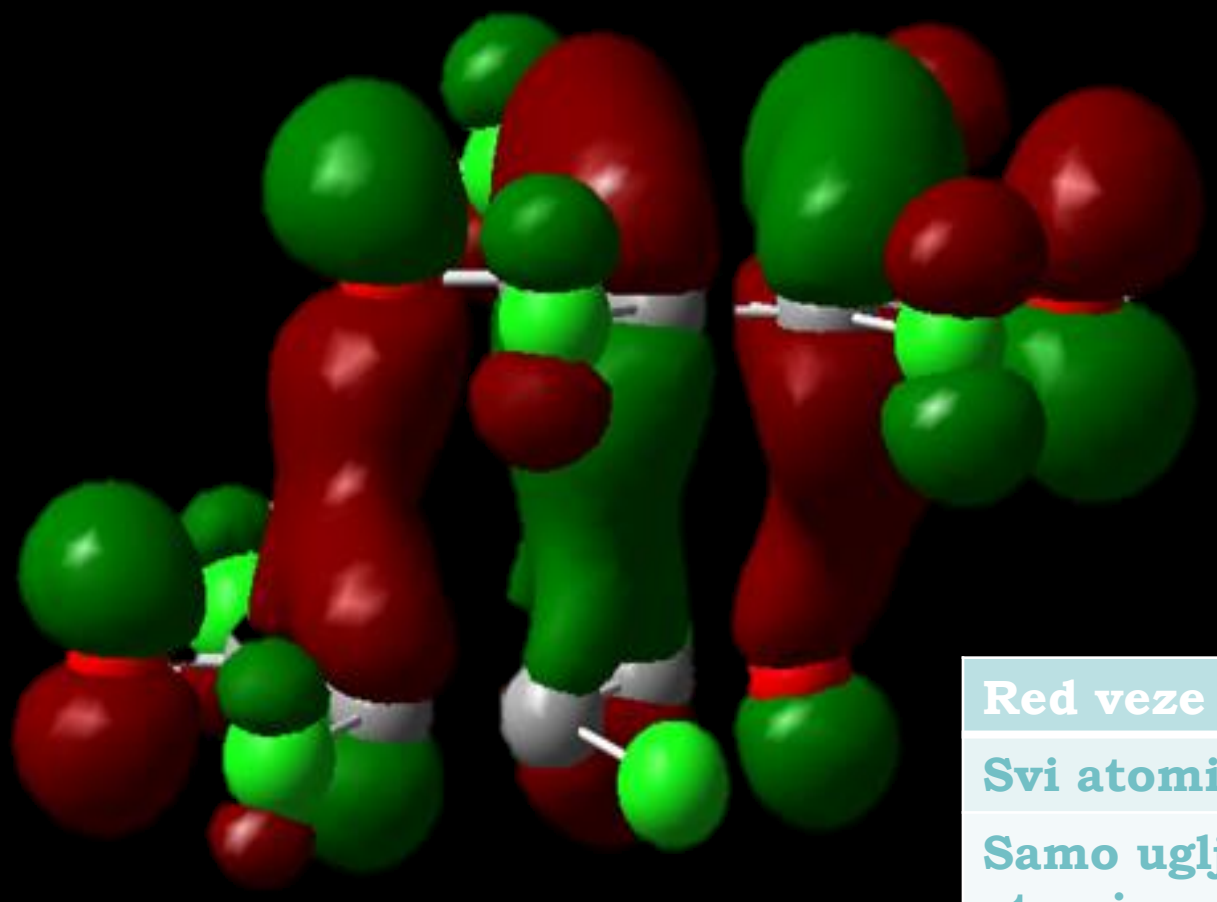


Figure 1. Illustration of the bonding (b_{3u}) and antibonding (b_{2g}) combinations of the two SOMOs in $TCNE_2^{2-}$ as obtained by using Hartree–Fock (HF) calculations. The energy level diagram is on the right.

Topologija elektronske gustoće u dimerima



HOMO orbitala dimera

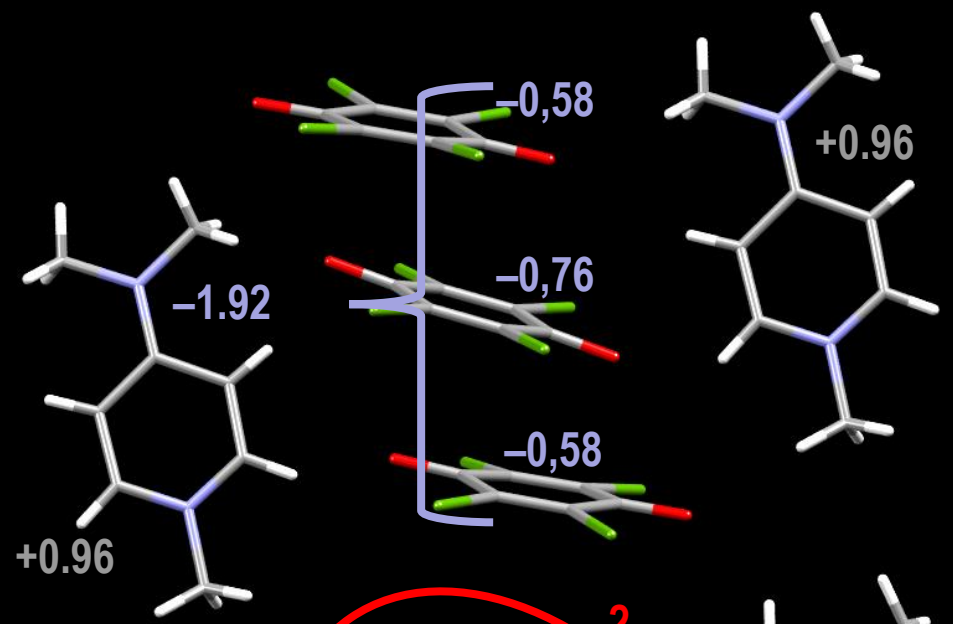


Red veze	
Svi atomi	0.80
Samo ugljikovi atomi	0.27

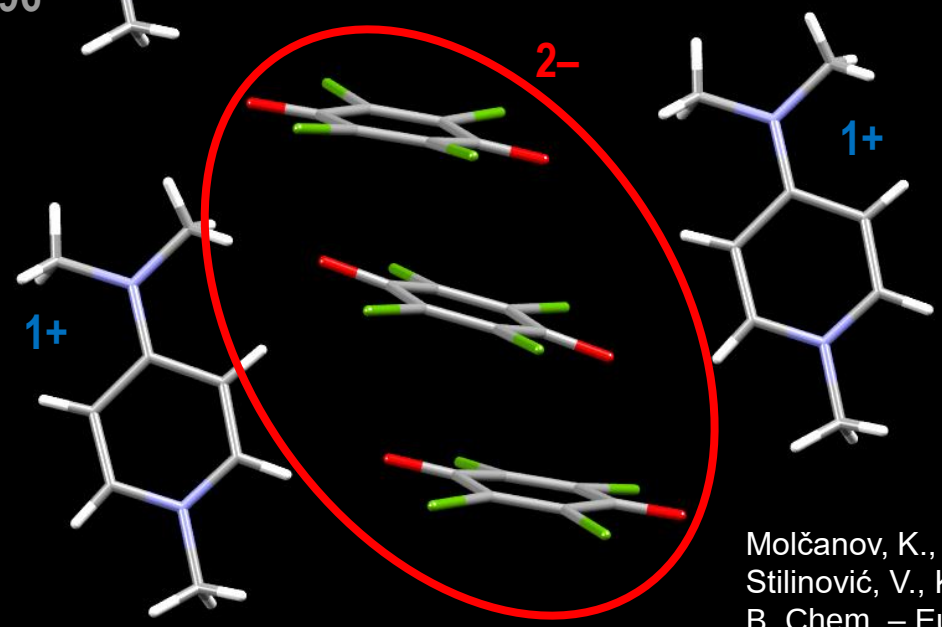
Energija veze (kovalentni doprinos): –39.4 kJ mol^{-1}

36c, 2e – $[N\text{-Me-4-(Me)}_2\text{NPy}]_2(\text{Cl}_4\text{Q})_3$

Naboji iz elektronske gustoće:



Naboji po kemijskom smislu:



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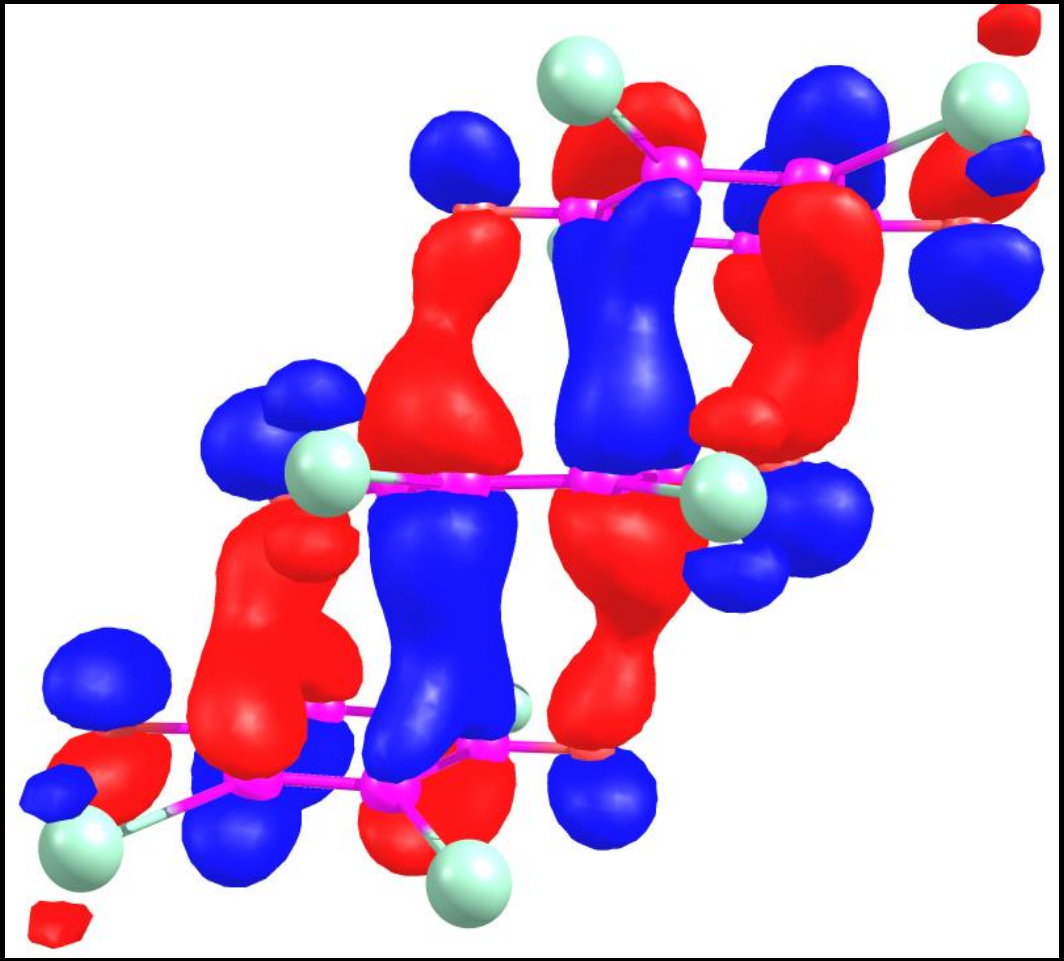
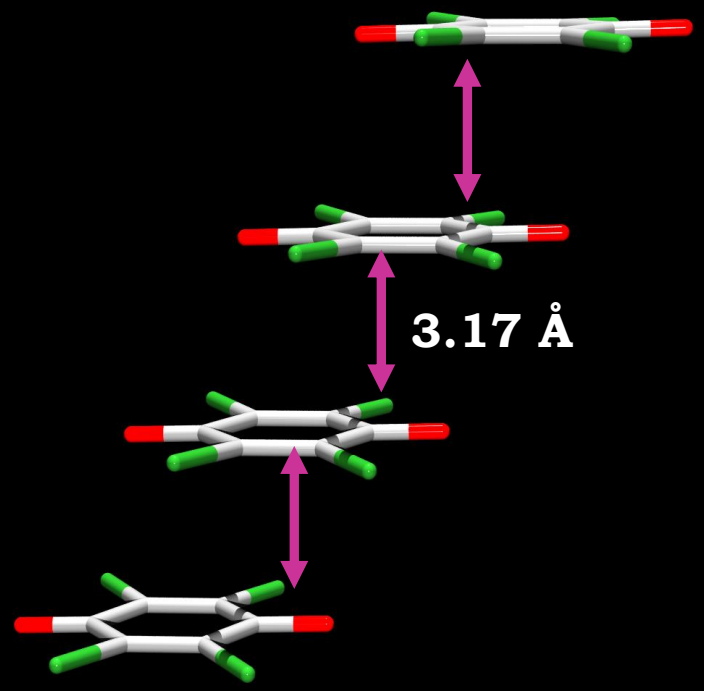
HOMO orbitala trimera

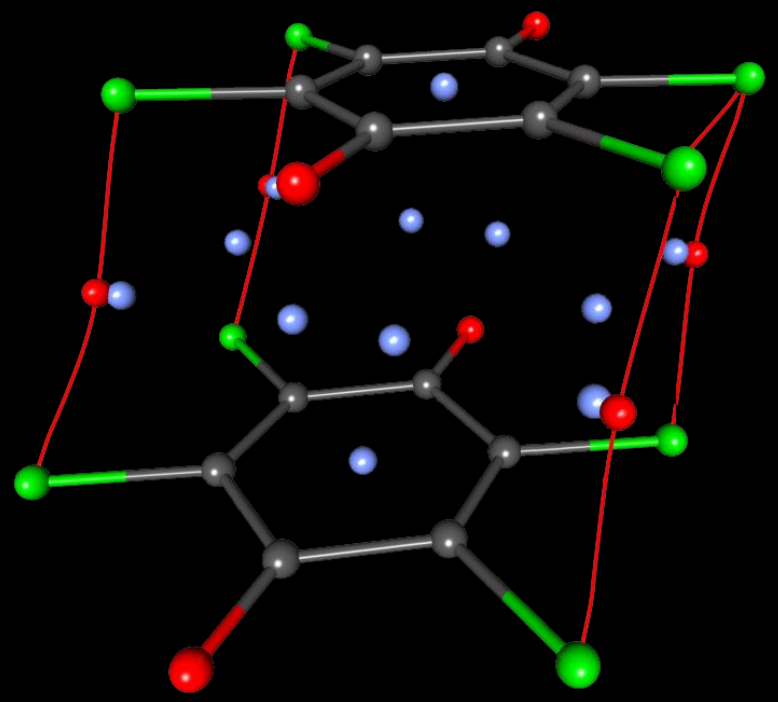


Energija veze (kovalentni doprinos): –17,2 kJ mol^{-1}

Red veze	
Svi atomi	≈ 0,5

12*n* cc, *n* e – polimer





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