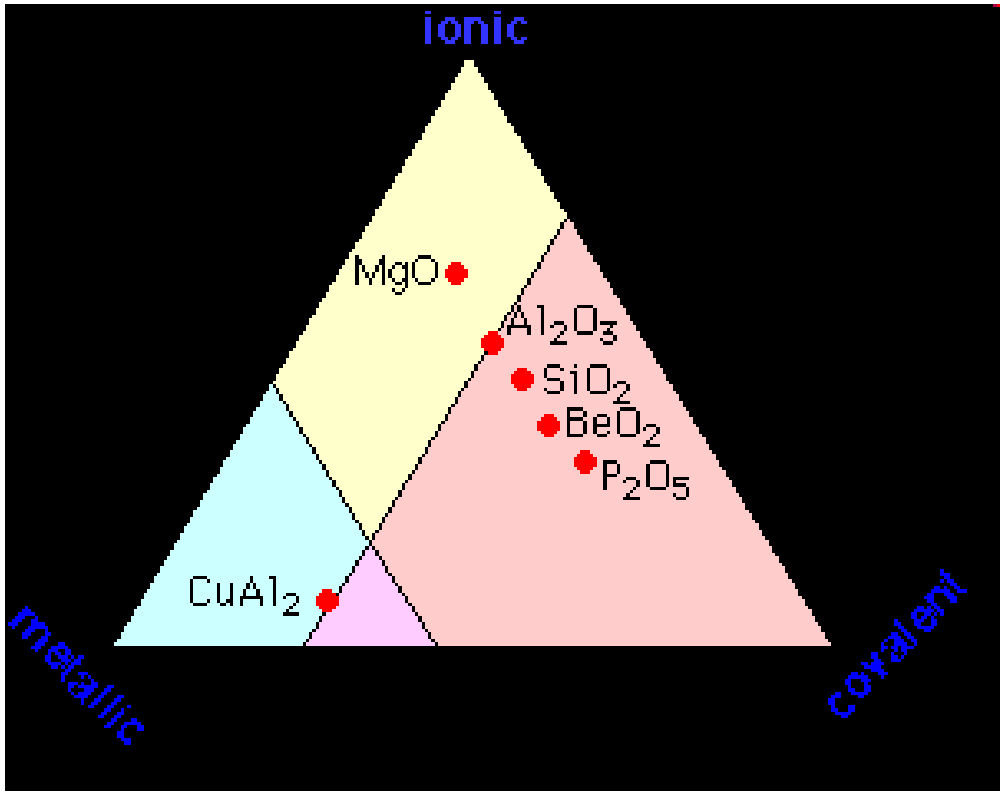
CAPVT II

VEZA

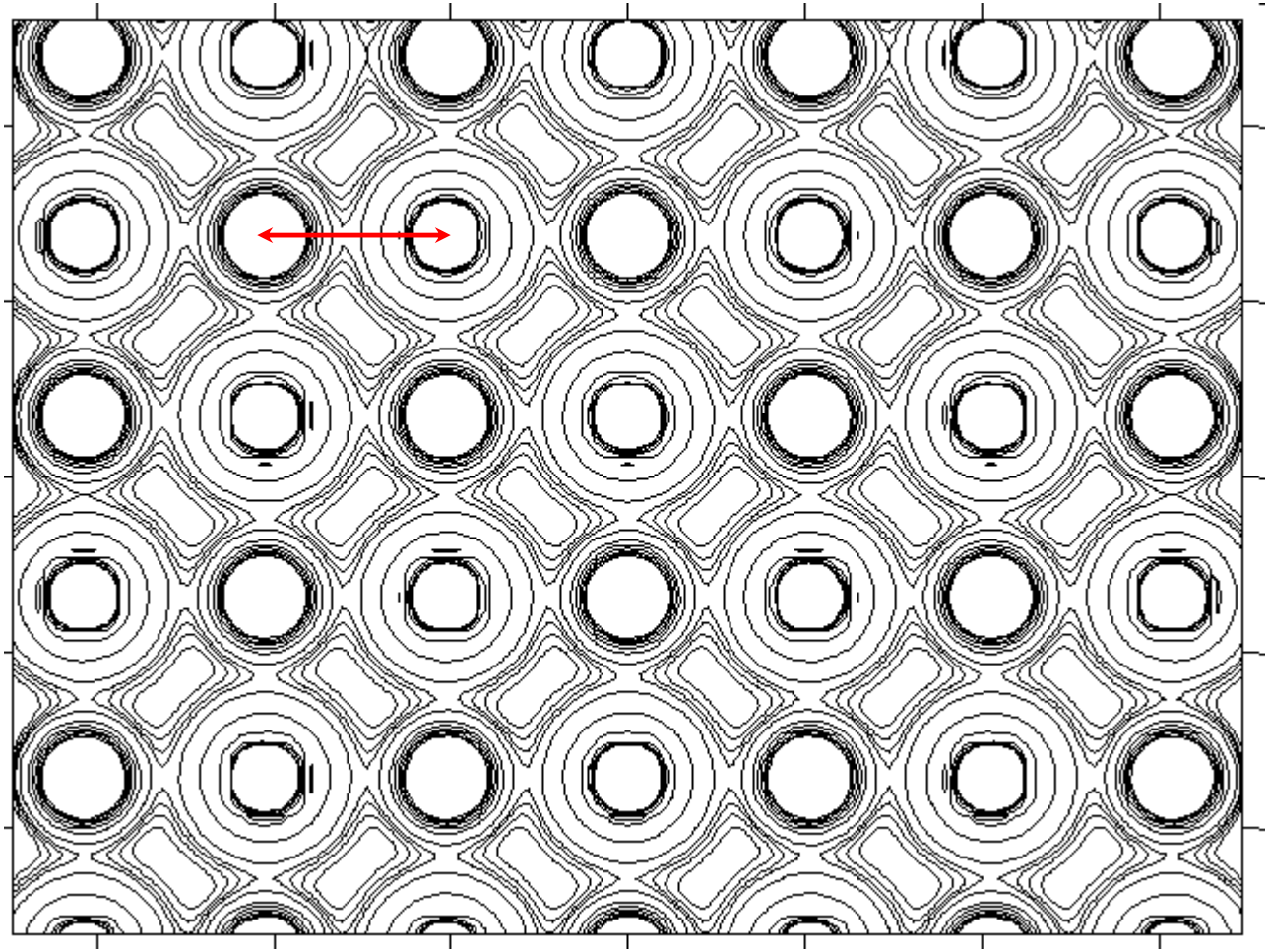
- Kakve kemijske veze mogu biti
  - Kovalentne, ionske, metalne
  - Jednostruke, dvostruke, trostruke...



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

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

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

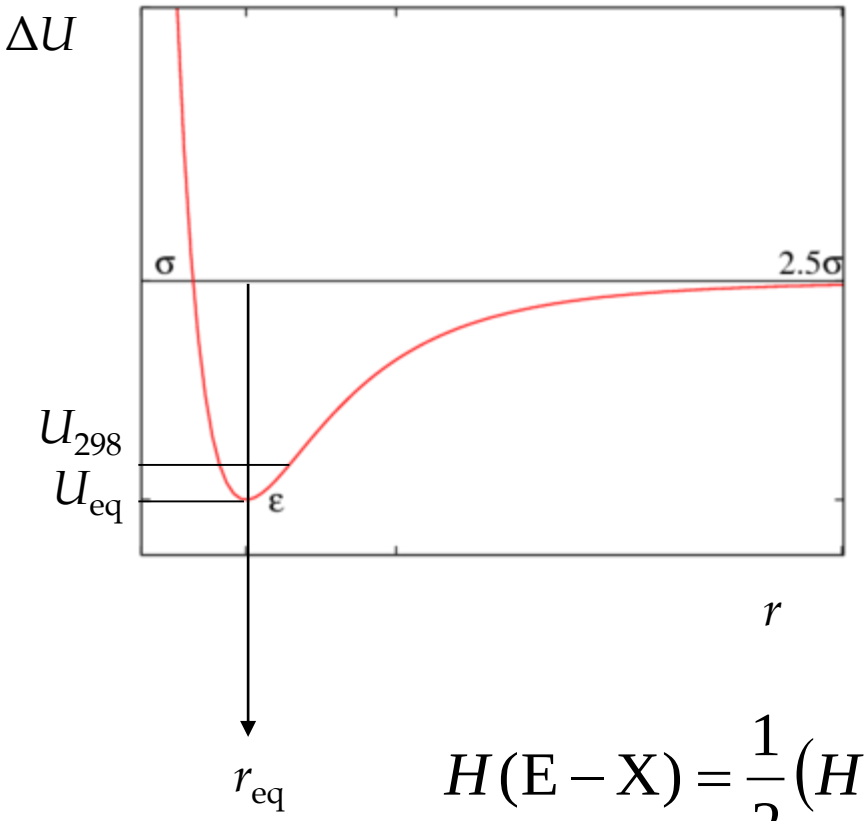
$$d(\mathrm{C}-\mathrm{C}) = r_{\mathrm{K}}(\mathrm{S}) + r_{\mathrm{K}}(\mathrm{C}) = 181 \text{ pm}$$

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

$$d(\mathrm{A}-\mathrm{B}) = r_{\mathrm{K}}(\mathrm{A}) + r_{\mathrm{K}}(\mathrm{B}) - k[\chi(\mathrm{A}) - \chi(\mathrm{B})]$$

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

Energija veze



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

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

Konstnta sile

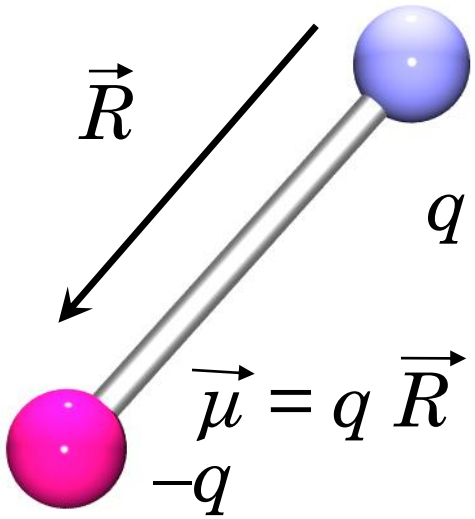
- Mjera za krutost veze (nagib Lennard-Jonesove krivulje)

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

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

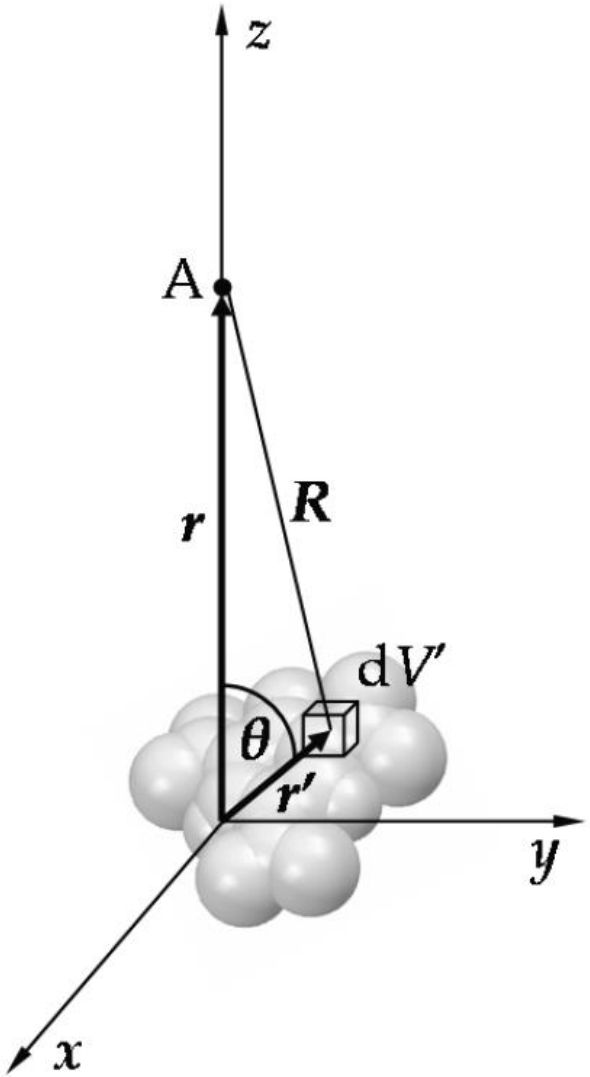
Dipolni moment

- Dipolni moment



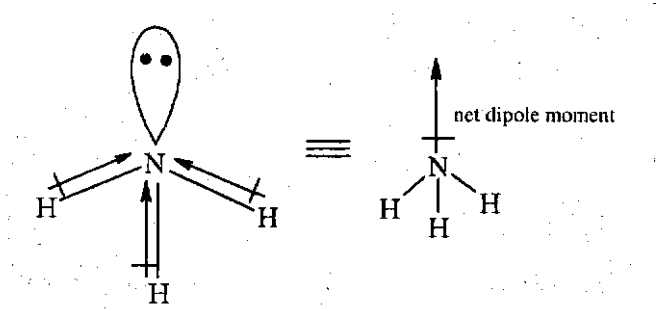
- Molekulski dipolni moment

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



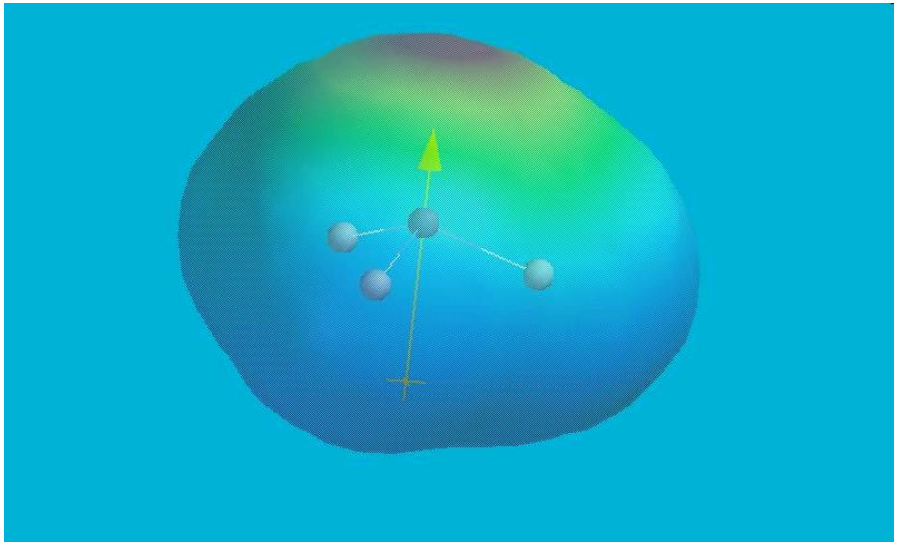
- Ukupni dipolni moment molekule kao suma dipolnih momenata veza.
- Dipolni moment veze sadrži:
  - Atomske dipolne momente
  - Moment prijenosa

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

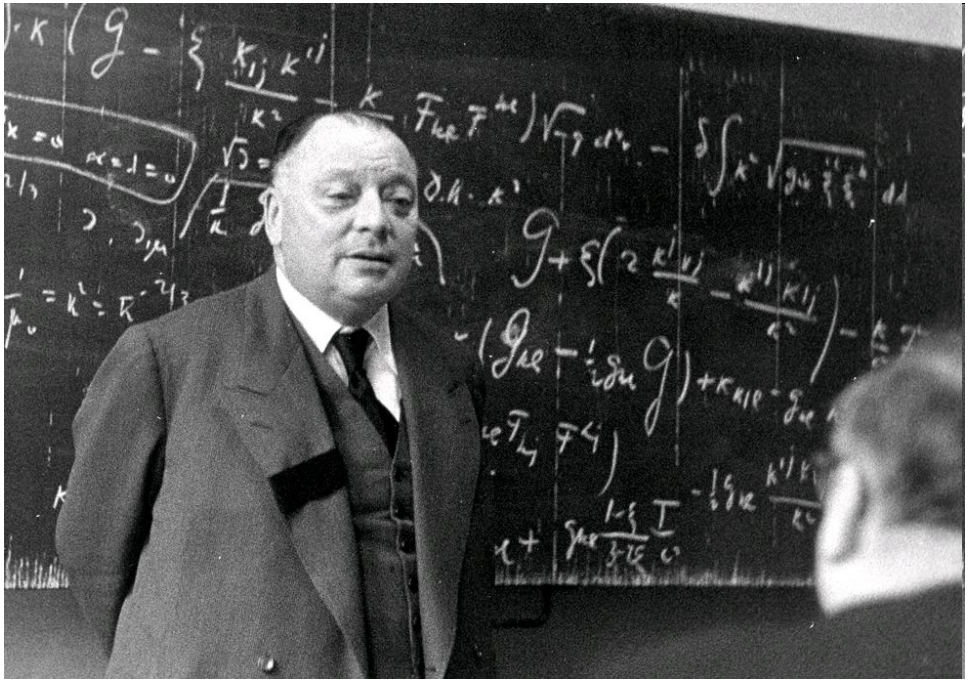
- Određena razmještajem elektrona u molekuli
- Elektroni se odbijaju, a po potrebi i sparuju.

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"*

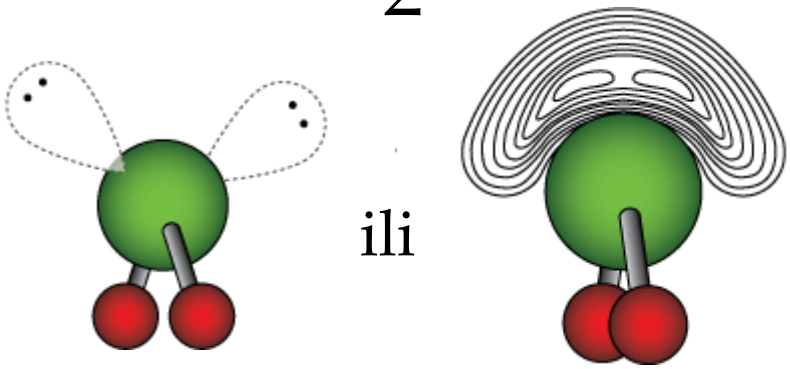


O sparivanju elektrona

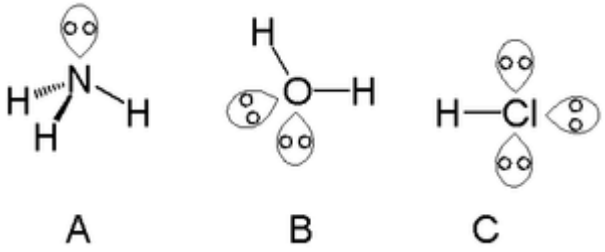
Kažu da zbog Paulija elektroni se sparuju.

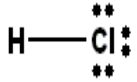
Zašto i koliko to elektroni čine?

H_2O



Monovalentni halogeni



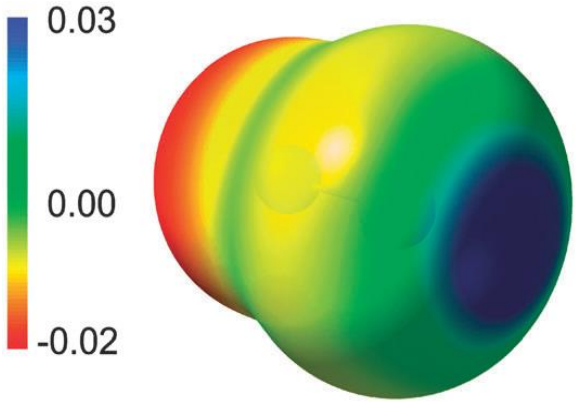


Central atom:	Cl
Cl contributes:	7 e^-
H contibutes:	1 e^-
Total VSE:	8
Total VSEP:	4
Geometry:	Linear (based on tetrahedral)

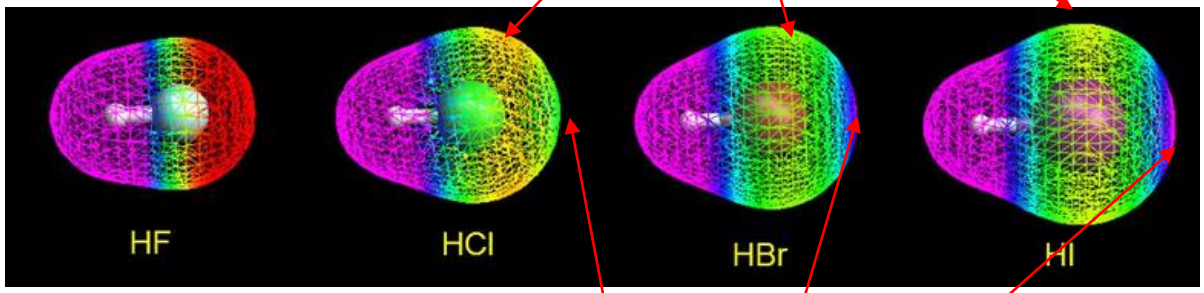
Što ne valja na ovoj slici?

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

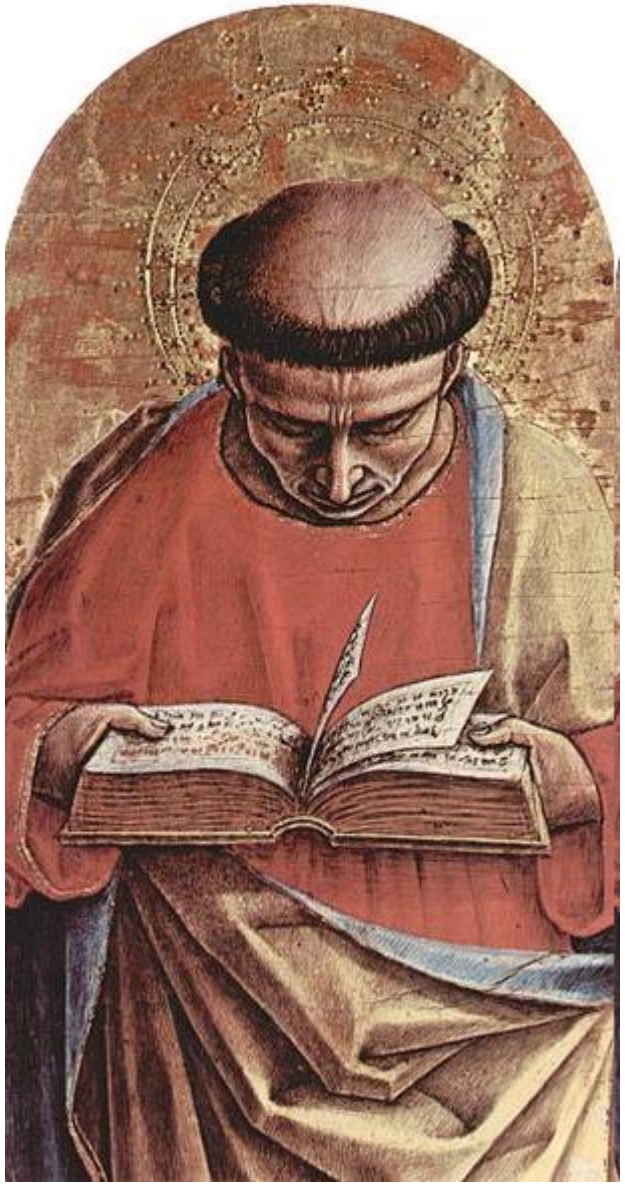
Monovalentni halogeni



povećana elektronska gustoća

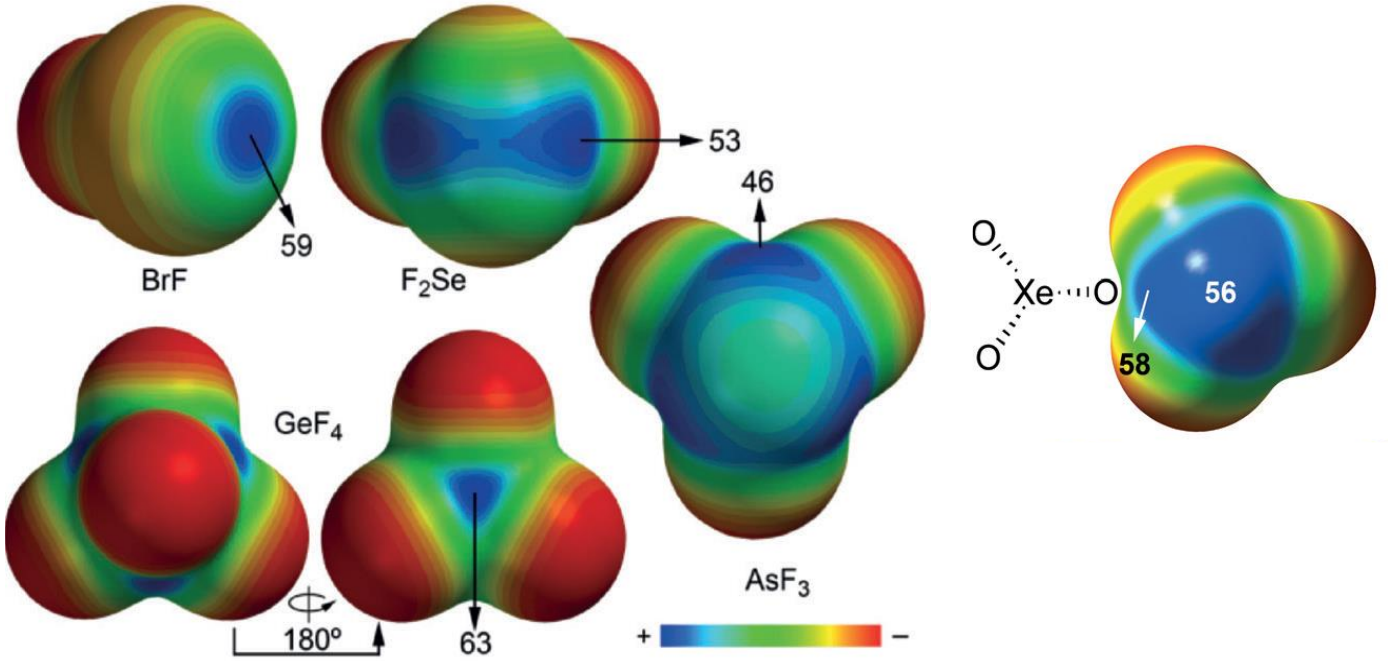


smanjena elektronska gustoća
σ-šupljina (*σ-hole*)

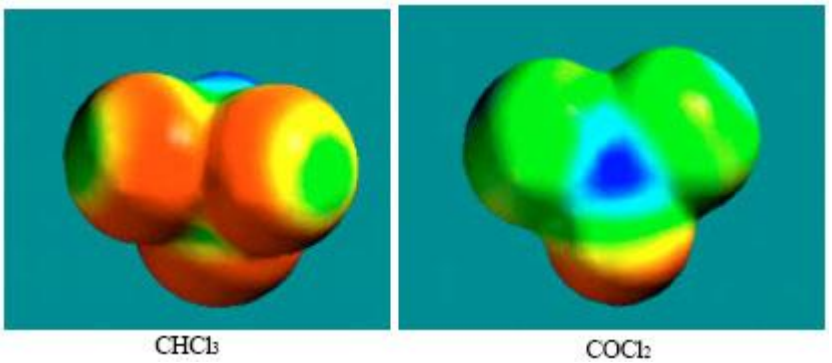


σ-, π- i ostale molekulske rupe

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



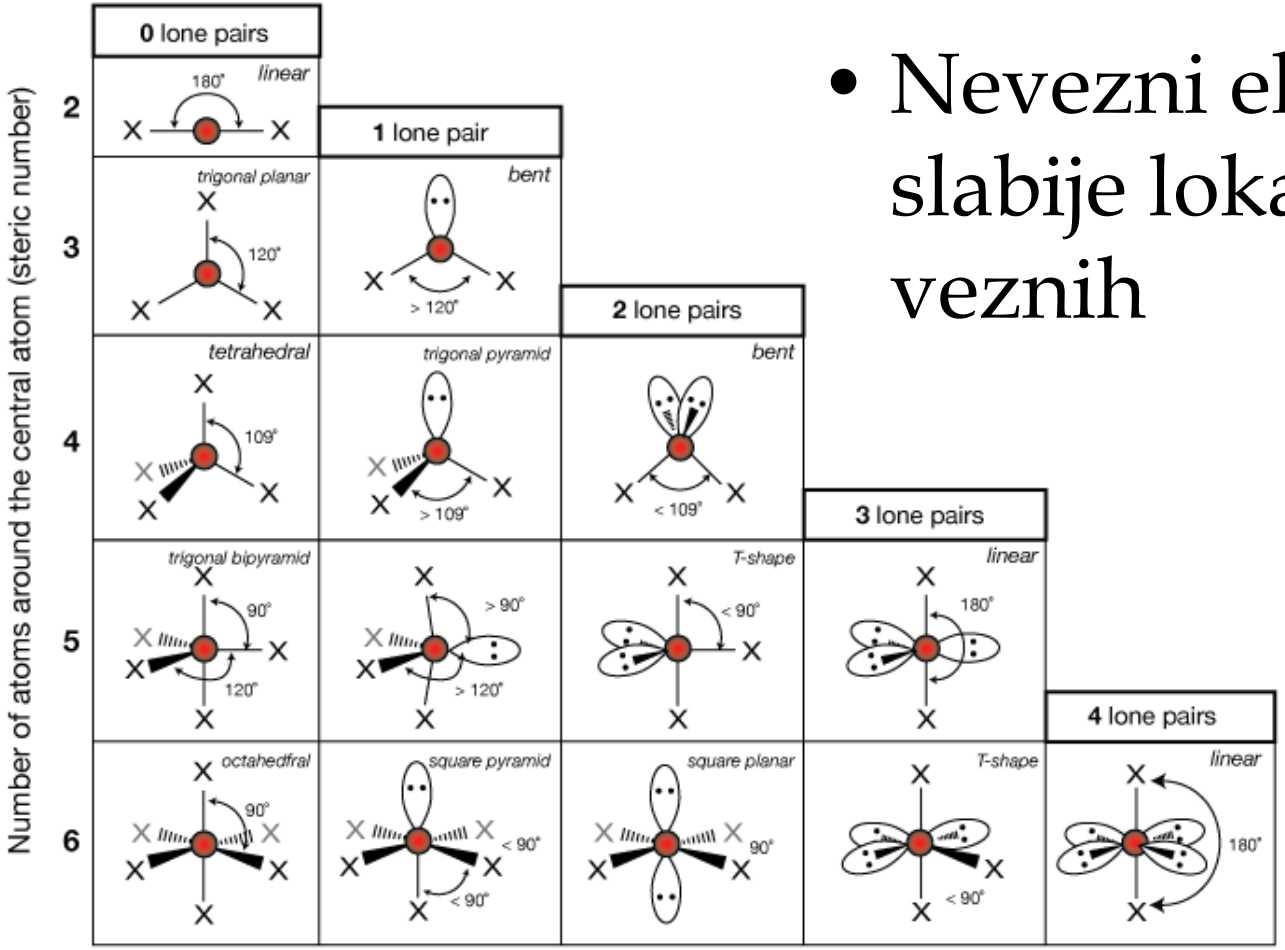
Nedostatak elektronske gustoće kadkad se javlja okomito na (višestruke) kovalentne veze – **π-šupljina**



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

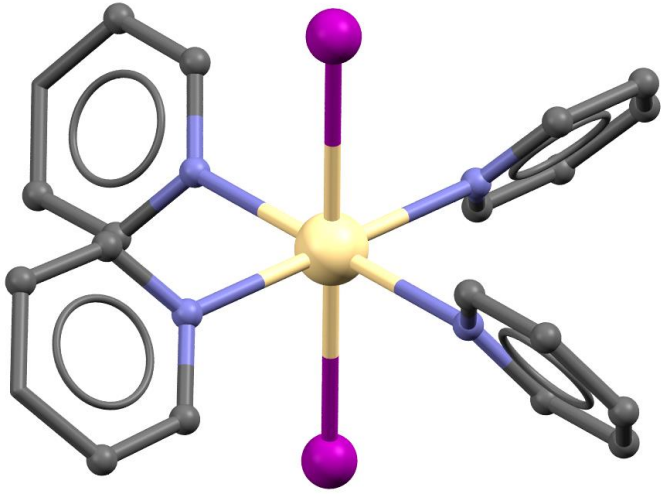


- Nevezni elektroni su slabije lokalizirani od veznih

VSEPR - ternarni spojevi

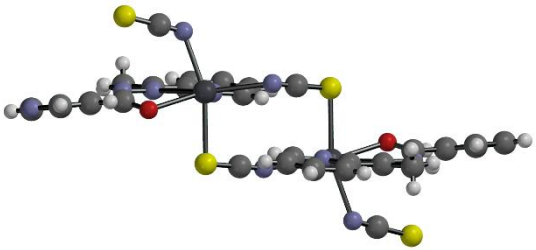
Bentovo pravilo – elektronegativniji supstituenti preferiraju aksijalni položaj (pripadni elektronski parovi su **jače** lokalizirani)

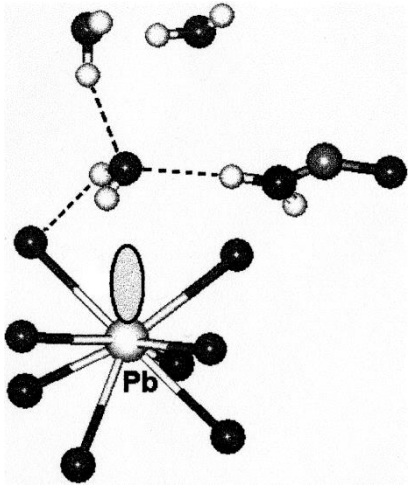
Vrijedi čak i za slučajeve s višeatomnim ligandima (npr. $CdI_2(pyr)_4$)



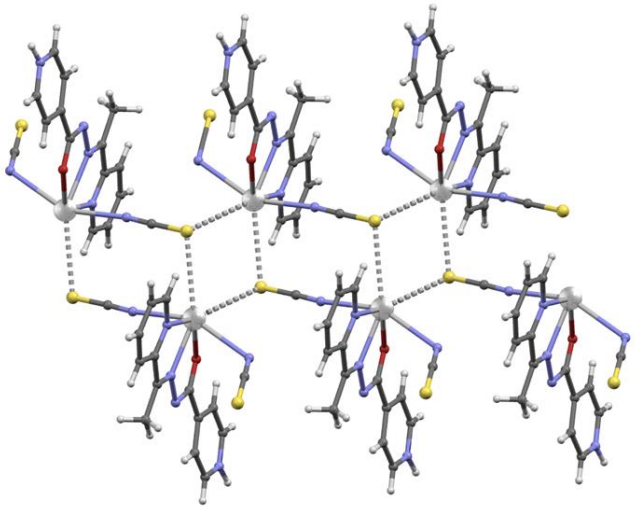
Olovo(II) i ‘sterički aktivni elektronski par’

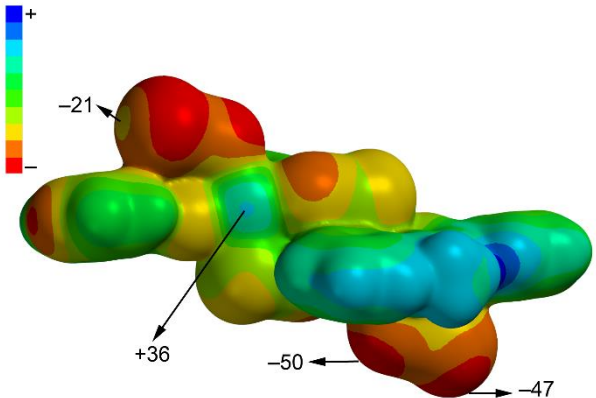
- Hemidirekcionalna koordinacija (‘sterički aktivan elektronski par’)



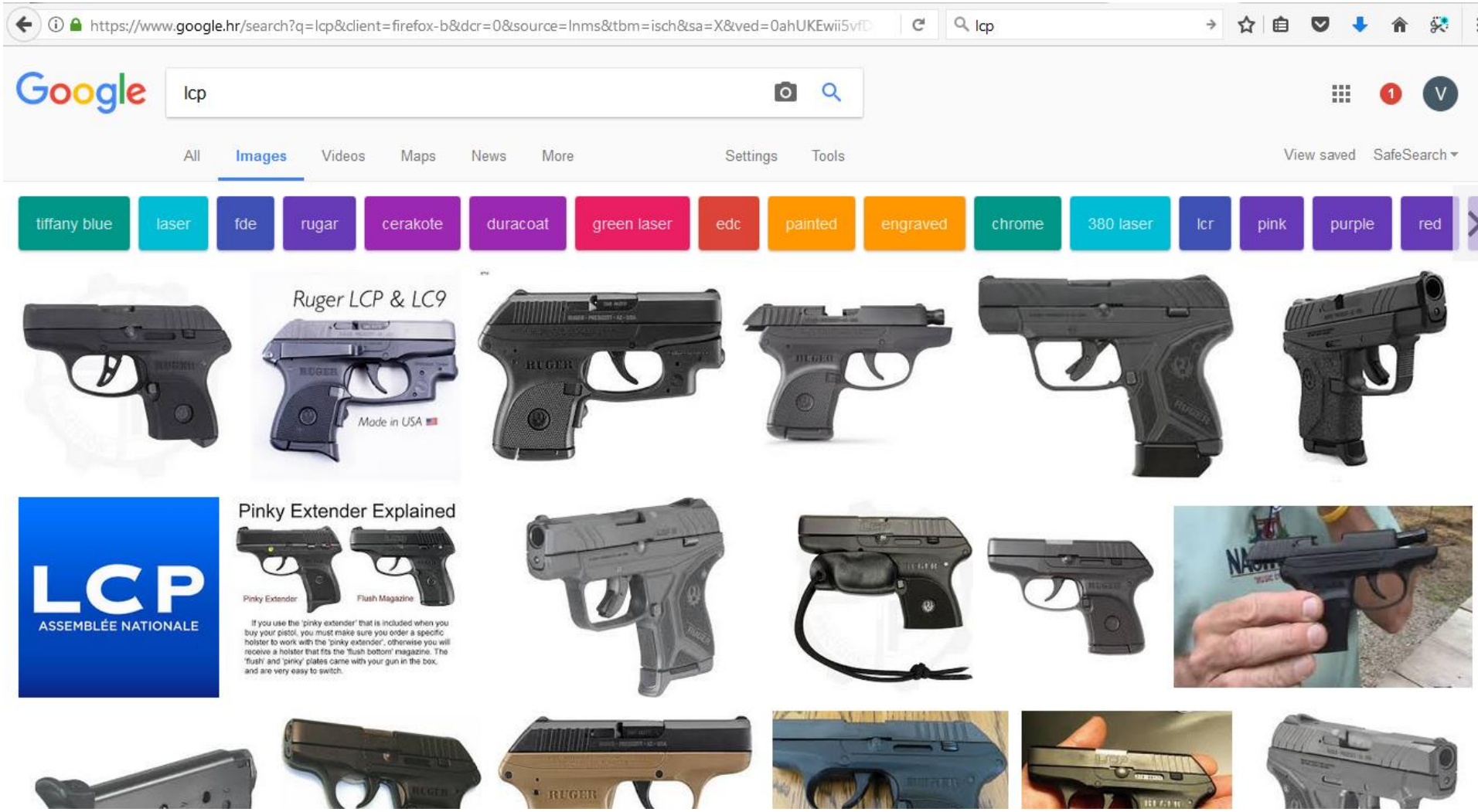


- ali





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

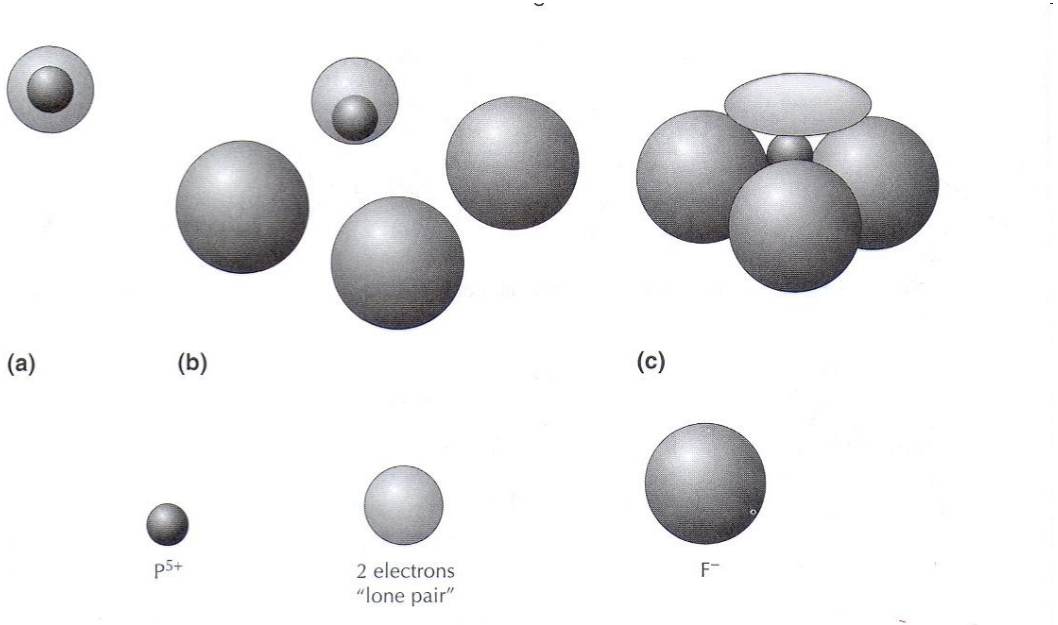
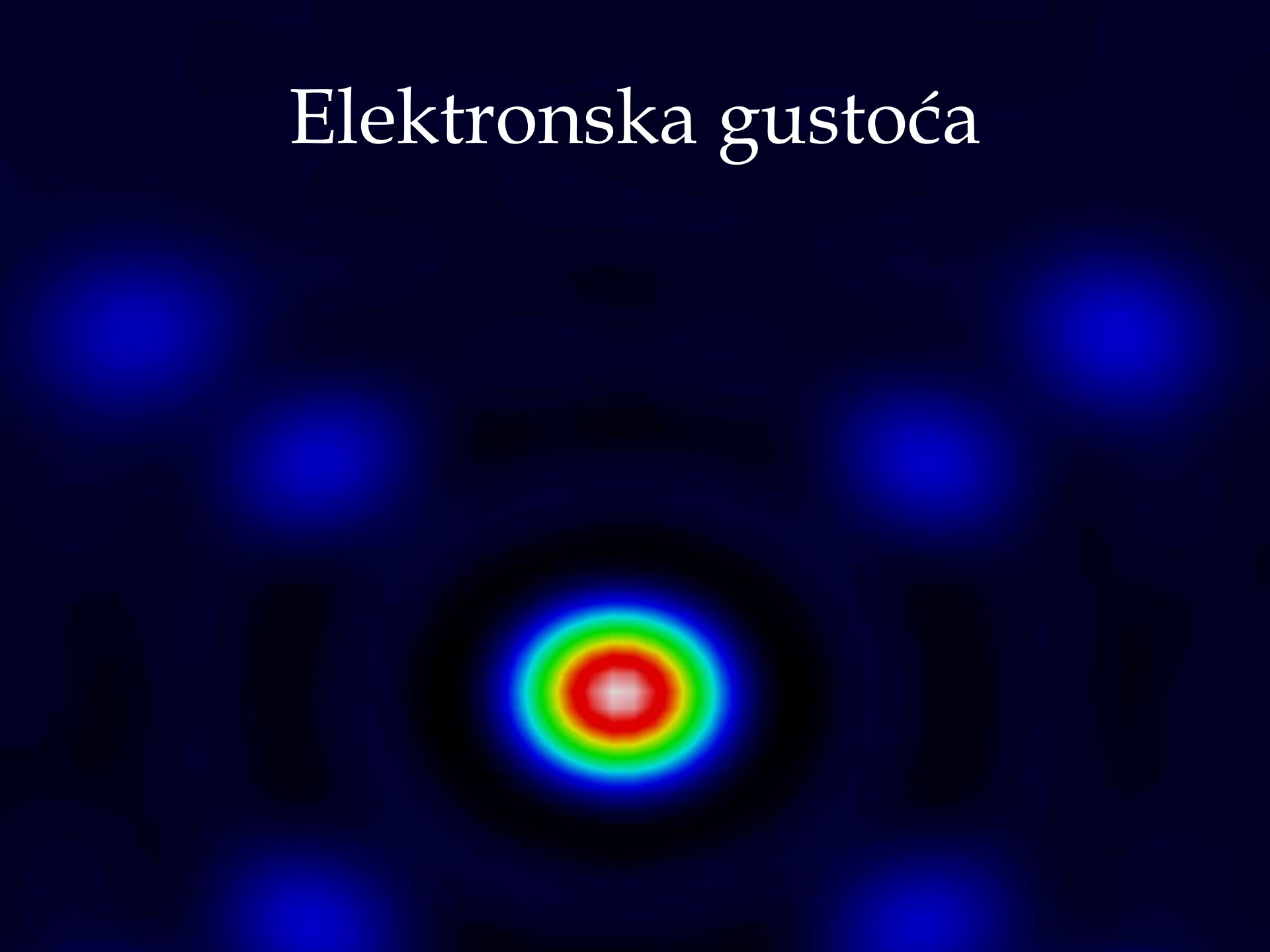


Figure 5.10 Representation of the formation of the lone pair in the PF_3 molecule. (a) An isolated P^{3+} ion consisting of a P^{5+} core surrounded by two nonbonding electrons in a spherical distribution. (b) Three approaching F^- ions distort the distribution of the two valence shell electrons pushing them to one side of the P^{5+} core. (c) When the F ligands reach their equilibrium positions, the two nonbonding electrons are localized into a lone pair, which acts as a pseudo-ligand giving the PF_3 molecule its pyramidal geometry.

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

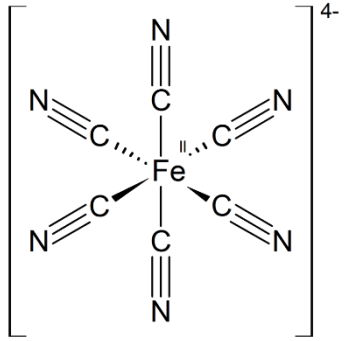
Elektronska gustoća

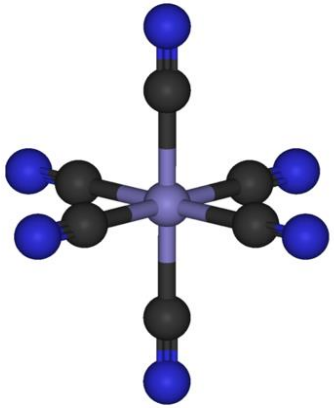


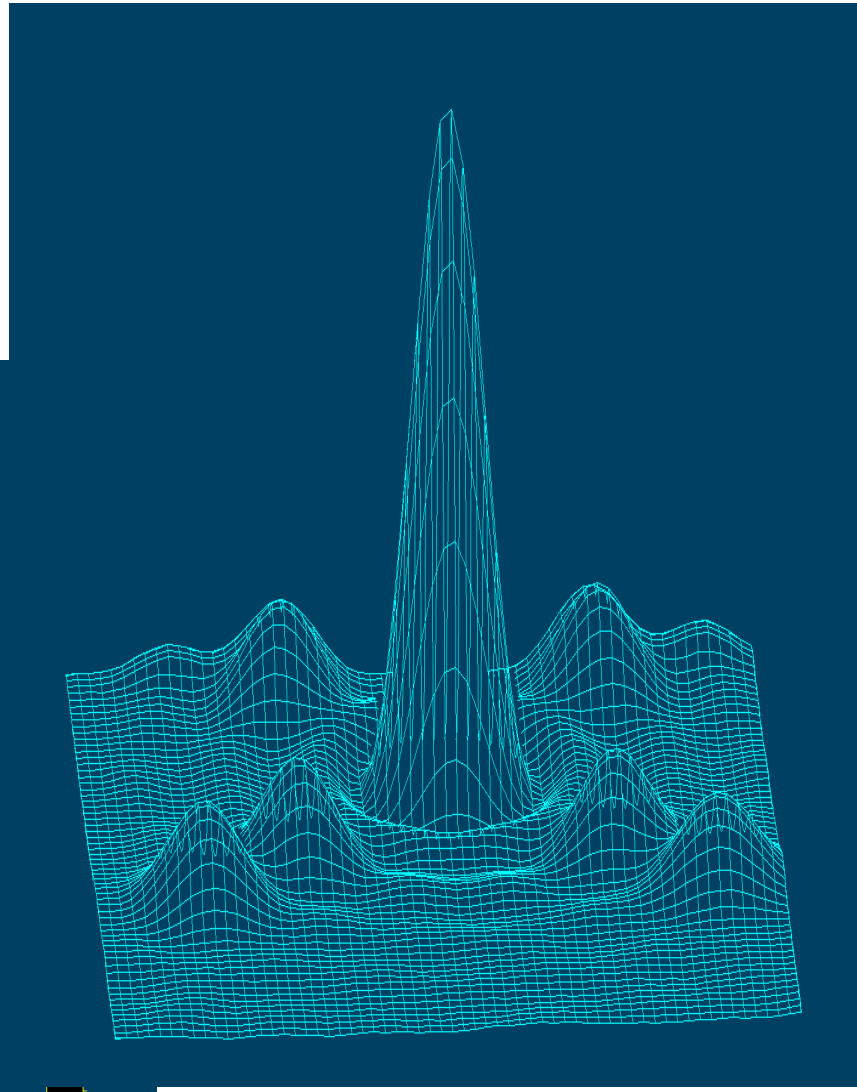
Kako do gustoće?

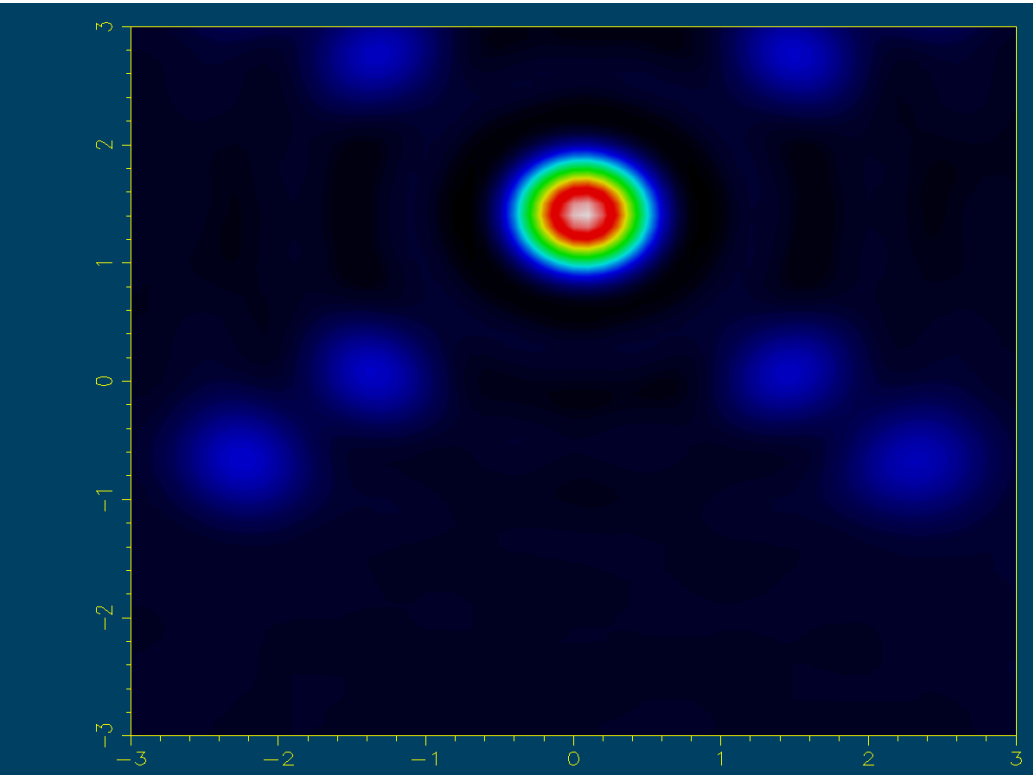
Računski: *ab initio,* semiempirijski

Mjerenjem: rentgenska i elektronska difrakcija


4-
N
C
Fe






3
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−2
−3
−3
−2
−1
0
1
2
3

Problemi

Nepotpuni podatci (‘*musavi Fourier*’)

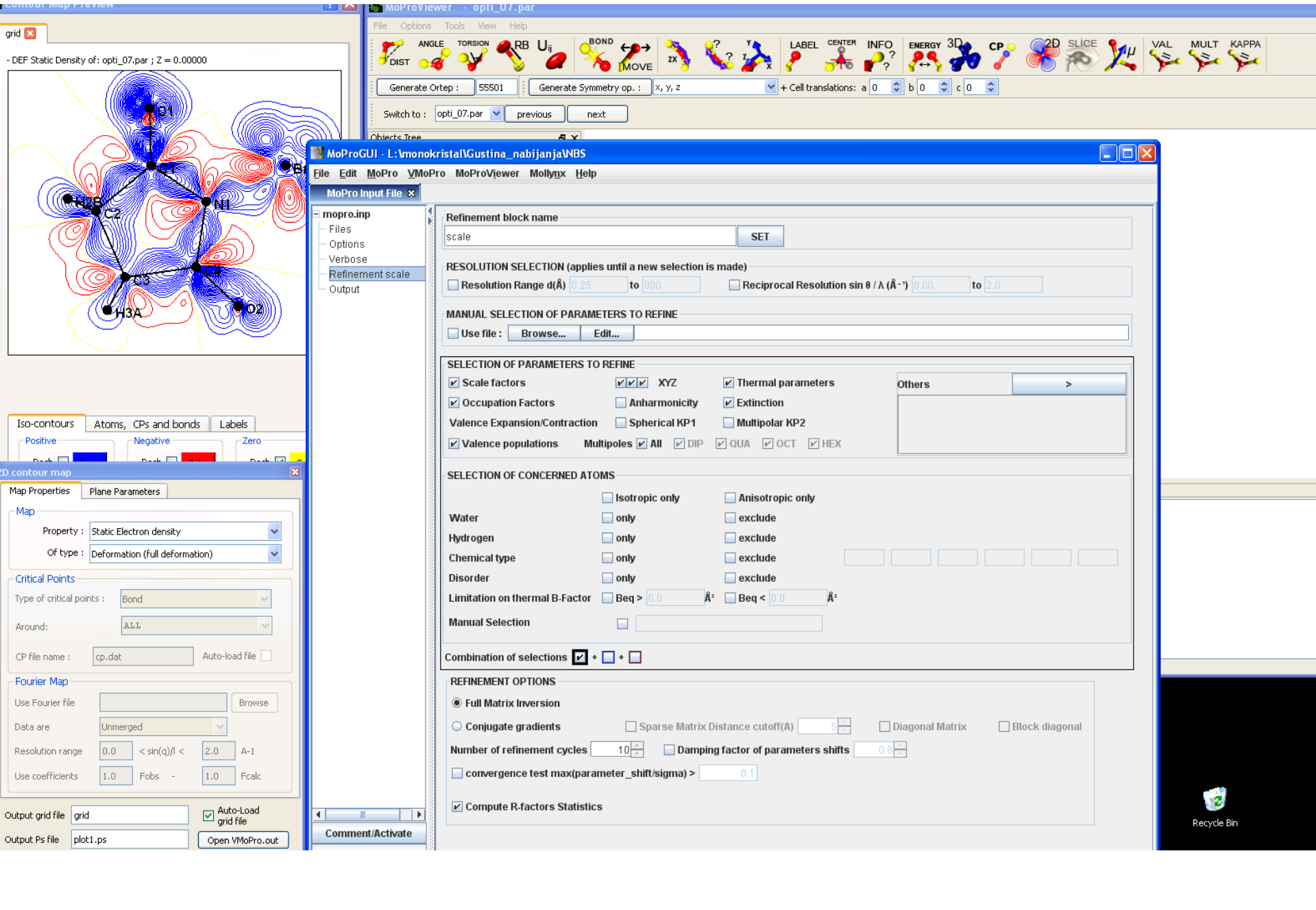
Termičko gibanje (dekonvolucija)

Nesavršenost kristala (artefakti)

Absorpcija i ekstinkcija

Cu – premala rezolucija; Mo,Ag – premali intenzitet

...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O1
C1
Br1
H1B
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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
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Use Fourier file
Browse
Data are Unmerged
Resolution range 0.0 < sin(q)/l < 2.0 A-1
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MoPro Input File
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Files
Options
Verbose
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Comment/Activate
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Resolution Range d(Å) 0.25 to 900
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MANUAL SELECTION OF PARAMETERS TO REFINE
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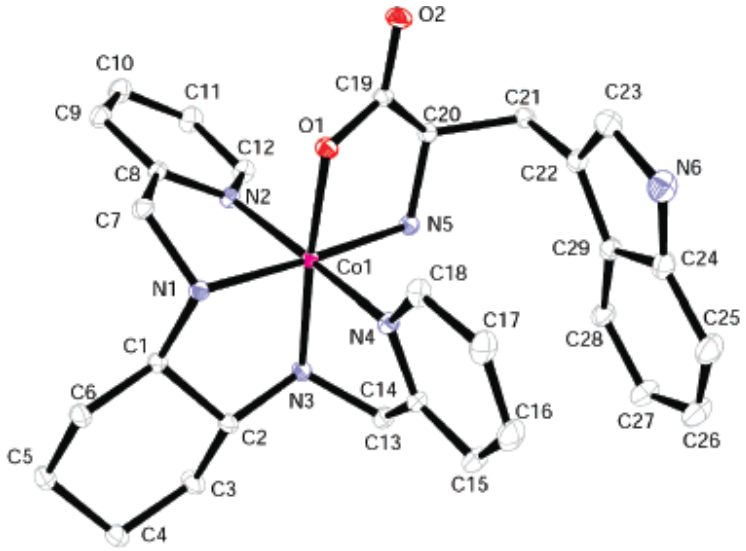
Occupation Factors
Anharmonicity
Extinction
Valence Expansion/Contraction
Spherical KP1
Multipolar KP2
Valence populations
Multipoles All DIP QUA OCT HEX
Others >
SELECTION OF CONCERNED ATOMS
Isotropic only
Anisotropic only
Water only exclude
Hydrogen only exclude
Chemical type only exclude
Disorder 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
C19
C9
O1
C20
C21
C23
C12
C22
N6
C8
N2
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C7
C29
C24
Co1
C18
N1
N4
C17
C1
C28
C25
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C14
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C2
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C26
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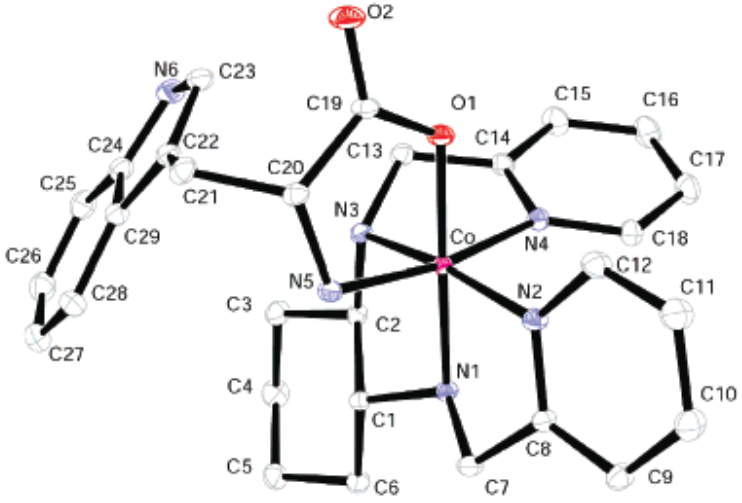
O2
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C16
C24
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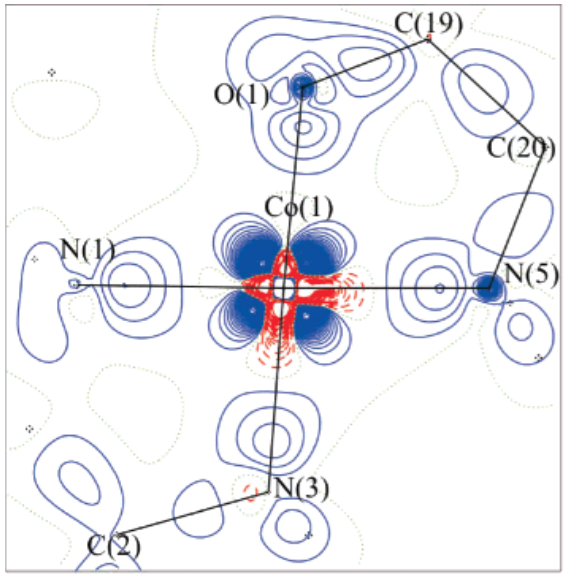
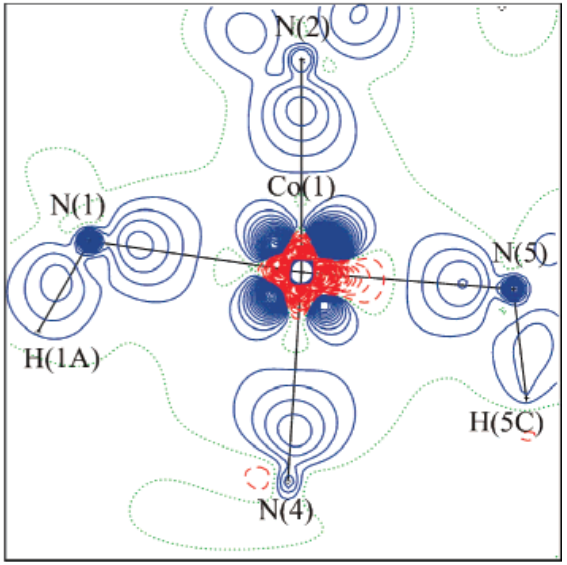
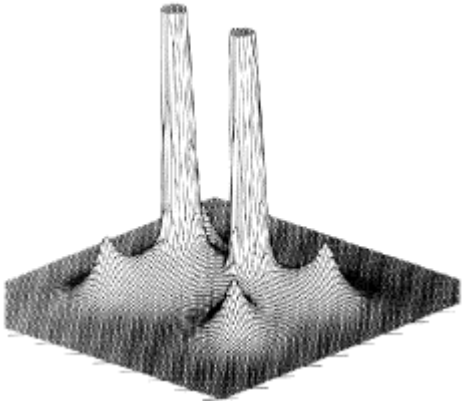
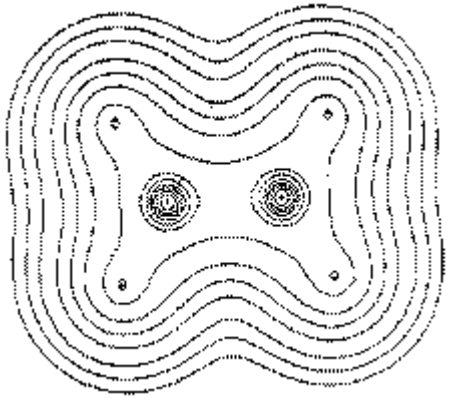
N3
Co
N4
C18
C29
C26
N5
C12
C28
N2
C11
C3
C2
C27
N1
C4
C10
C1
C8
C5
C6
C7
C9

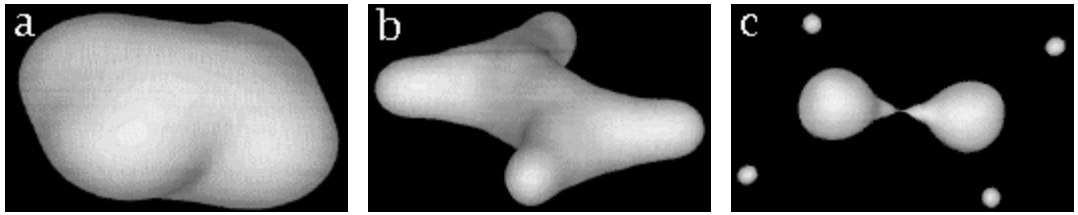

C(19)
O(1)
C(20)
Co(1)
N(1)
N(5)
N(3)
C(2)


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

Prikazi elektronske gustoće





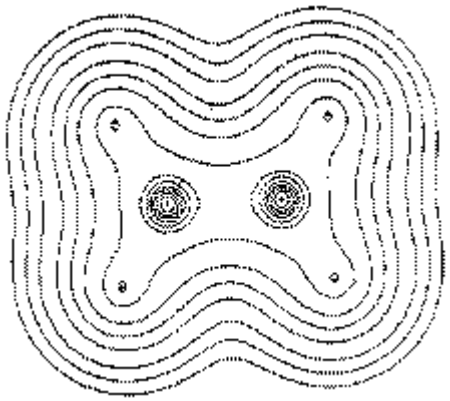


AIM

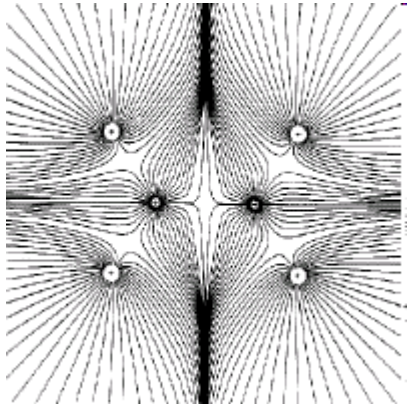
- Atoms In Molecules
- Raspodjela elektronske gustoće u prostoru definira strukturu molekule
- Kako definirati atome, veze itd. u oblaku molekulske elekreonske gustoće?

Topologija funkcije gustoće

- Gradijenti, polja, kritične točke i atraktori



envelopa



gradijent

Gradijent – $\nabla\rho$

Vektorsko polje gradijenta – skup svih gradijenatnih putanja

Kritična točka

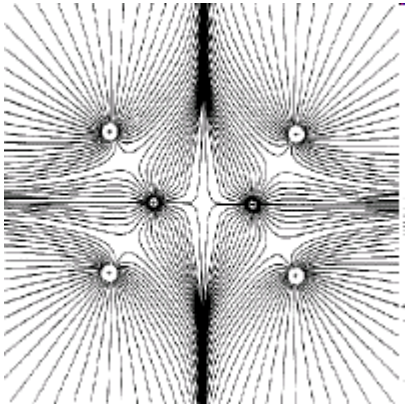
Atraktor – točka u kojoj se spajaju putanje gradijenata – razdjeljuju molekulu na područja pod utjecajem pojedinih atraktora

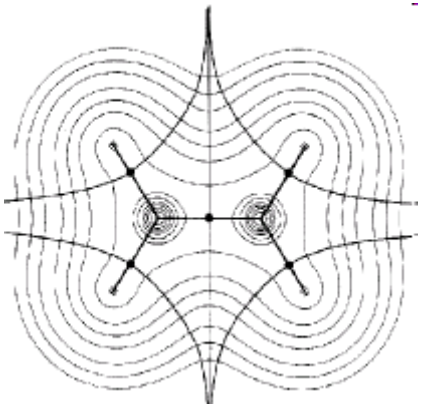
Kritične točke

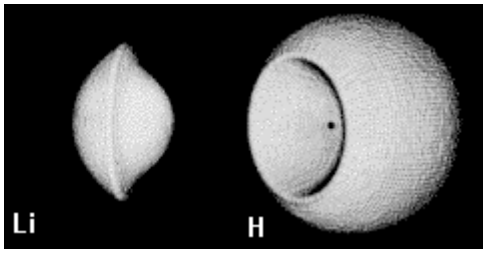
- Atraktori – maksimumi
- Kritične točke veze – sedlaste točke (u 2 smjera maksimum)
- Kritične točke prstena – sedlaste točke (u 2 smjera minimum)
- Kritične točke kaveza - minimumi

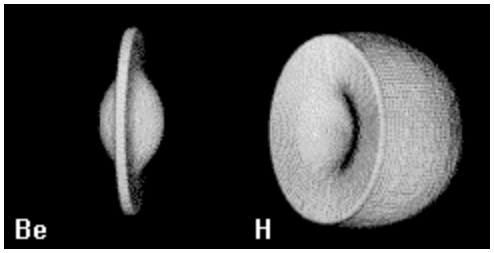
Atom

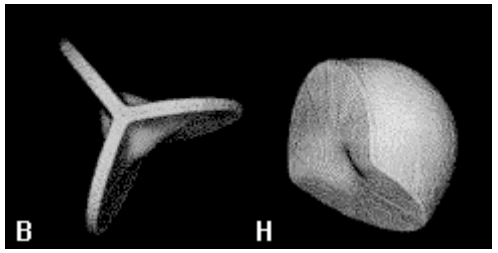
- Jezgra je atraktor
- Pripadni atom je dio prostora u kojemu sve putanje gradijenata imaju isti atraktor
- Postoji skup putanja gradijenata bez atraktora – granice među atomima

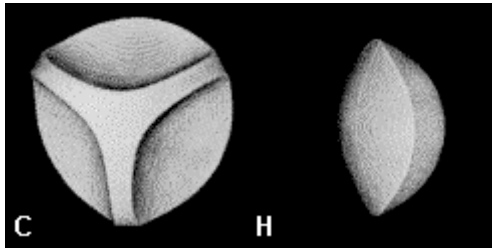


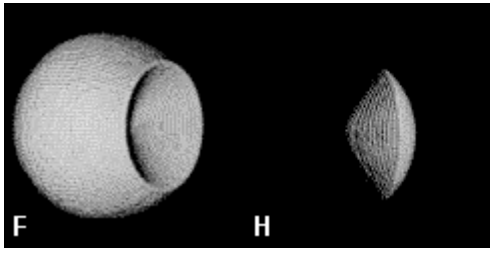


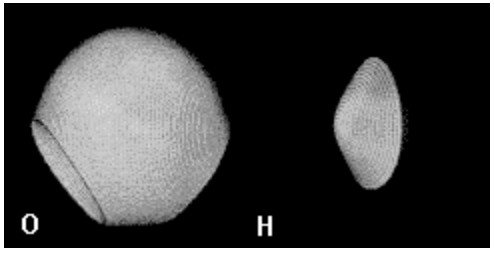

Li
H

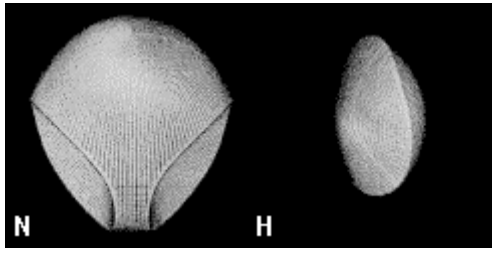

Be
H


B
H


C
H

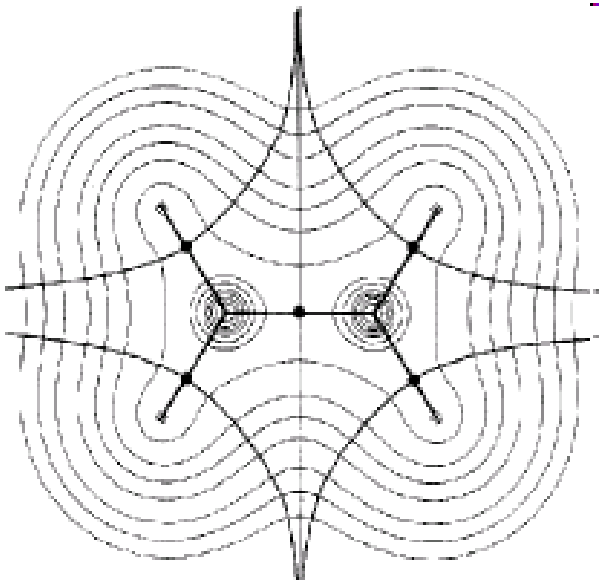

F
H


O
H


N
H

Veza

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



Svojstva veze

- Vezna udaljenost
- Gustoća naboja u kritičnoj točki
- Eliptičnost

Kovalentnost i ionskost veze

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

‘Udio ionske veze’

- Pauling:

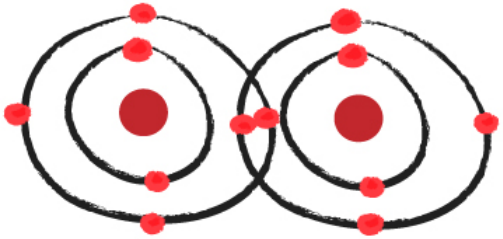
$$\left(1 - e^{-\left(\frac{\Delta\chi}{2}\right)^2}\right) * 100\%$$

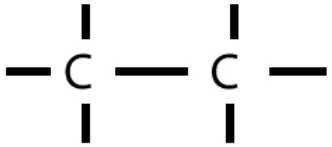
- Preko dipolâ:

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

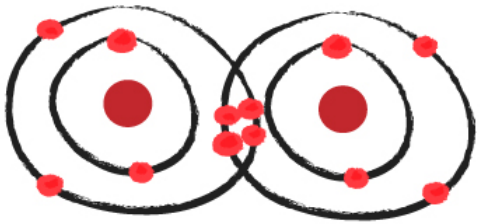
$(\mu_{\text{calc}}) =$ molekulski dipol za slučaj da je veza potpuno ionska ($q = Z$)

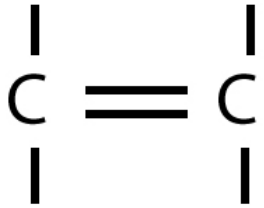
Red veze



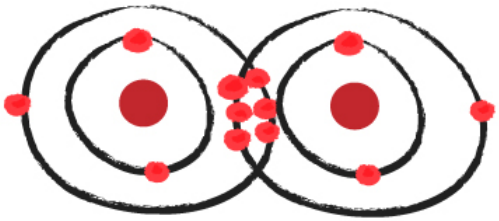


JEDNOSTRUKA



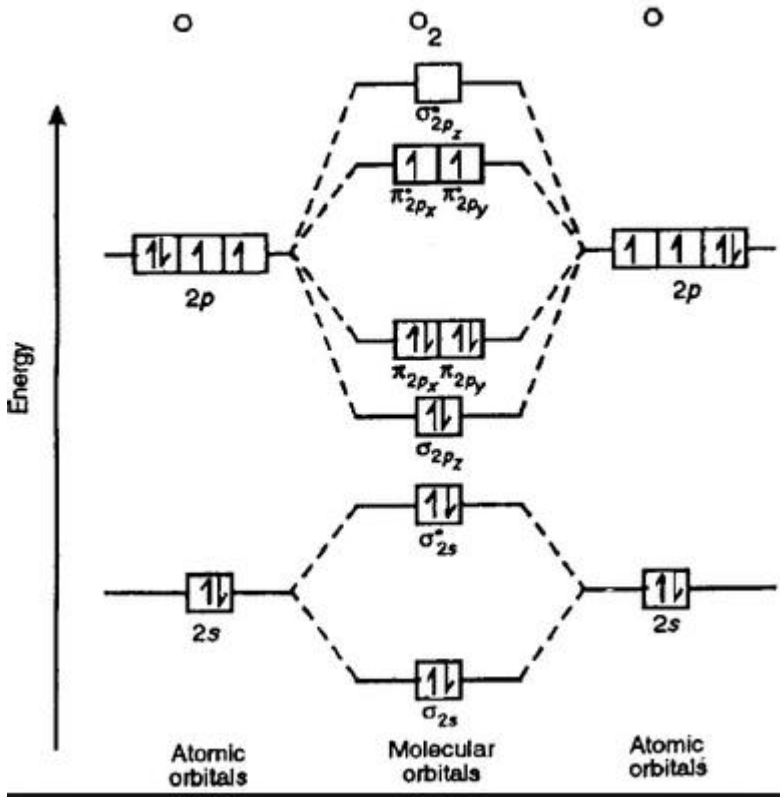


DVOSTRUKA



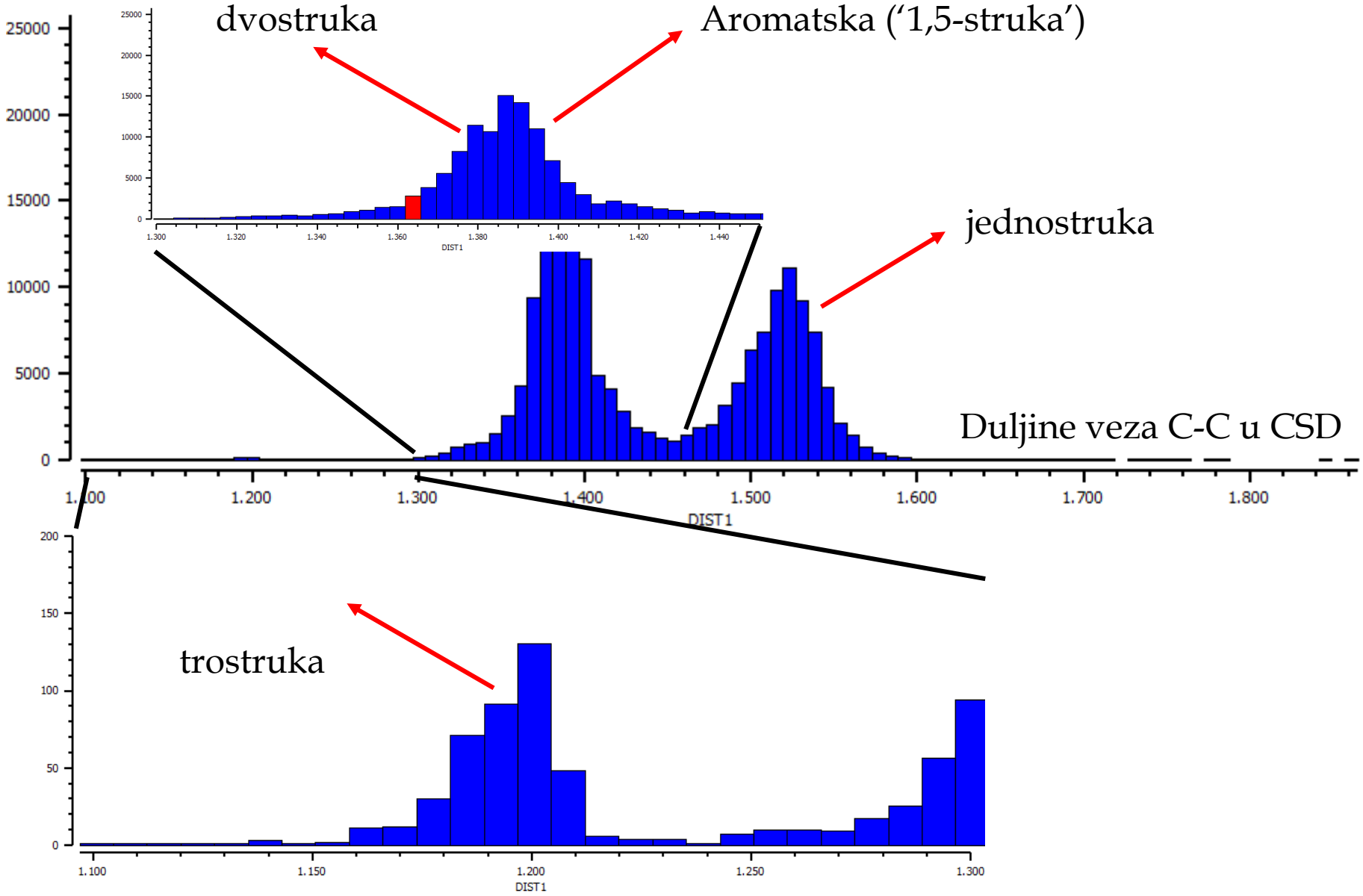
TROSTRUKA

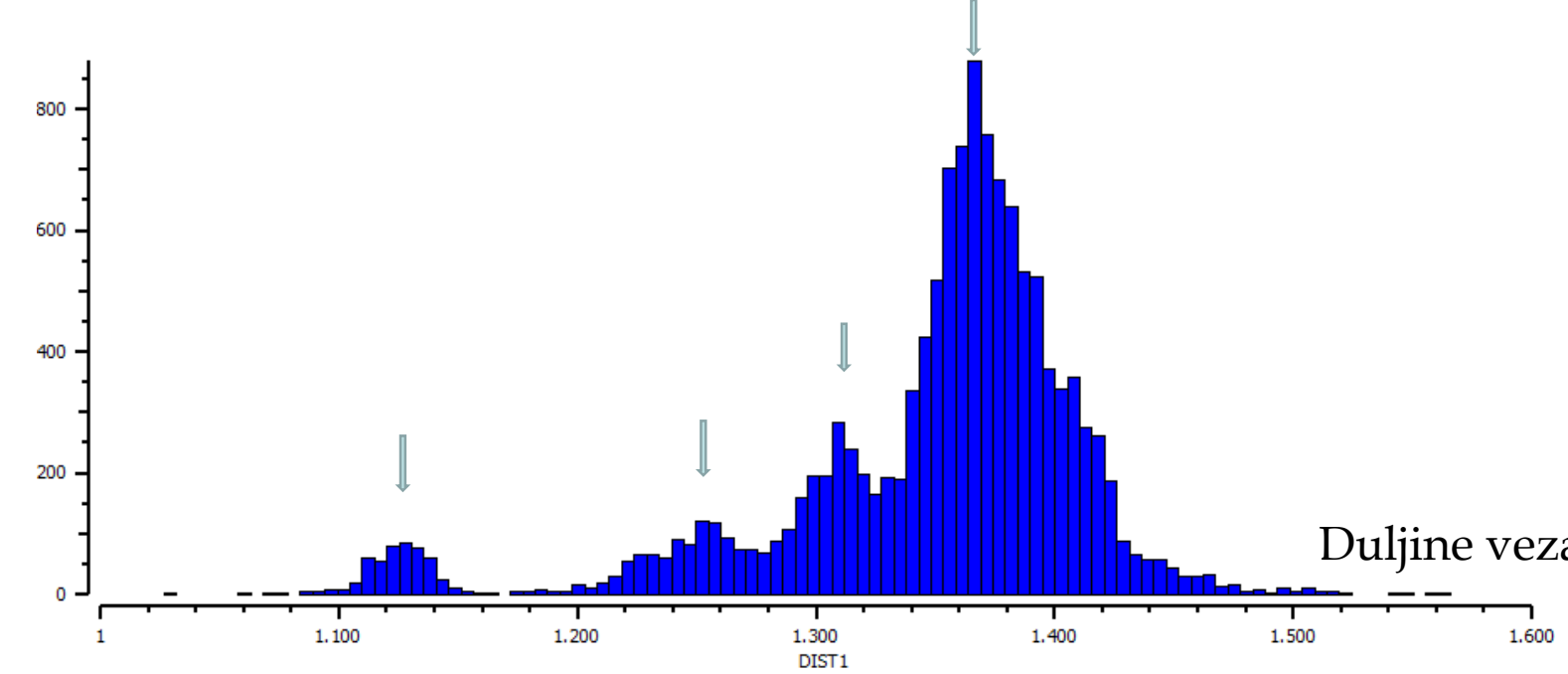
Molekulske orbitale



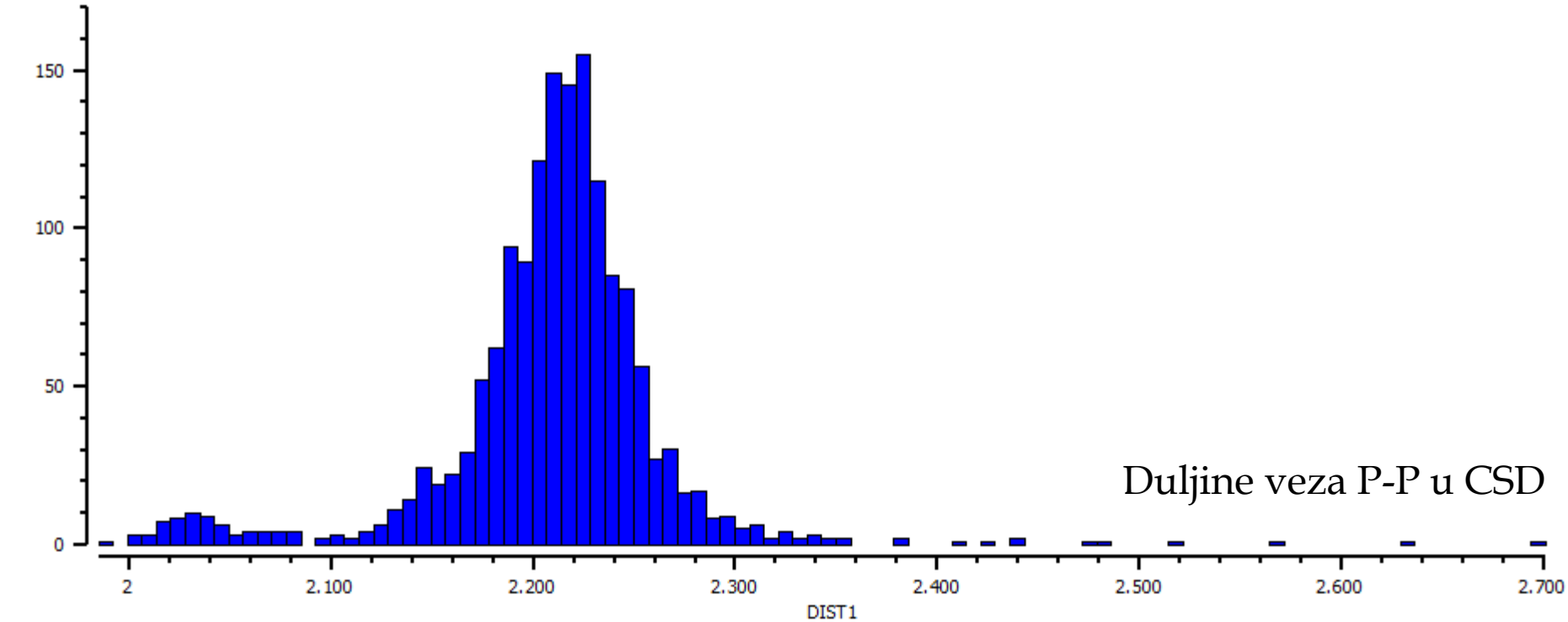
Red veze = $(N(\mathrm{e}_{\mathrm{vezni}}) - N(\mathrm{e}_{\mathrm{protuvezni}}))/2$

Red veze i duljina veze

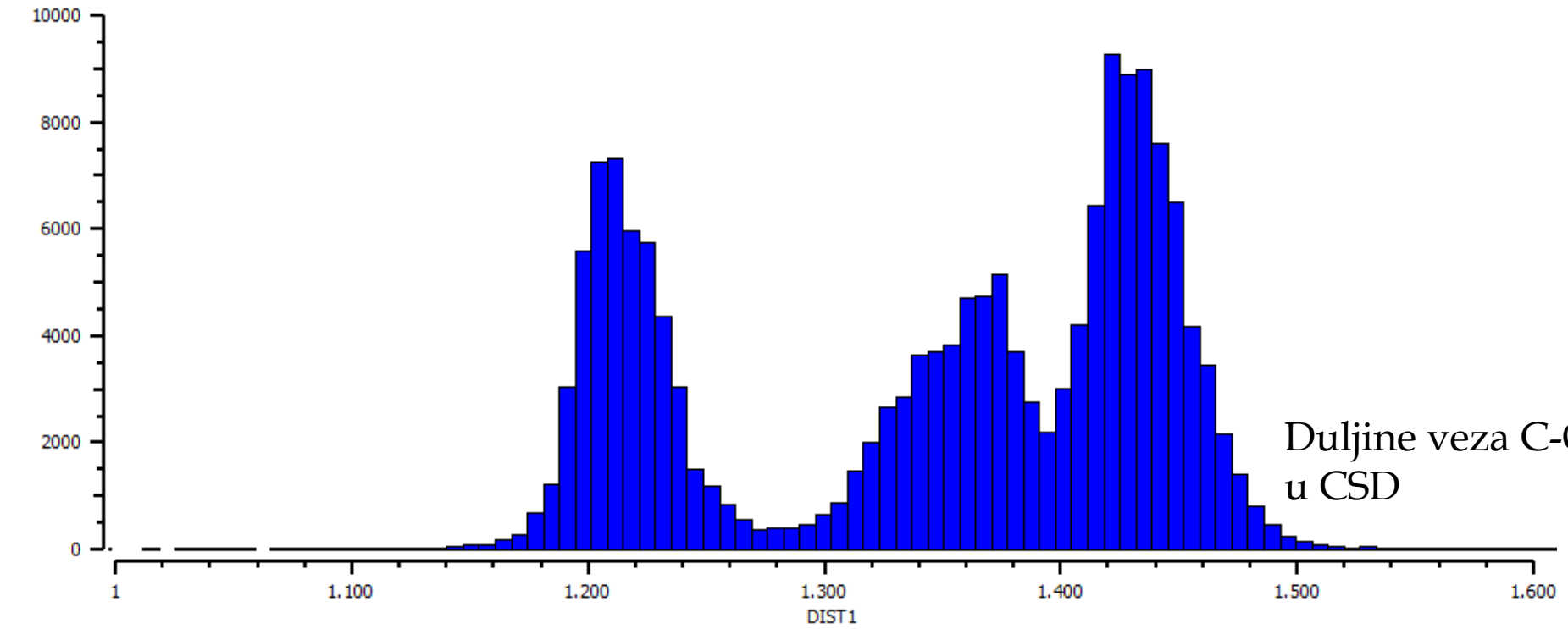




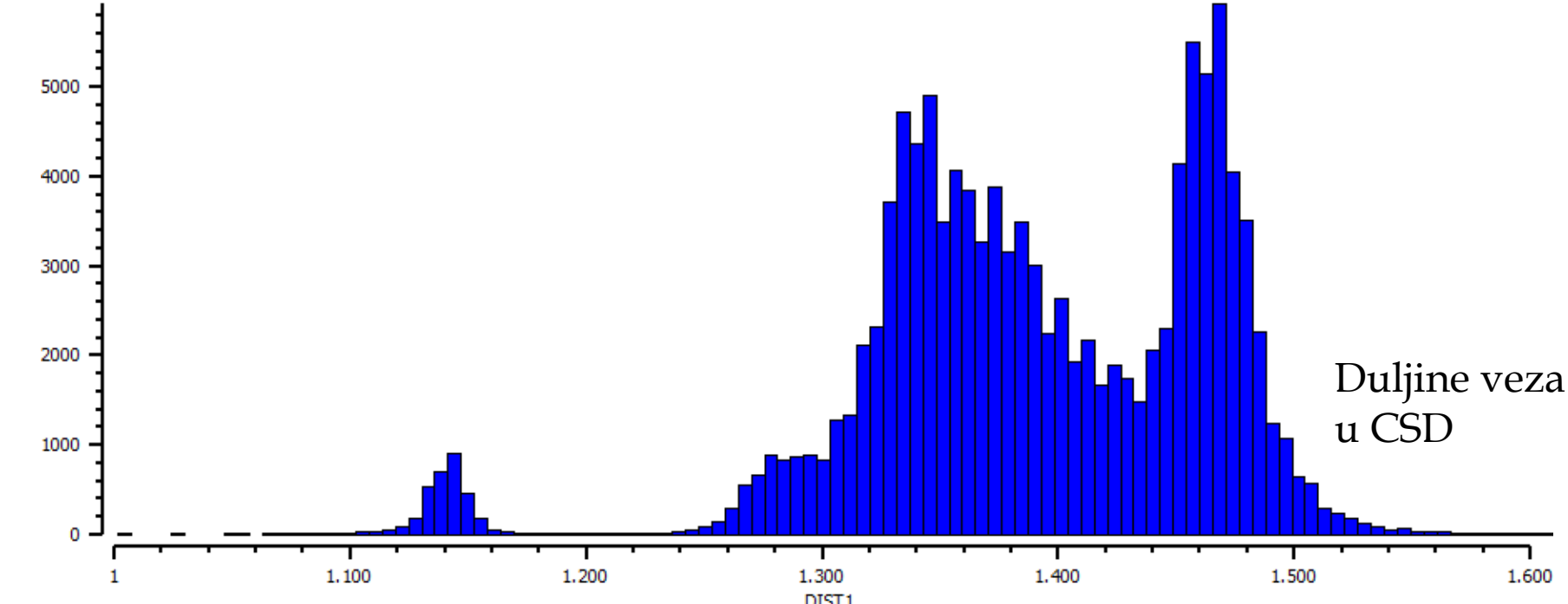
Duljine veza N-N u CSD



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

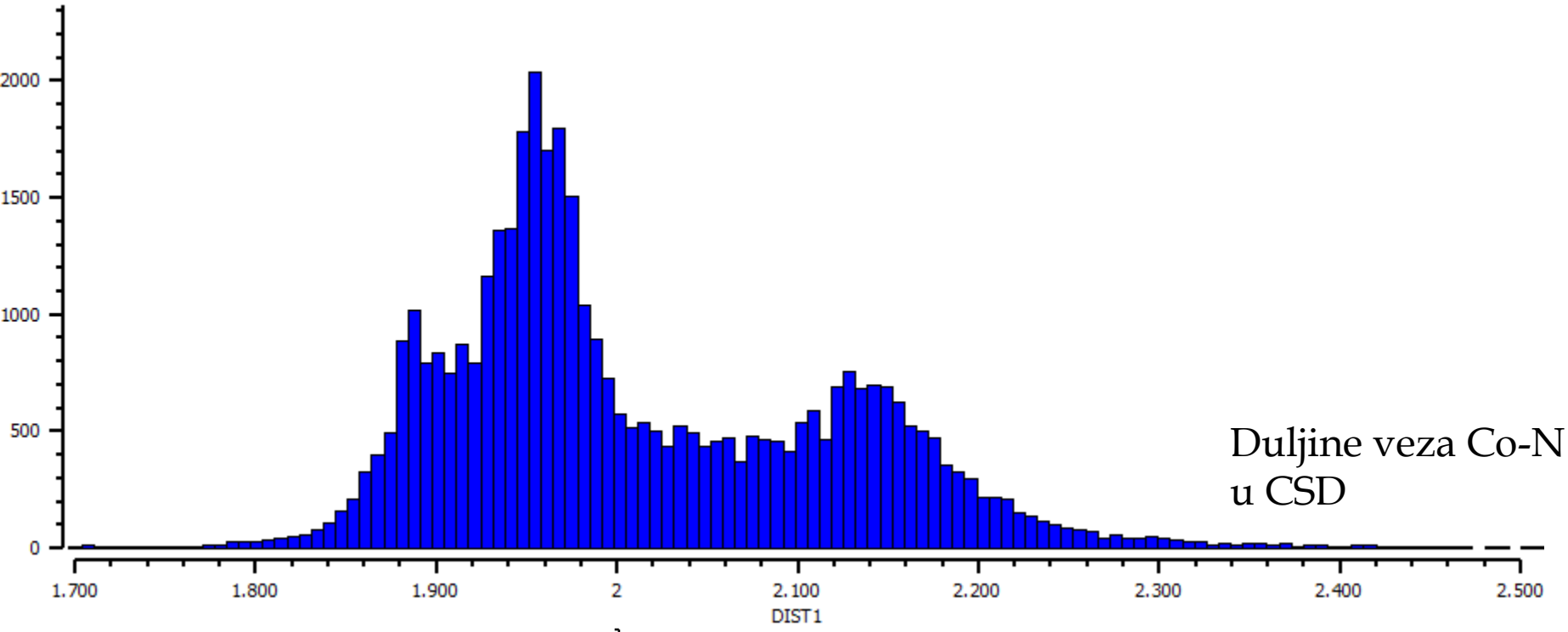
duljina veze

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

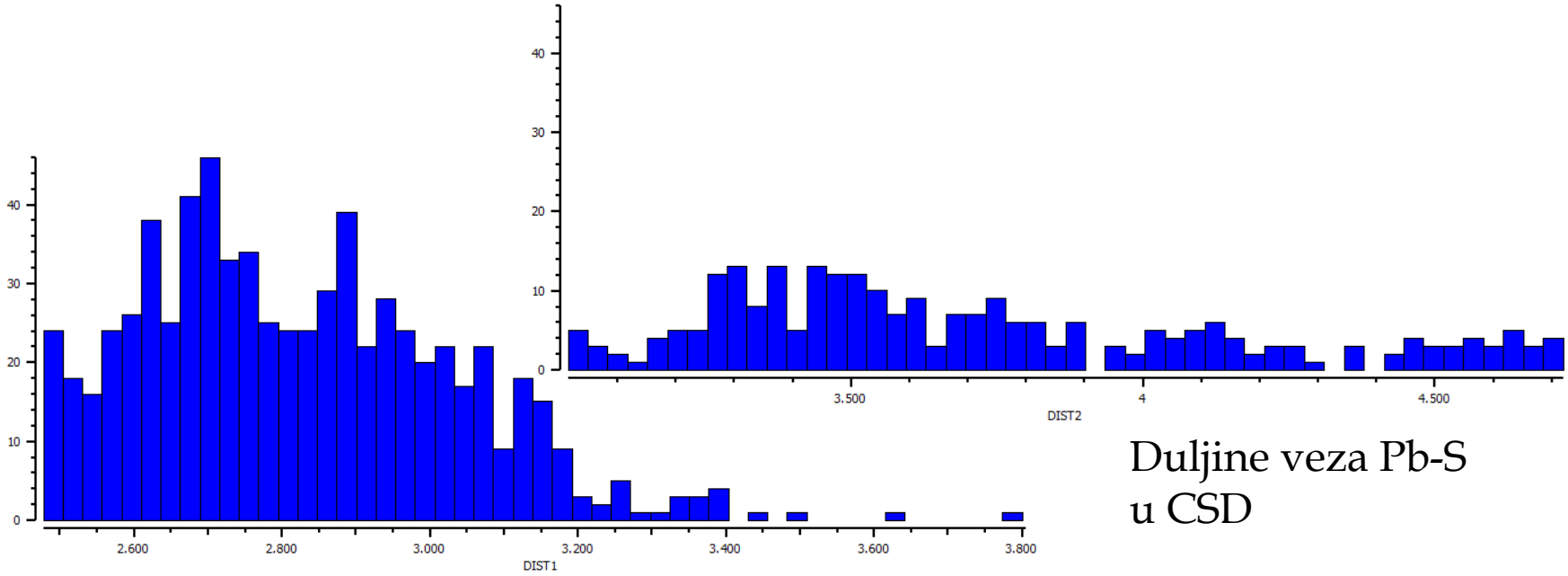
Ugodivi parametar (obično oko 0,37 Å, npr za C 0,352 Å)

Alternativno:

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



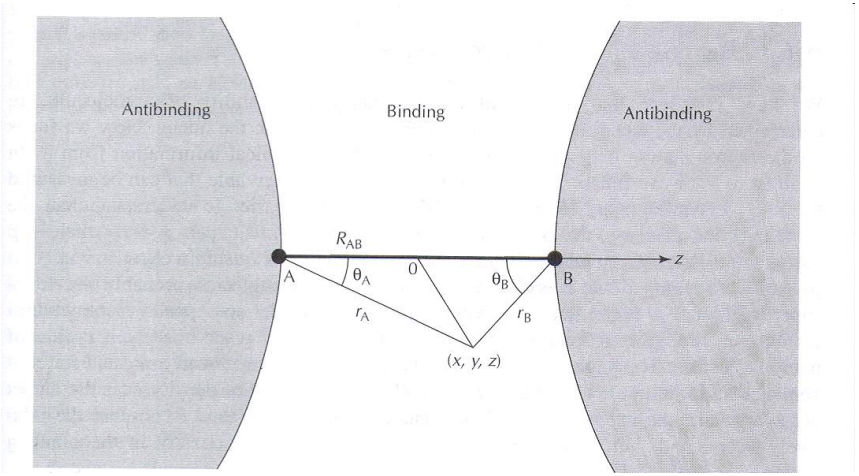
Duljine veza Co-N u CSD



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

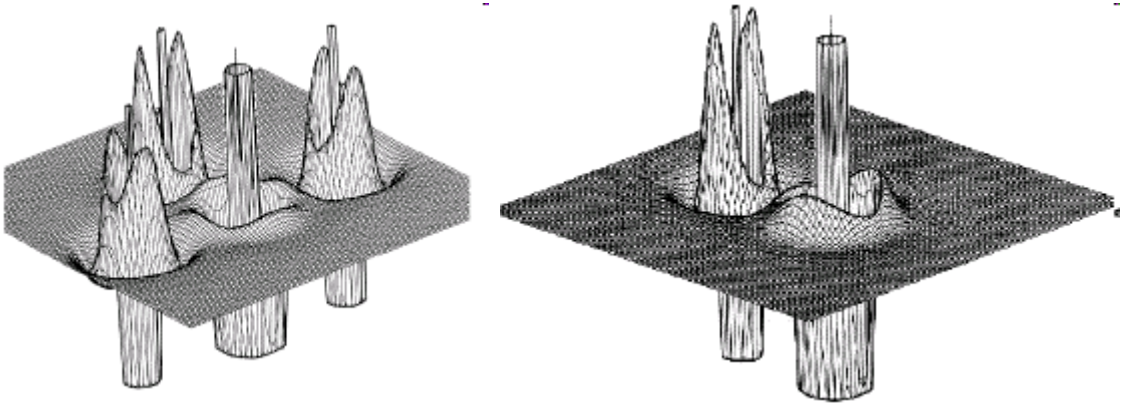
Valencija

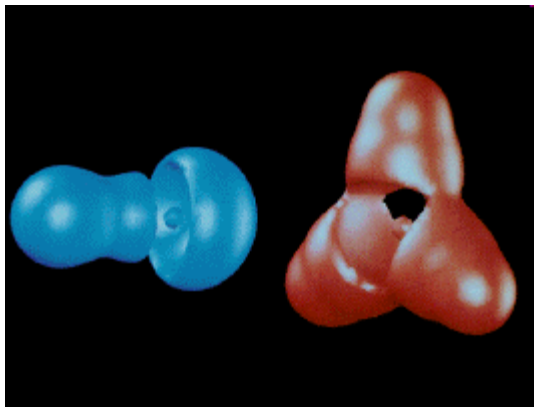
Metoda vezne valencije:

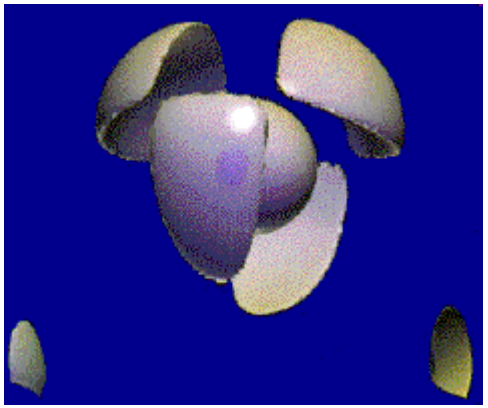
Valencija atoma = zbroj redova svih veza koje neki atom čini

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...