Ab initio proučavanje neadijabatskih efekata kod malih molekula

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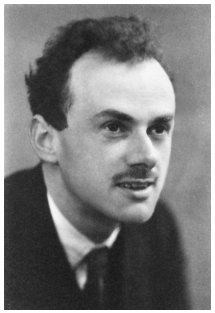
Uvod



"Fizički zakoni na kojima počiva veliki deo fizike i **cela** hemija su, dakle, potpuno poznati i problem je **samo** u tome što egzaktna primena tih zakona vodi do jednačina koje su isuviše komplikovane da bi se mogle rešiti."

— P. A. M. Dirak, 1929.

Sadržaj izlaganja

Sadržaj izlaganja

Šredingerova jednačina

- Molekul $\Longrightarrow$ S jezgara $(A, B, \ldots, S)$, N elektrona $(\alpha, \beta, \ldots, N)$
- Talasna funkcija

$$\Psi = \Psi(r_A, s_A, \ldots, r_S, s_S, r_\alpha, s_\alpha, \ldots, r_N, s_N)$$

- Šredingerova jednačina

$$\hat{H}\Psi = E\Psi$$

Born-Openhajmerova aproksimacija

- Šredingerova jednačina

$$\hat{H}\Psi(\vec{r},\vec{R}) = E\Psi(\vec{r},\vec{R})$$

- Nerelativistički hamiltonijan molekula

$$\hat{H} = \hat{T}_n + \hat{T}_e + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn} = -\frac{1}{2}\sum_{K=A}^{S}\frac{1}{m_K}\Delta_K - \frac{1}{2}\sum_{\mu=\alpha}^{N}\Delta_\mu$$
$$-\sum_{\mu=\alpha}^{N}\sum_{K=A}^{S}\frac{Z_K}{|\vec{r}_{\mu K}|} + \sum_{\mu=\alpha}^{N}\sum_{\nu>\mu}^{N}\frac{1}{|\vec{r}_{\mu\nu}|} + \sum_{K=A}^{S}\sum_{L>K}^{S}\frac{Z_K Z_L}{|\vec{R}_{KL}|}$$

Born-Openhajmerova aproksimacija

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$$-\sum_{\mu=\alpha}^{N}\sum_{K=A}^{S}\frac{Z_K}{|\vec{r}_{\mu K}|} + \sum_{\mu=\alpha}^{N}\sum_{\nu>\mu}^{N}\frac{1}{|\vec{r}_{\mu\nu}|} + \sum_{K=A}^{S}\sum_{L>K}^{S}\frac{Z_K Z_L}{|\vec{R}_{KL}|}$$

- Elektronski hamiltonijan

$$\hat{H}_e = \hat{T}_e + \hat{V}_{en} + \hat{V}_{ee} + \hat{V}_{nn}$$

Born-Openhajmerova aproksimacija

- Rešavamo elektronsku Šredingerovu jednačinu

$$\hat{H}_e\psi(\vec{r};\vec{R}) = E_{el}(\vec{R})\psi(\vec{r};\vec{R})$$

- Rešavamo jezgarnu Šredingerovu jednačinu

$$\Psi(\vec{r},\vec{R}) = \sum_j \Phi_j(\vec{R})\psi_j(\vec{r};\vec{R})$$

$$[\hat{T}_n + E_{el}(\vec{R}) - E]\Phi_j(\vec{R}) + \sum_j \Lambda_{ij}\Phi_j(\vec{R}) = 0$$

gde je

$$\Lambda_{ij} = -\frac{1}{2}\sum_{K=A}^{S}\frac{1}{m_K}\left[2\left\langle\psi_i(\vec{r};\vec{R})\middle|\vec{\nabla}_K\psi_j(\vec{r};\vec{R})\right\rangle\vec{\nabla}_K + \left\langle\psi_i(\vec{r};\vec{R})\middle|\Delta\psi_j(\vec{r};\vec{R})\right\rangle\right]$$

Born-Openhajmerova aproksimacija

- Zanemarivanje Λ_{ij}
  - nedijagonalni članovi $(i \neq j) \Rightarrow$ adijabatska aproksimacija
  - $(i \neq j) \wedge (i = j) \Rightarrow$ B-O aproksimacija

- Dobijamo sistem jednačina

$$[\hat{T}_n + E_{el}(\vec{R})]\Phi_j(\vec{R}) = E\Phi_j(\vec{R}), \qquad j = 1, 2, \ldots$$

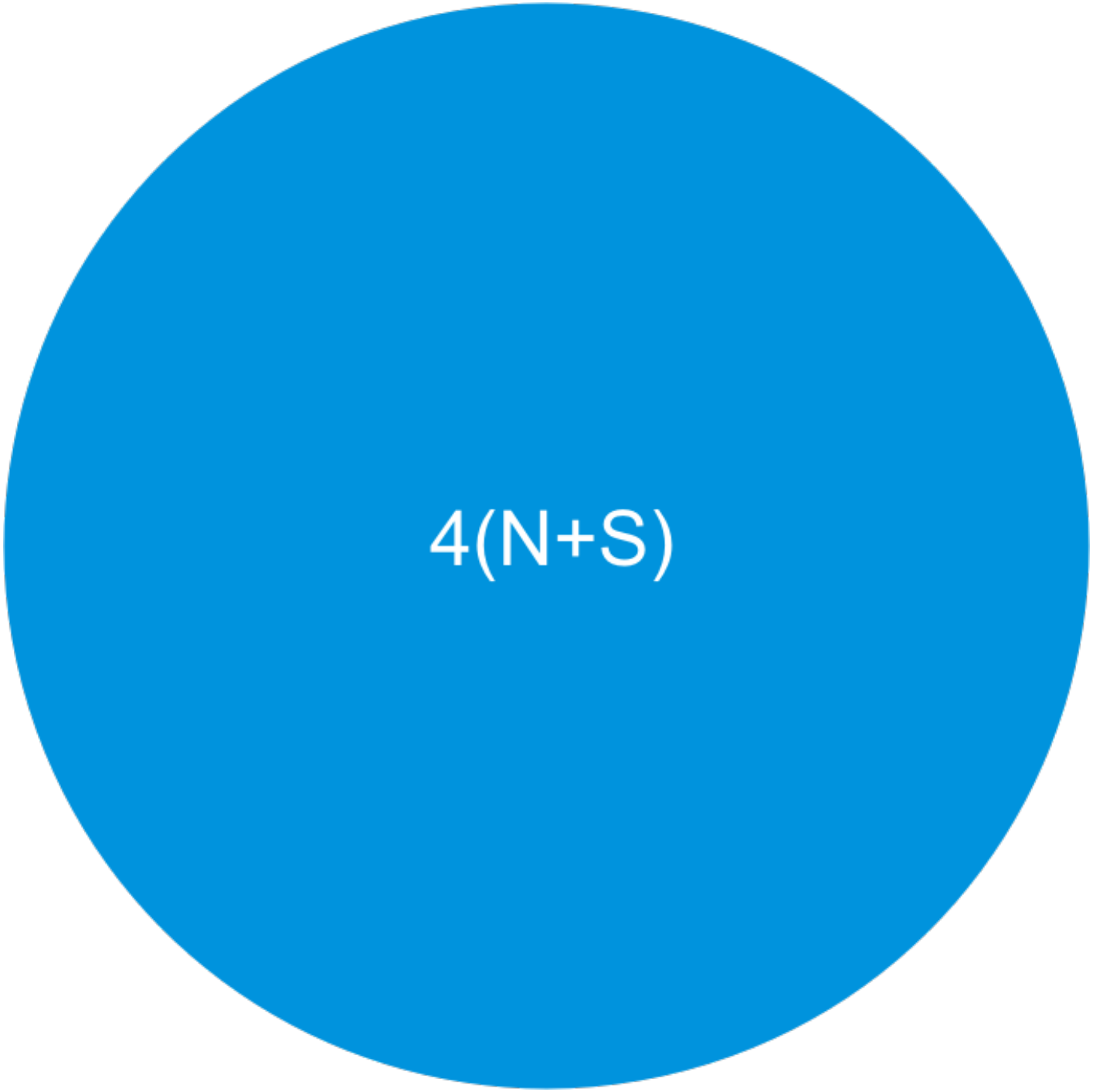
- Narušavanje B-O aproksimacije $\Longrightarrow$ neadijabatski efekti
  i) izbegnuta presecanja potencijalnih površi
  ii) Jan-Telerov efekat
  iii) Rener-Telerov efekat

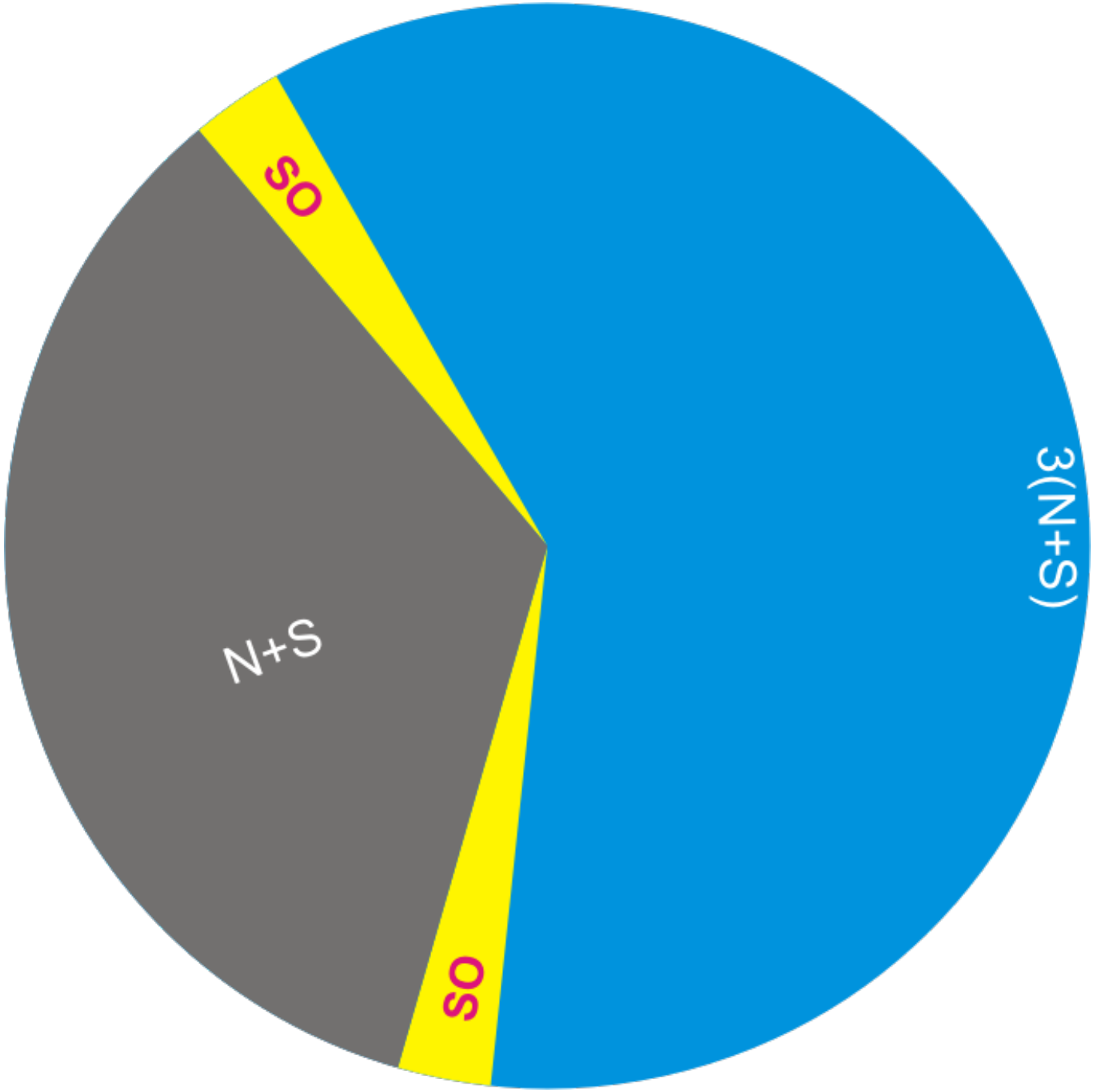
Metode kvantne hemije

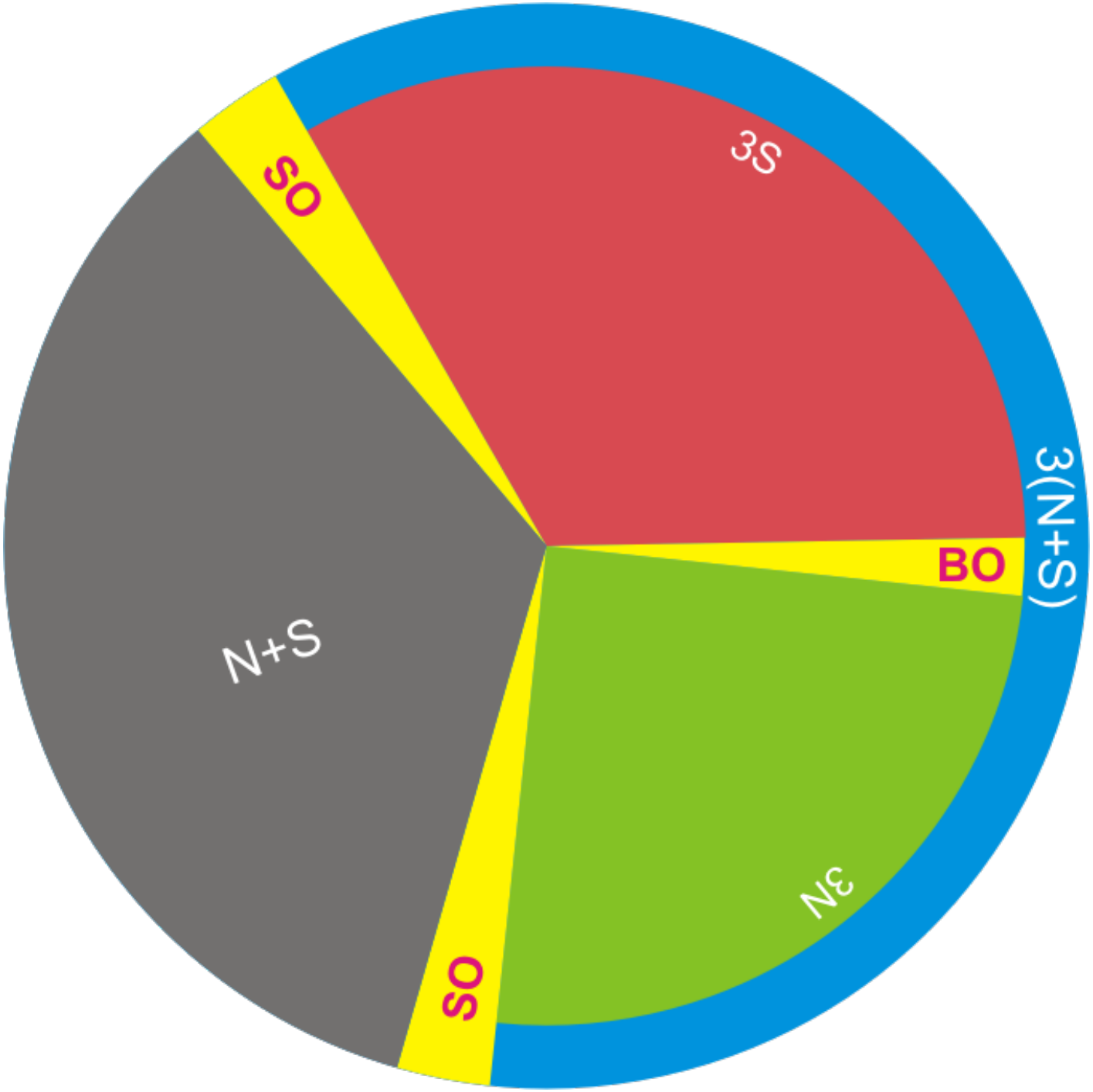
- "*Brute force*" metode
- Semiempirijske metode
- *Ab initio* metode

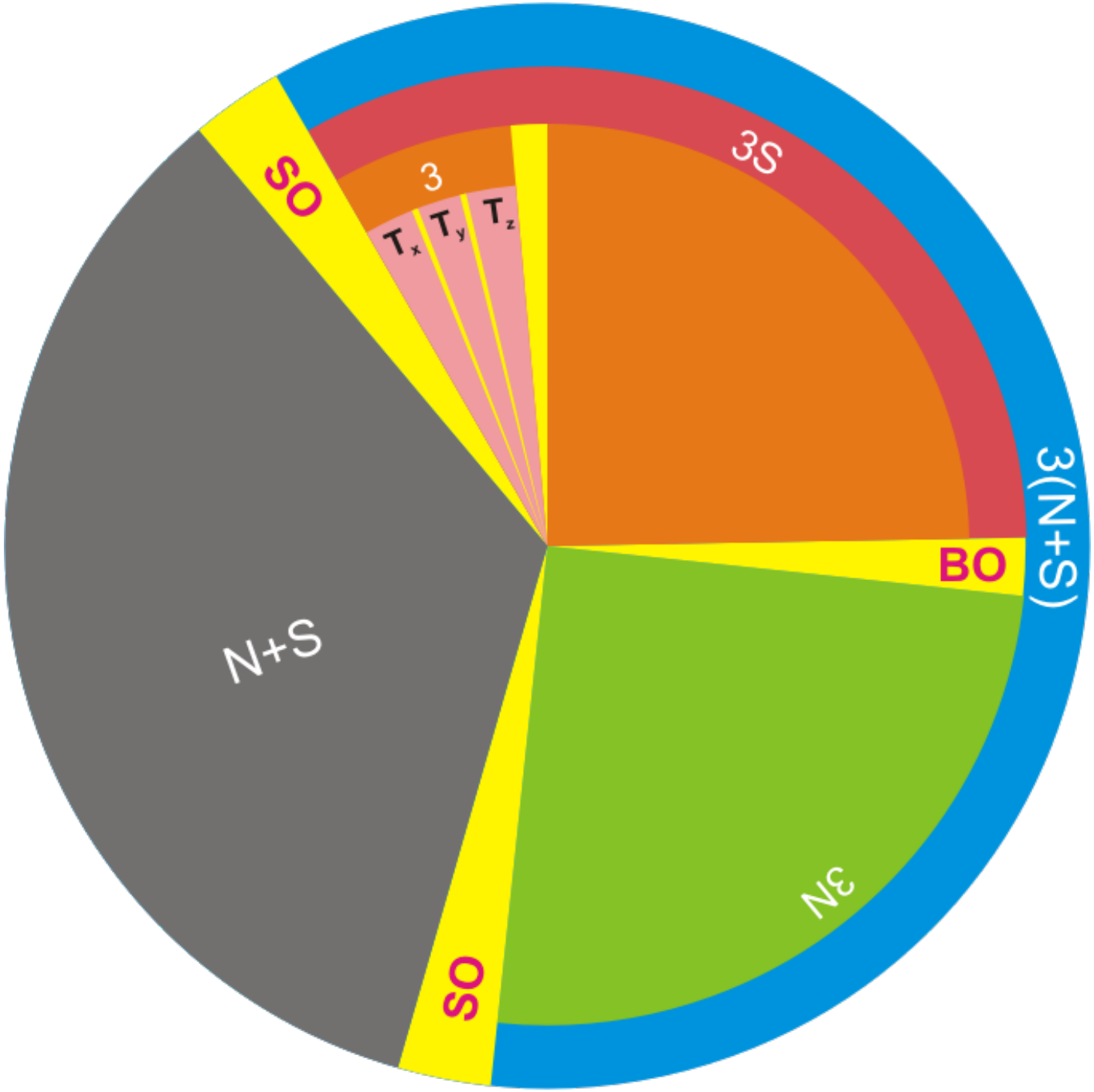
Približne metode

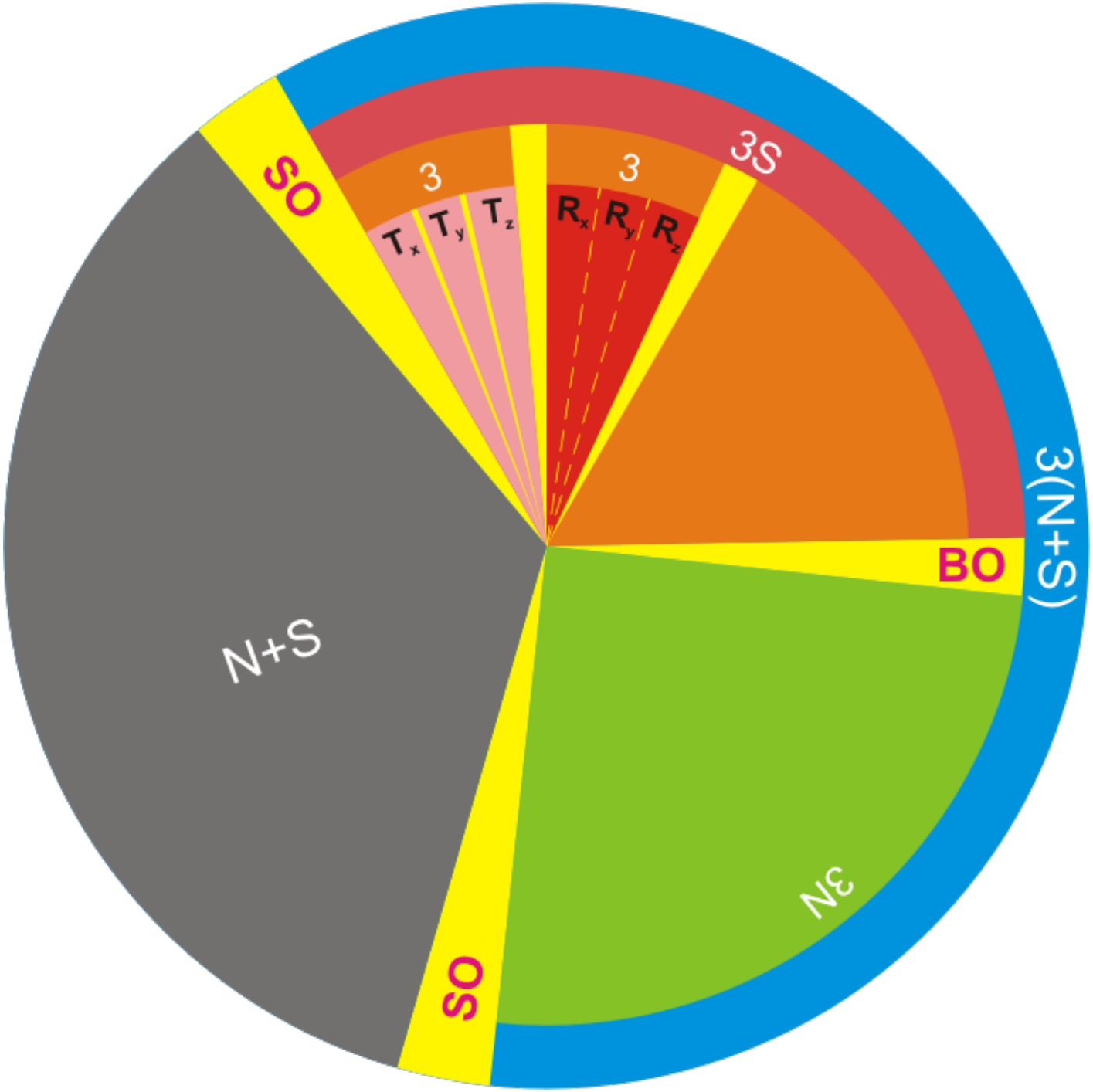
- Perturbacioni račun
- Varijacioni račun

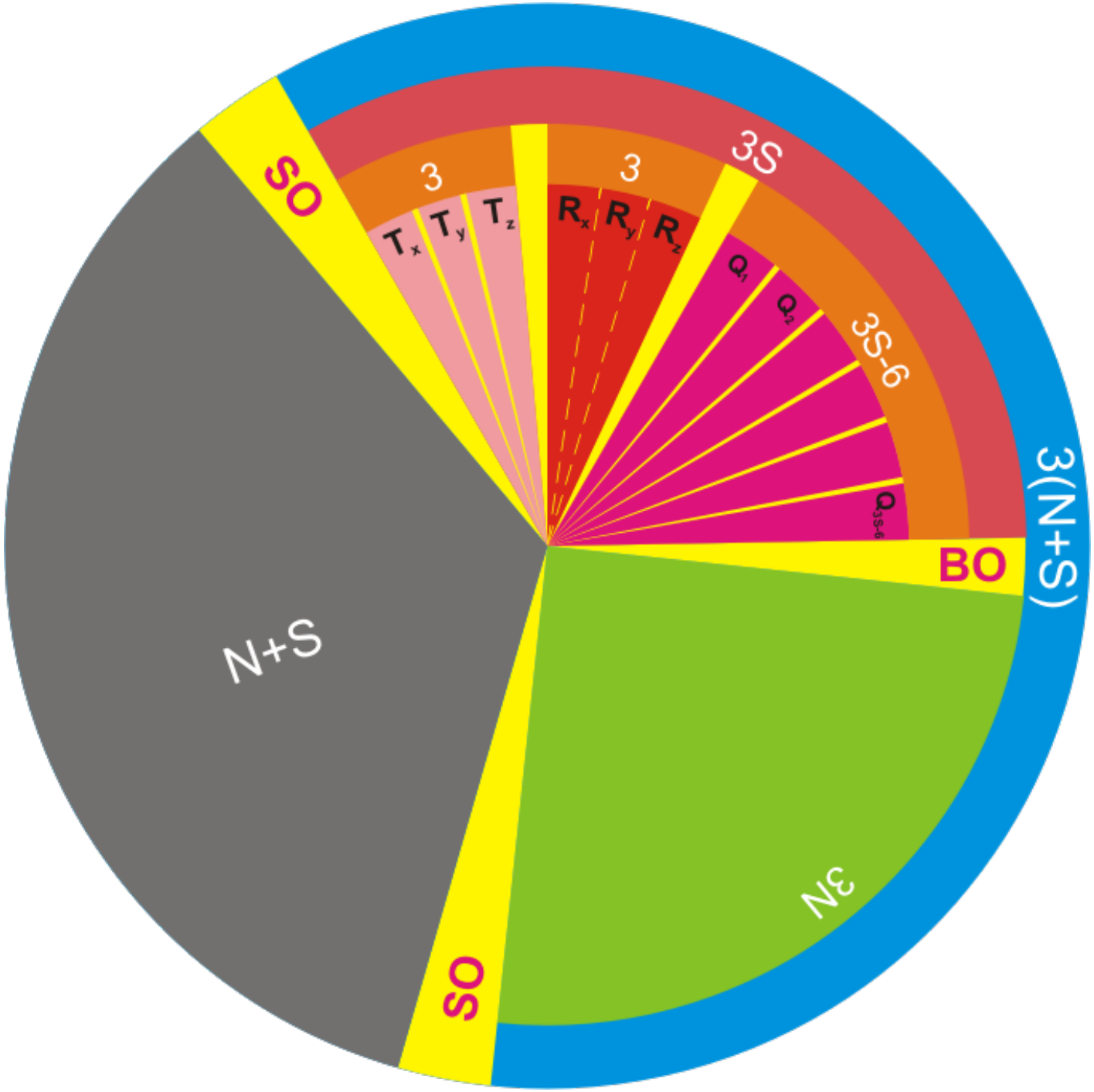

4(N+S)

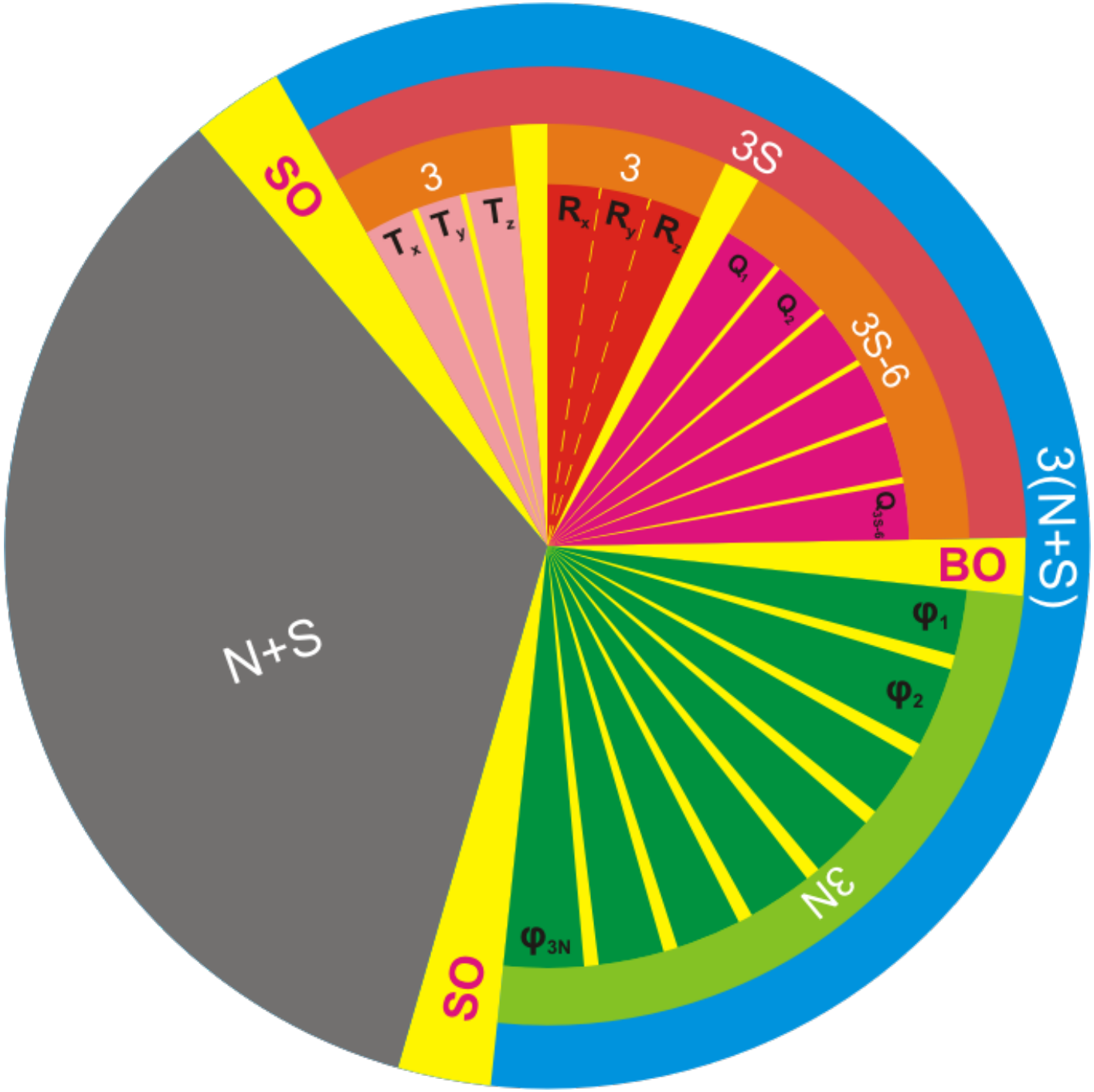

SO
3(N+S)
N+S
SO


SO
3S
3(N+S)
BO
N+S
SO
3N


SO
3
T_x
T_y
T_z
3S
3(N+S)
BO
N+S
SO
3N

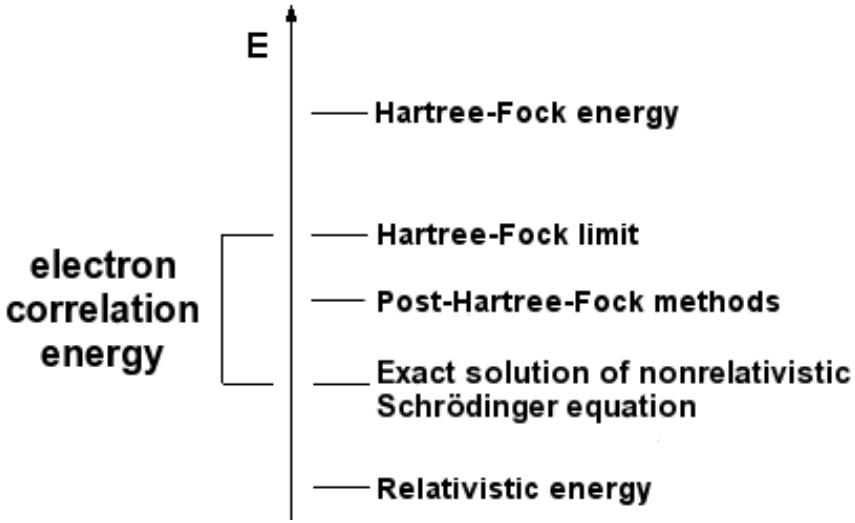

SO
3
T_x
T_y
T_z
3
R_x
R_y
R_z
3S
3(N+S)
BO
N+S
SO
Nε


SO
3
T_x
T_y
T_z
3
R_x
R_y
R_z
3S
3S-6
Q_1
Q_2
Q_{3S-6}
BO
3(N+S)
N+S
SO
3N


3(N+S)
3S
3S-6
3
3
SO
BO
SO
Nε
N+S
T_x
T_y
T_z
R_x
R_y
R_z
Q_1
Q_2
Q_{3S-6}
φ_1
φ_2
φ_{3N}

Ab initio metode za rešavanje elektronskog problema

- Hartree-Fock method (HF)
- Density functional theory (DFT)
  (*ab initio*?)



Post-Hartree-Fock methods

- Møller–Plesset perturbation theory (MPn)
- Configuration interaction (CI)
- Coupled cluster (CC)

Multi-reference methods

- Multi-configurational self-consistent field (MCSCF, CASSCF)
- Multi-reference configuration interaction (MRCI)
- Complete active space perturbation theory (CASPTn)
- Multi-reference coupled-cluster (MRCC)

Sadržaj izlaganja

Mali molekuli

The Cologne Database for Molecular Spectroscopy
Universität zu Köln, Physikalisches Institut
http://www.astro.uni-koeln.de/cdms/molecules

Molecules in the Interstellar Medium or Circumstellar Shells (as of 02/2016)

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	>12 atoms
H_2	C_3 *	*c*-C_3H	C_5 *	C_5H	C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N	HC_9N	*c*-C_6H_6 *	$HC_{11}N$
AlF	C_2H	*l*-C_3H	C_4H	*l*-H_2C_4	CH_2CHCN	$HC(O)OCH_3$	CH_3CH_2CN	$(CH_3)_2CO$	CH_3C_6H	*n*-C_3H_7CN	C_{60} *
AlCl	C_2O	C_3N	C_4Si	C_2H_4*	CH_3C_2H	CH_3COOH	$(CH_3)_2O$	$(CH_2OH)_2$	C_2H_5OCHO	*i*-C_3H_7CN 2014	C_{70} *
C_2**	C_2S	C_3O	*l*-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH	CH_3CH_2CHO	$CH_3OC(O)CH_3$	$C_2H_5OCH_3$?	C_{60}^+ *
CH	CH_2	C_3S	*c*-C_3H_2	CH_3NC	CH_3CHO	C_6H_2	HC_7N				
CH^+	HCN	C_2H_2*	H_2CCN	CH_3OH	CH_3NH_2	CH_2OHCHO	C_8H				
CN	HCO	NH_3	CH_4 *	CH_3SH	*c*-C_2H_4O	*l*-HC_6H *	$CH_3C(O)NH_2$				
CO	HCO^+	HCCN	HC_3N	HC_3NH^+	H_2CCHOH	CH_2CHCHO (?)	C_8H^-				
CO^+	HCS^+	$HCNH^+$	HC_2NC	HC_2CHO	C_6H^-	CH_2CCHCN	C_3H_6				
CP	HOC^+	HNCO	HCOOH	NH_2CHO	CH_3NCO 2015	H_2NCH_2CN	CH_3CH_2SH (?)				
SiC	H_2O	HNCS	H_2CNH	C_5N		CH_3CHNH					
HCl	H_2S	$HOCO^+$	H_2C_2O	*l*-HC_4H *							
KCl	HNC	H_2CO	H_2NCN	*l*-HC_4N							
NH	HNO	H_2CN	HNC_3	*c*-H_2C_3O							
NO	MgCN	H_2CS	SiH_4 *	H_2CCNH (?)							
NS	MgNC	H_3O^+	H_2COH^+	C_5N^-							
NaCl	N_2H^+	*c*-SiC_3	C_4H^-	HNCHCN							
OH	N_2O	CH_3 *	HC(O)CN								
PN	NaCN	C_3N^-	HNCNH								
SO	OCS	PH_3	CH_3O								
SO^+	SO_2	HCNO	NH_4^+								
SiN	*c*-SiC_2	HOCN	H_2NCO^+ (?)								
SiO	CO_2 *	HSCN	$NCCNH^+$ 2015								

Mali molekuli

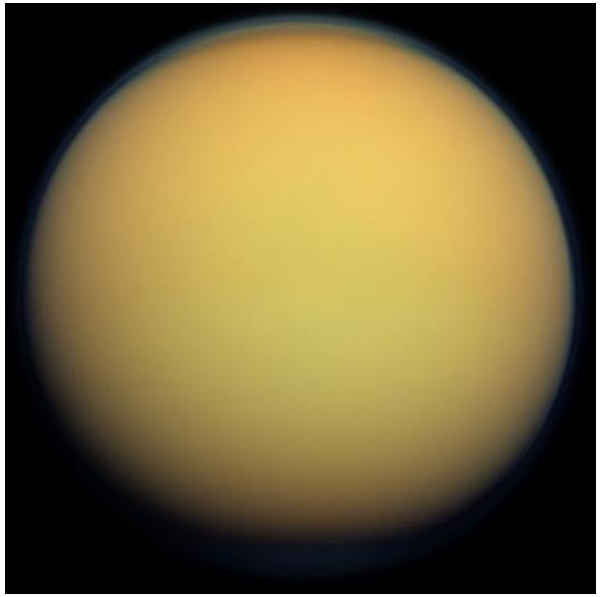
Extragalactic Molecules (as of 10/2015)

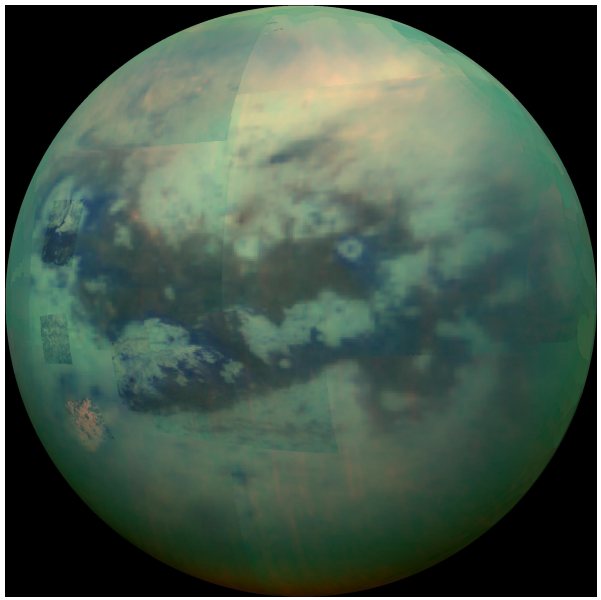
2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	>8 atoms
OH	H_2O	H_2CO	*c*-C_3H_2	CH_3OH	CH_3CCH	HC_6H	*c*-C_6H_6 *
CO	HCN	NH_3	HC_3N	CH_3CN	CH_3NH_2		C_{60}* (?)
H_2 *	HCO^+	HNCO	CH_2NH	HC_4H *	CH_3CHO		
CH	C_2H	C_2H_2 *	NH_2CN	$HC(O)NH_2$			
CS	HNC	H_2CS ?	*l*-C_3H_2				
CH^+ **	N_2H^+	$HOCO^+$	H_2CCN				
CN	OCS	*c*-C_3H	H_2CCO				
SO	HCO	H_3O^+	C_4H				
SiO	H_2S	*l*-C_3H					
CO^+	SO_2						
NO	HOC^+						
NS	C_2S						
NH	H_2O^+						
OH^+	HCS^+						
HF	H_2Cl^+ 2014						
SO^+	NH_2 2014						
ArH^+ 2015							

Mali molekuli - atmosfera Titana

N≡C−C≡C−C≡N Dicijanoacetilen (C_4N_2)
H−C≡C−C≡C−H Diacetilen (C_4H_2)

- Cijanoacetilen i cijanodiacetilen opaženi u interstelarnom prostoru, dicijanoacetilen?
- Atmosfera Titana (N_2, CH_4, ...)
- $C_4N_{2(s)}$ detektovan
- C_4N_2 značajan za meteorologiju Titana
- $X\ ^2\Pi_u$ elektronsko stanje katjona $C_4N_2^+$, ispoljava Rener-Telerov efekat

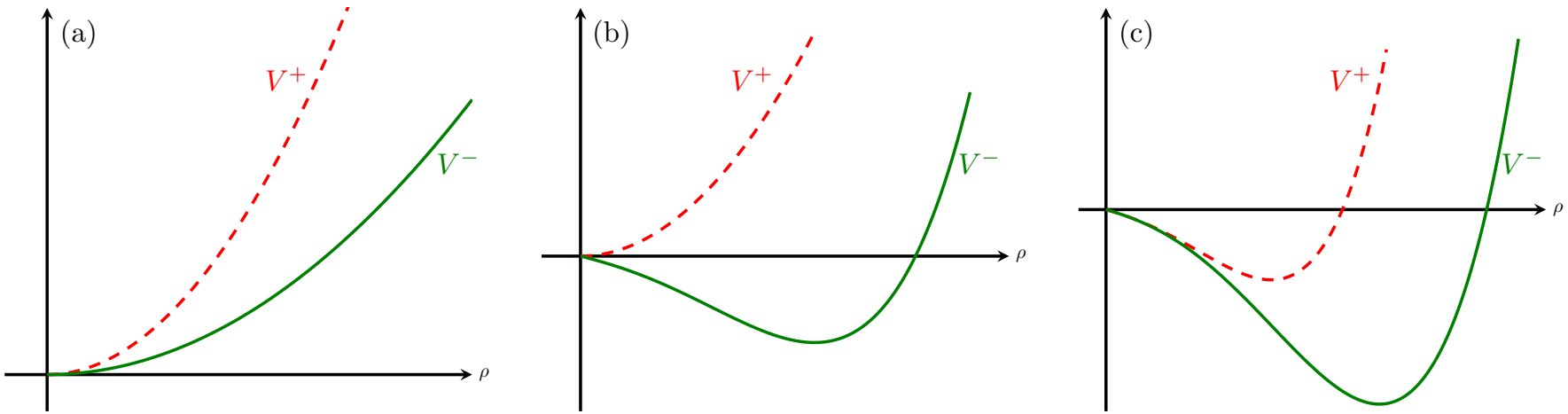




Sadržaj izlaganja

Rener-Telerov efekat - opšta razmatranja

- Linearni molekuli (elektronska stanja Π, Δ, Φ, ...)
- $C_{\infty v}$, $D_{\infty h} \rightarrow C_s$, C_{2v}, C_{2h}, ...
- Vibraciono-elektronska (vibronska) sprega



- Troatomski molekuli
- Četvoroatomski molekuli

Sadržaj izlaganja

Modelni hamiltonijan

a) Razmatrano elektronsko stanje je dovoljno odvojeno od drugih elektronskih stanja
b) Ravnotežna geometrija molekula je linearna
c) Harmonijska aproksimacija
d) Sprega između savijajućih i istežućih vibracija je zanemarena
e) Rotacija molekula u celini zanemarena
f) Korišćene krivolinijske unutrašnje koordinate
g) Primenjen operator kinetičke energije jezgara za infinitezimalne savijajuće vibracije
h) Primenjen fenomenološki spin-orbitni operator
i) Asimptotske (linearne) elektronske talasne funkcije su korišćene za matričnu reprezentaciju operatora kinetičke energije jezgara

Modelni hamiltonijan

- Molekulski hamiltonijan

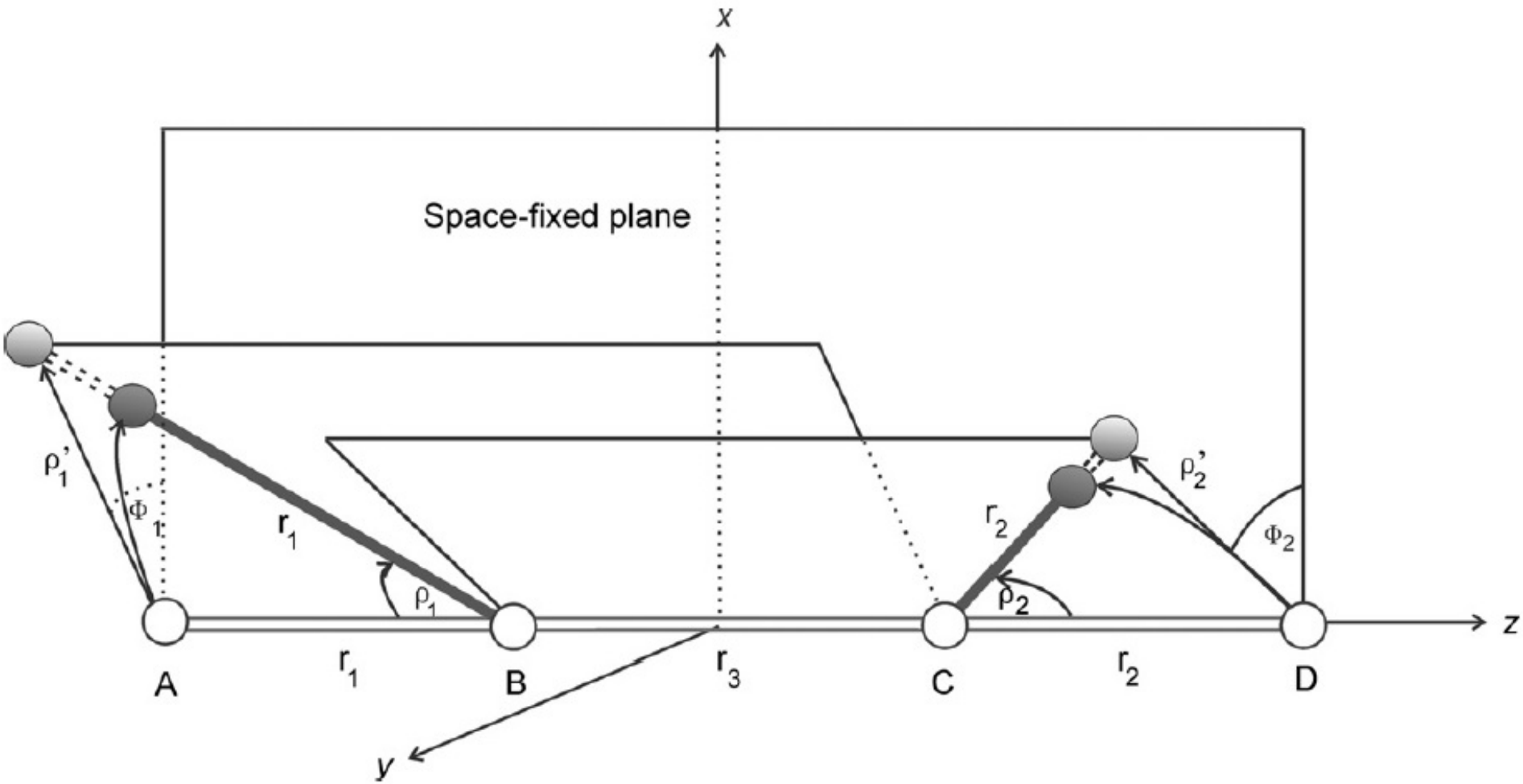
$$\hat{H} = \hat{H}_e + \hat{T}_n + \hat{H}_{SO}$$

- Elektronski spin-orbitni operator

$$\hat{H}_{SO} = A_{SO}\hat{L}_z\hat{S}_z$$

- Operator kinetičke energije za savijajuća kretanja jezgara
  - i) krivolinijske unutrašnje koordinate (ρ_1, ϕ_1, ρ_2, ϕ_2)
  - ii) krivolinijske simetrijske koordinate (ρ_C, ϕ_C, ρ_T, ϕ_T)
  - iii) pravolinijske unutrašnje/simetrijske koordinate
  - iv) normalne koordinate

Modelni hamiltonijan



[Perić *et al.* 2006]

Modelni hamiltonijan

- $\hat{T}_n$ u krivolinijskim unutrašnjim koordinatama za dve (dvostruko degenerisane) infinitezimalne savijajuće vibracije

$$\begin{aligned}\hat{T}_n = &-\frac{1}{2\mu_1}\left(\frac{\partial^2}{\partial\rho_1^2}+\frac{1}{\rho_1}\frac{\partial}{\partial\rho_1}+\frac{1}{\rho_1^2}\frac{\partial^2}{\partial\phi_1^2}\right)-\frac{1}{2\mu_2}\left(\frac{\partial^2}{\partial\rho_2^2}+\frac{1}{\rho_2}\frac{\partial}{\partial\rho_2}+\frac{1}{\rho_2^2}\frac{\partial^2}{\partial\phi_2^2}\right)\\ &+\frac{1}{\mu_{12}}\left[\cos(\phi_2-\phi_1)\left(\frac{\partial^2}{\partial\rho_1\partial\rho_2}+\frac{1}{\rho_1\rho_2}\frac{\partial^2}{\partial\phi_1\partial\phi_2}\right)\right.\\ &\left.+\sin(\phi_2-\phi_1)\left(\frac{1}{\rho_1}\frac{\partial^2}{\partial\rho_2\partial\phi_1}-\frac{1}{\rho_2}\frac{\partial^2}{\partial\rho_1\partial\phi_2}\right)\right]\end{aligned}$$

$$V=\frac{1}{2}k_1\rho_1^2+\frac{1}{2}k_2\rho_2^2+k_{12}\rho_1\rho_2\cos(\phi_2-\phi_1)$$

Elektronske bazne funkcije

- Vibronska talasna funkcija u obliku

$$\Psi = f_1\psi_1 + f_2\psi_2$$

- Izbor elektronskih talasnih funkcija $\Rightarrow$ adijabatske talasne funkcije

$$\hat{H}_e\psi^+ = V^+\psi^+, \qquad \hat{H}_e\psi^- = V^-\psi^-$$

- Matrični elementi od $\hat{H}_{el}$ dijagonalni
- Matrični elementi od $\hat{T}_n$ sadrže članove:

$$\left\langle \psi^+ \middle| \frac{\partial}{\partial q_i} \middle| \psi^+ \right\rangle = \left\langle \psi^- \middle| \frac{\partial}{\partial q_i} \middle| \psi^- \right\rangle = \frac{\partial}{\partial q_i}$$

$$\left\langle \psi^+ \middle| \frac{\partial}{\partial q_i} \middle| \psi^- \right\rangle = \left\langle \psi^+ \middle| \frac{\partial \psi^-}{\partial q_i} \right\rangle = -\left\langle \psi^- \middle| \frac{\partial}{\partial q_i} \middle| \psi^+ \right\rangle$$

- B-O aproksimacija?
- Izbegnuta presecanja; članovi ρ_i^{-1} i $\rho_i^{-1}\rho_j^{-1}$

Elektronske bazne funkcije - dijabatizacija

- Dijabatske elektronske talasne funkcije

$$\eta_1 = \psi^+ \cos(\Lambda\tau) - \psi^- \sin(\Lambda\tau)$$
$$\eta_2 = \psi^+ \sin(\Lambda\tau) + \psi^- \cos(\Lambda\tau)$$

- Matrični elementi elektronskog operatora u ovoj bazi

$$E_{11} = \langle \eta_1 | \hat{H}_e | \eta_1 \rangle = V^+ \cos^2(\Lambda\tau) + V^- \sin^2(\Lambda\tau)$$
$$E_{22} = \langle \eta_2 | \hat{H}_e | \eta_2 \rangle = V^+ \sin^2(\Lambda\tau) + V^- \cos^2(\Lambda\tau)$$
$$E_{12} = \langle \eta_1 | \hat{H}_e | \eta_2 \rangle = \frac{V^+ - V^-}{2} \sin(2\Lambda\tau) = \langle \eta_2 | \hat{H}_e | \eta_1 \rangle$$

- Ugao τ određujemo kao

$$\left\langle \eta_1 \middle| \frac{\partial \eta_2}{\partial q_i} \right\rangle = 0, \quad \frac{\partial \tau}{\partial q_i} = -\frac{1}{\Lambda} \left\langle \psi^+ \middle| \frac{\partial \psi^-}{\partial q_i} \right\rangle = \frac{1}{\Lambda} \left\langle \psi^- \middle| \frac{\partial \psi^+}{\partial q_i} \right\rangle$$

Elektronske bazne funkcije - dijabatizacija

- Sledeća transformacija - linearne bazne funkcije

$$\psi_1 = \frac{1}{\sqrt{2}}(\eta_1 + i\eta_2) = \frac{1}{\sqrt{2}} e^{i\Lambda\tau}(\psi^+ + i\psi^-)$$
$$\psi_2 = \frac{1}{\sqrt{2}}(\eta_1 - i\eta_2) = \frac{1}{\sqrt{2}} e^{-i\Lambda\tau}(\psi^+ - i\psi^-)$$

- U linearnoj bazi matrični elementi elektronskog operatora oblika

$$E_{11}^{lin} = \langle\psi_1|\hat{H}_e|\psi_1\rangle = \frac{V^+ + V^-}{2} = \langle\psi_2|\hat{H}_e|\psi_2\rangle = E_{22}^{lin}$$
$$E_{12}^{lim} = \langle\psi_1|\hat{H}_e|\psi_2\rangle = \frac{V^+ - V^-}{2} e^{-2i\tau}$$
$$E_{21}^{lim} = \langle\psi_2|\hat{H}_e|\psi_1\rangle = \frac{V^+ - V^-}{2} e^{2i\tau}$$

- Kompleksni matrični elementi "linearnih" el. funkcija po koordinatama jezgara

Mala odstupanja od linearnosti

- Asimptotske forme adijabatskih el. talasnih funkcija

$$\psi_0^+ = \lim_{\rho_1 \to 0,\ \rho_2 \to 0} \psi^+ = \xi \frac{1}{\sqrt{\pi}} \cos[\Lambda(\theta - \tau)]$$

$$\psi_0^- = \lim_{\rho_1 \to 0,\ \rho_2 \to 0} \psi^- = \xi \frac{1}{\sqrt{\pi}} \sin[\Lambda(\theta - \tau)]$$

- Dijabatske elektronske funkcije

$$\eta_0^1 = \lim_{\rho_1 \to 0,\ \rho_2 \to 0} \eta_1 = \xi \frac{1}{\sqrt{\pi}} \cos(\Lambda\theta)$$

$$\eta_0^2 = \lim_{\rho_1 \to 0,\ \rho_2 \to 0} \eta_2 = \xi \frac{1}{\sqrt{\pi}} \sin(\Lambda\theta)$$

- "Linearne" elektronske funkcije

$$\psi_0^1 = \lim_{\rho_1 \to 0,\ \rho_2 \to 0} \psi_1 = \xi \frac{1}{\sqrt{2\pi}} e^{i\Lambda\theta}$$

$$\psi_0^2 = \lim_{\rho_1 \to 0,\ \rho_2 \to 0} \psi_2 = \xi \frac{1}{\sqrt{2\pi}} e^{-i\Lambda\theta}$$

Ugao τ

- U okviru harm. aproksimacije i za Π elektronsko stanje, sledi

$$\tau = -\frac{1}{2}\arctan\left\{\frac{\epsilon_1\rho_1^2\sin(2\phi_1)+\epsilon_1\rho_2^2\sin(2\phi_2)+2\epsilon_{12}\rho_1\rho_2\sin(\phi_1+\phi_2)}{\epsilon_1\rho_1^2\cos(2\phi_1)+\epsilon_1\rho_2^2\cos(2\phi_2)+2\epsilon_{12}\rho_1\rho_2\cos(\phi_1+\phi_2)}\right\}$$

- Izvodi

$$\frac{\partial\tau}{\partial\rho_2} = \frac{\rho_1\sin(\phi_2-\phi_1)\left[\epsilon_1\epsilon_{12}\rho_1^2+\epsilon_2\epsilon_{12}\rho_2^2+2\epsilon_1\epsilon_2\rho_1\rho_2\cos(\phi_2-\phi_1)\right]}{(V^+-V^-)^2}$$

$$\frac{\partial\tau}{\partial\phi_2} = \frac{\epsilon_2^2\rho_2^4+2\epsilon_{12}^2\rho_1^2\rho_2^2+\epsilon_{12}\rho_1\rho_2(\epsilon_1\rho_1^2+\epsilon_2\rho_2^2)\cos(\phi_2-\phi_1)+\epsilon_1\epsilon_2\rho_1^2\rho_2^2\cos 2(\phi_2-\phi_1)}{(V^+-V^-)^2}$$

S-O matrični elementi

- Matrični elementi operatora S-O sprege u "linearnoj" asimptotskoj bazi

$$\left\langle \psi_0^1 \middle| \hat{H}_{SO} \middle| \psi_0^1 \right\rangle = \Lambda\Sigma A_{SO}$$
$$\left\langle \psi_0^2 \middle| \hat{H}_{SO} \middle| \psi_0^2 \right\rangle = -\Lambda\Sigma A_{SO}$$
$$\left\langle \psi_0^1 \middle| \hat{H}_{SO} \middle| \psi_0^2 \right\rangle = \left\langle \psi_0^2 \middle| \hat{H}_{SO} \middle| \psi_0^1 \right\rangle = 0$$

- Elektronski matrični elementi su operatori koji treba da deluju na vibracione bazne funkcije
- Svojstvene funkcije 2D harmonijskog oscilatora

Kvantni brojevi

$$\hat{N}_z = \hat{R}_z + \hat{L}_z \quad \Rightarrow \quad K = l \pm \Lambda$$

$$\hat{J}_z = \hat{N}_z + \hat{S}_z \quad \Rightarrow \quad P = K + \Sigma$$

$$l = v, v-2, \ldots, 1 \quad \text{ili} \quad 0$$

Kompjutacioni detalji

- Adijabatske energije $\Rightarrow$ FV-SA-CASSCF(9,10)/cc-pVQZ
- Dužine veza konstantne

  C–H $\equiv r = 2{,}04$ bohr $= 1{,}0795$ Å
  C–C $\equiv R = 2{,}37$ bohr $= 1{,}2542$ Å

- MOLPRO 2012.1 [Werner *et al.* 2012]

Parametri koji ulaze u model

TABLE I. Adiabatic electronic energies (V^+, V^-) for the components of the $X^2\Pi_u$ electronic state of $C_2H_2^+$ derived from CASSCF calculations at the C–H and C–C bond lengths kept fixed at 2.04 and 2.37 bohrs, respectively. $\bar{V} = (V^+ + V^-)/2, \Delta V = (V^+ - V^-), V_e$ is the energy at linear (equilibrium) geometry (computed in the D_{2h} point group).

ρ_1 (deg)	ϕ_1 (deg)	ρ_2 (deg)	ϕ_2 (deg)	V^+ (hartree)	V^- (hartree)	$\bar{V} - V_e$ (hartree)	ΔV (hartree)
0	0	0	0	−76.621 734 28	−76.621 734 28	0.0	0.0
10	0	9.99	0.01	−76.619 367 82	−76.619 272 02	0.002 414 36	−0.000 095 80
10	0	9.99	179.99	−76.619 846 90	−76.620 680 52	0.001 470 57	0.000 833 62

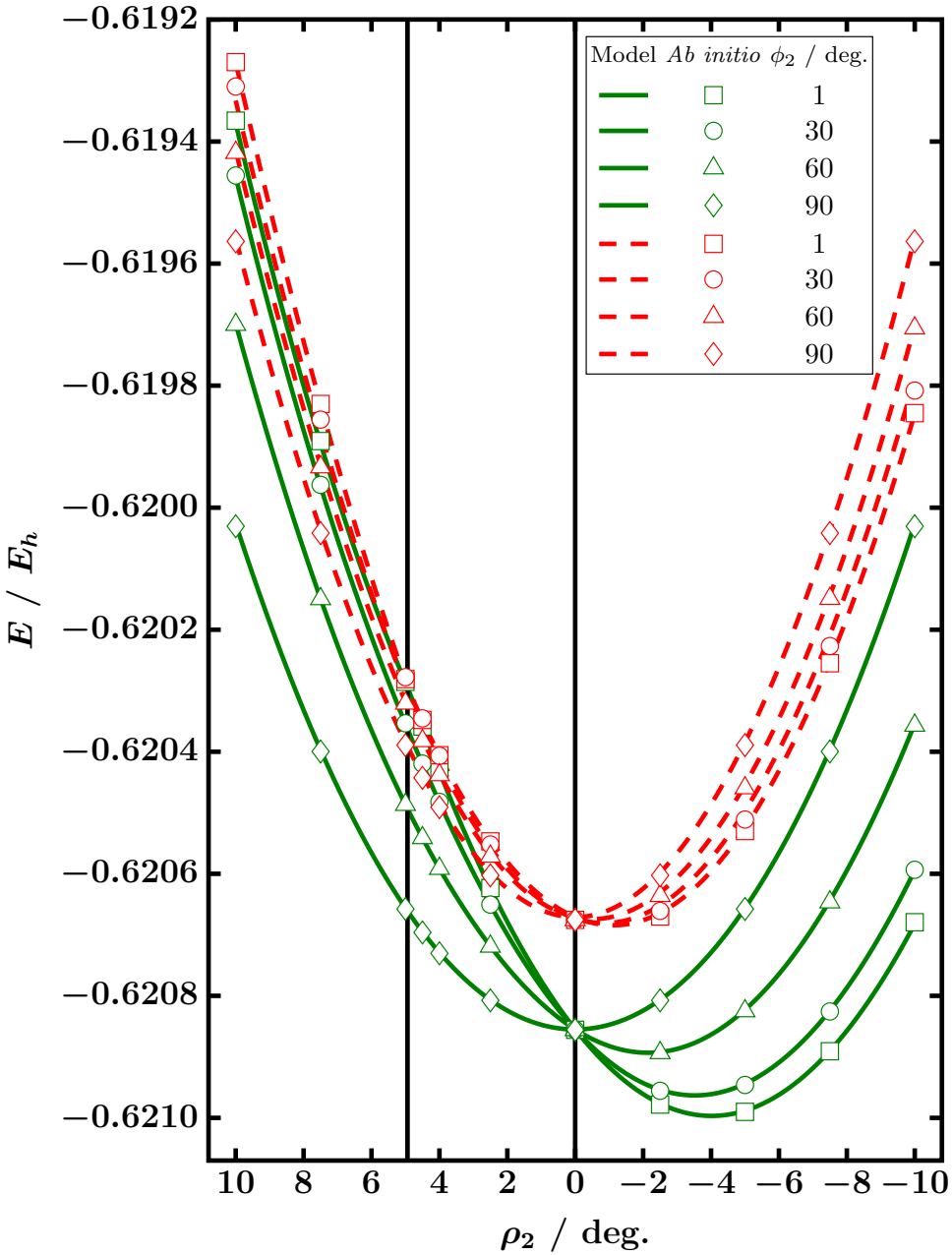
TABLE II. Molecular parameters for the $X^2\Pi_u$ electronic state of $C_2H_2^+$ derived from CASSCF calculations. All quantities are given in atomic units (hartree/rad^2) except of u_1, u_2, which are dimensionless.

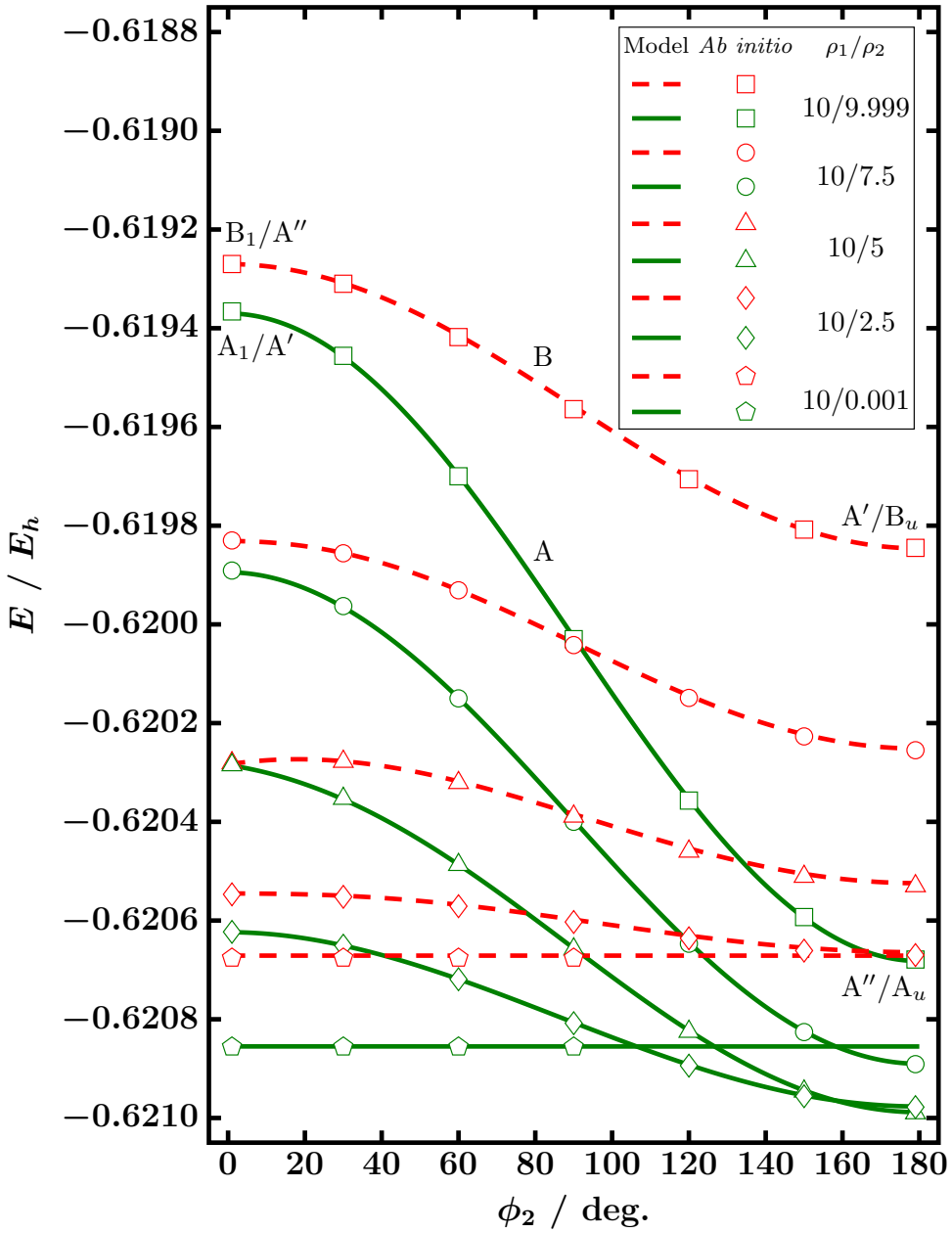
$k_T = 0.096\,542$	$k_C = 0.158\,508$	$\varepsilon_T = 0.027\,366$	$\varepsilon_C = -0.003\,145$
$k_1 = k_2 = 0.063\,763$	$k_{12} = 0.015\,492$	$\varepsilon_1 = \varepsilon_2 = 0.006\,055$	$\varepsilon_{12} = -0.007\,628$
$u_1 = 2.025\,715$	$u_2 = 0.493\,653$		

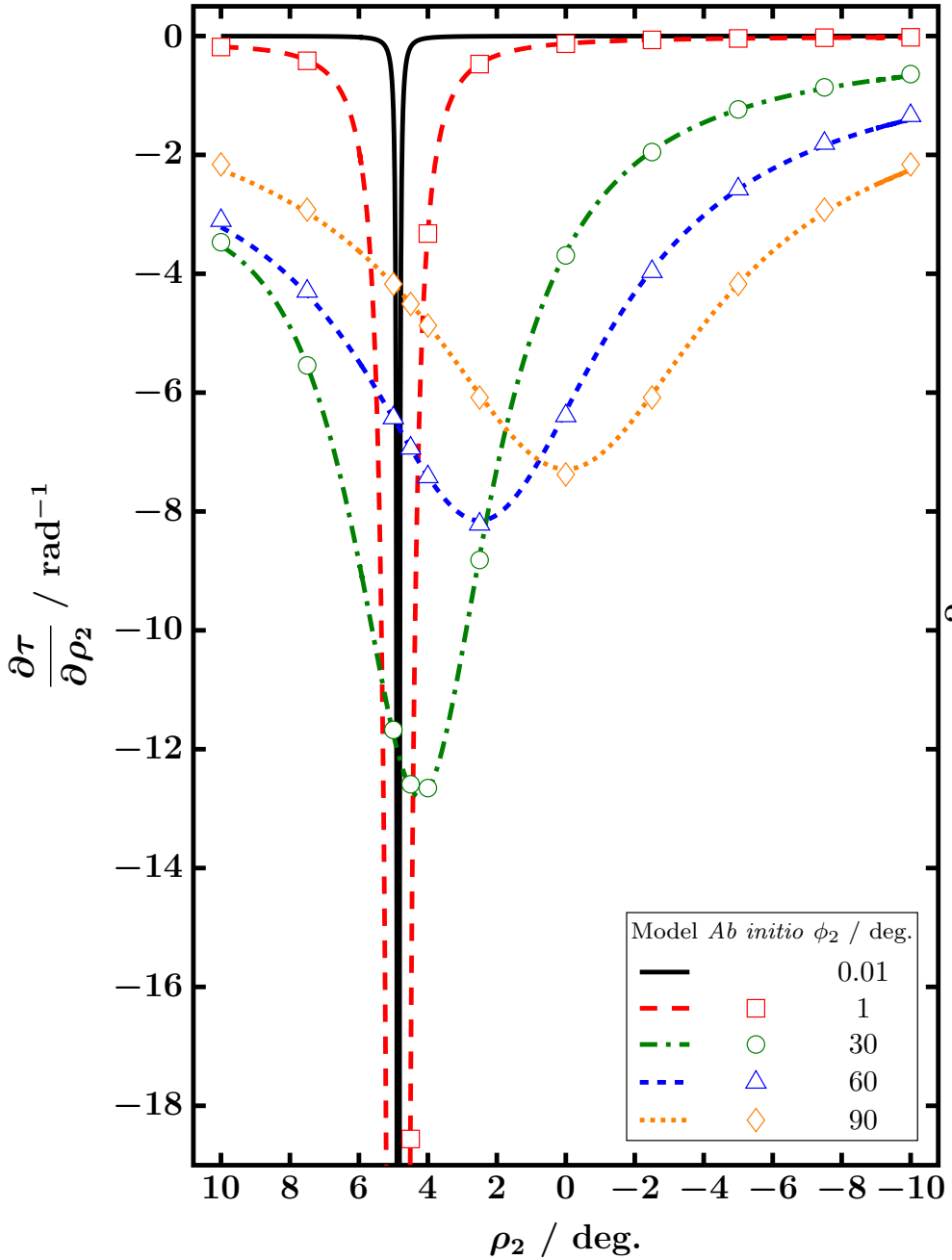
- Presecanja pri planarnim geometrijama [Perić 2006]

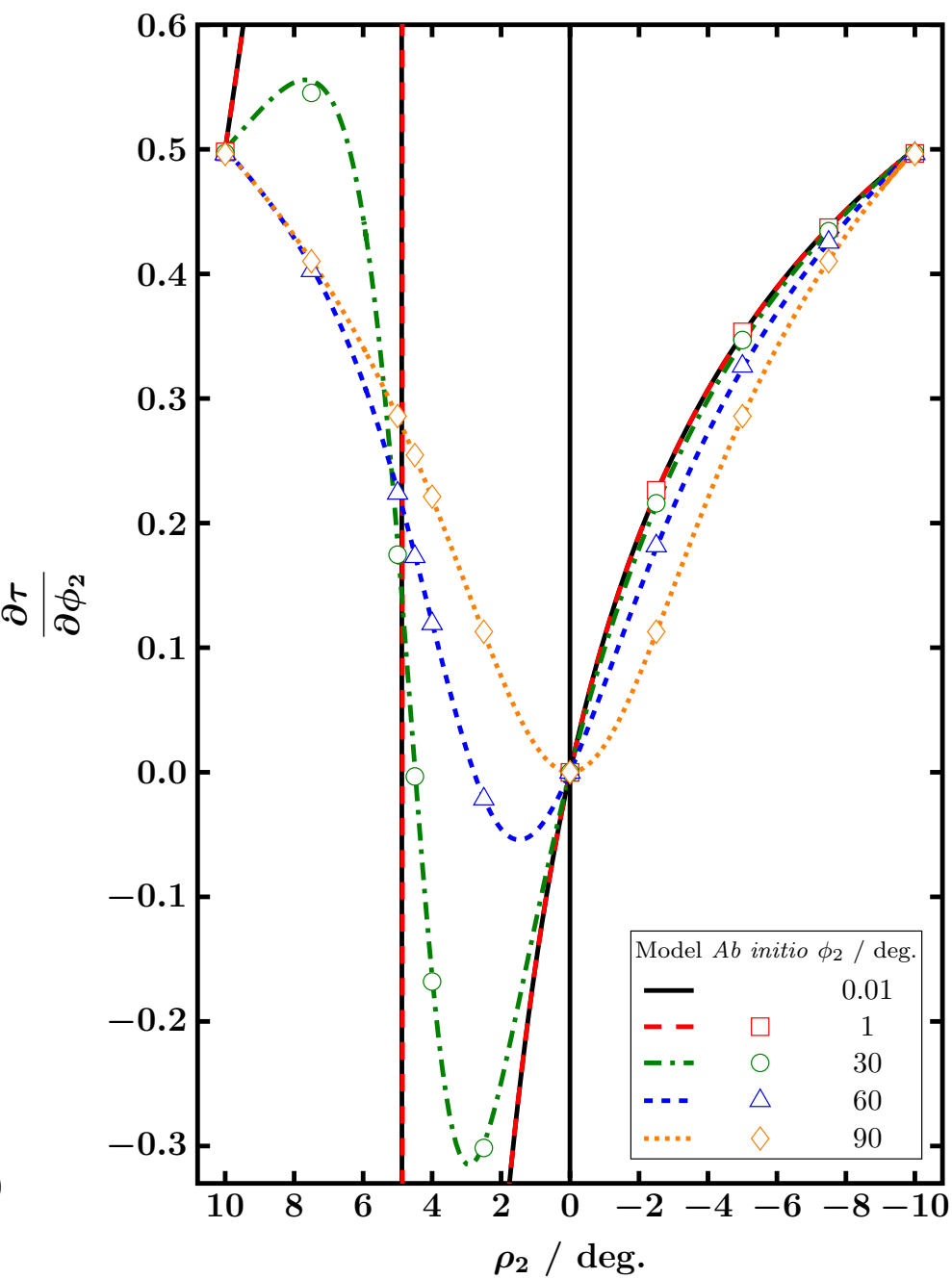
$$\rho_2 = u\rho_1, \qquad u = \frac{-\epsilon_{12} \pm \sqrt{\epsilon_{12}^2 - \epsilon_1\epsilon_2}}{\epsilon_2}$$

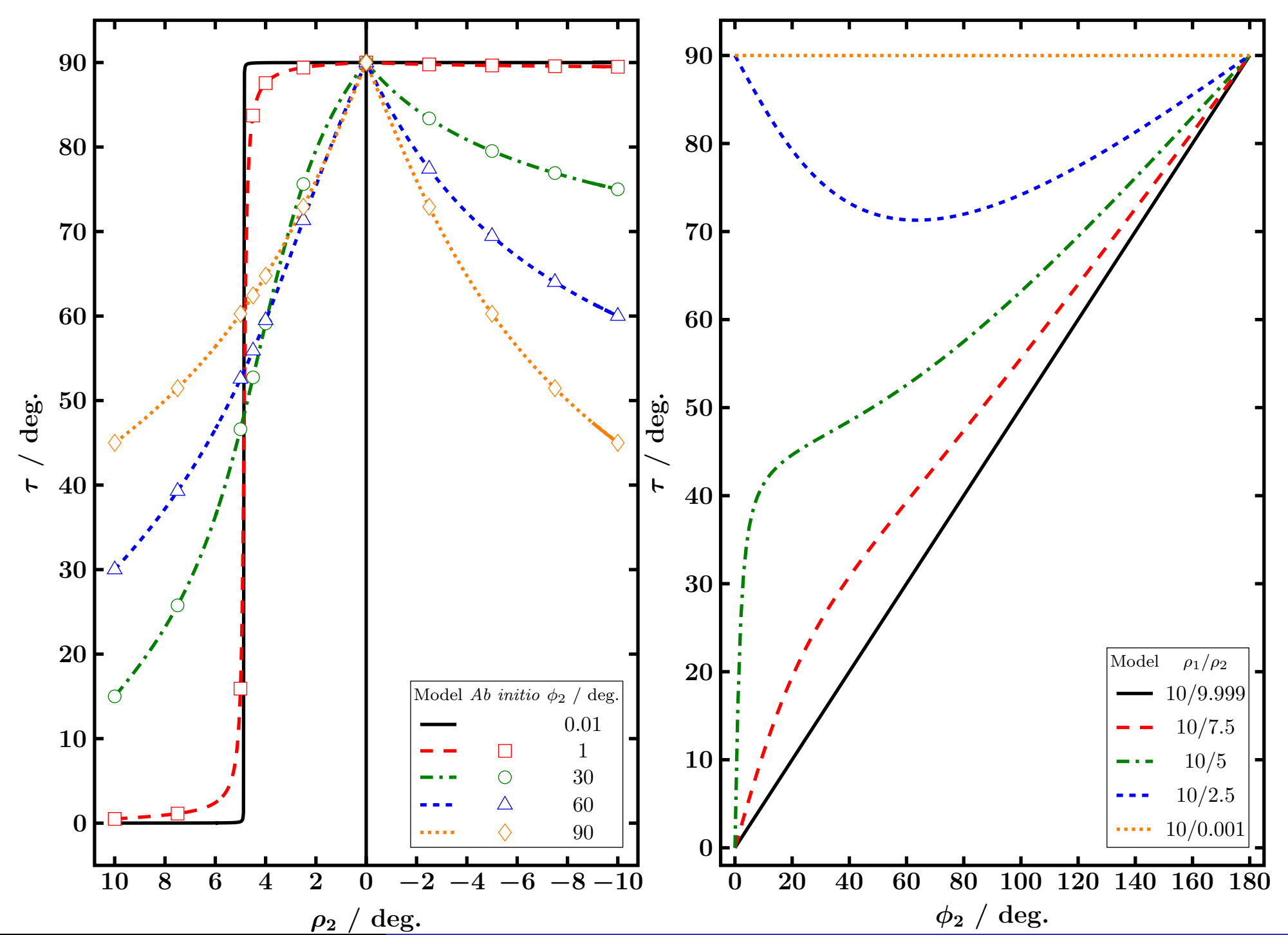
- Ukupno 5 *ab initio* računa!

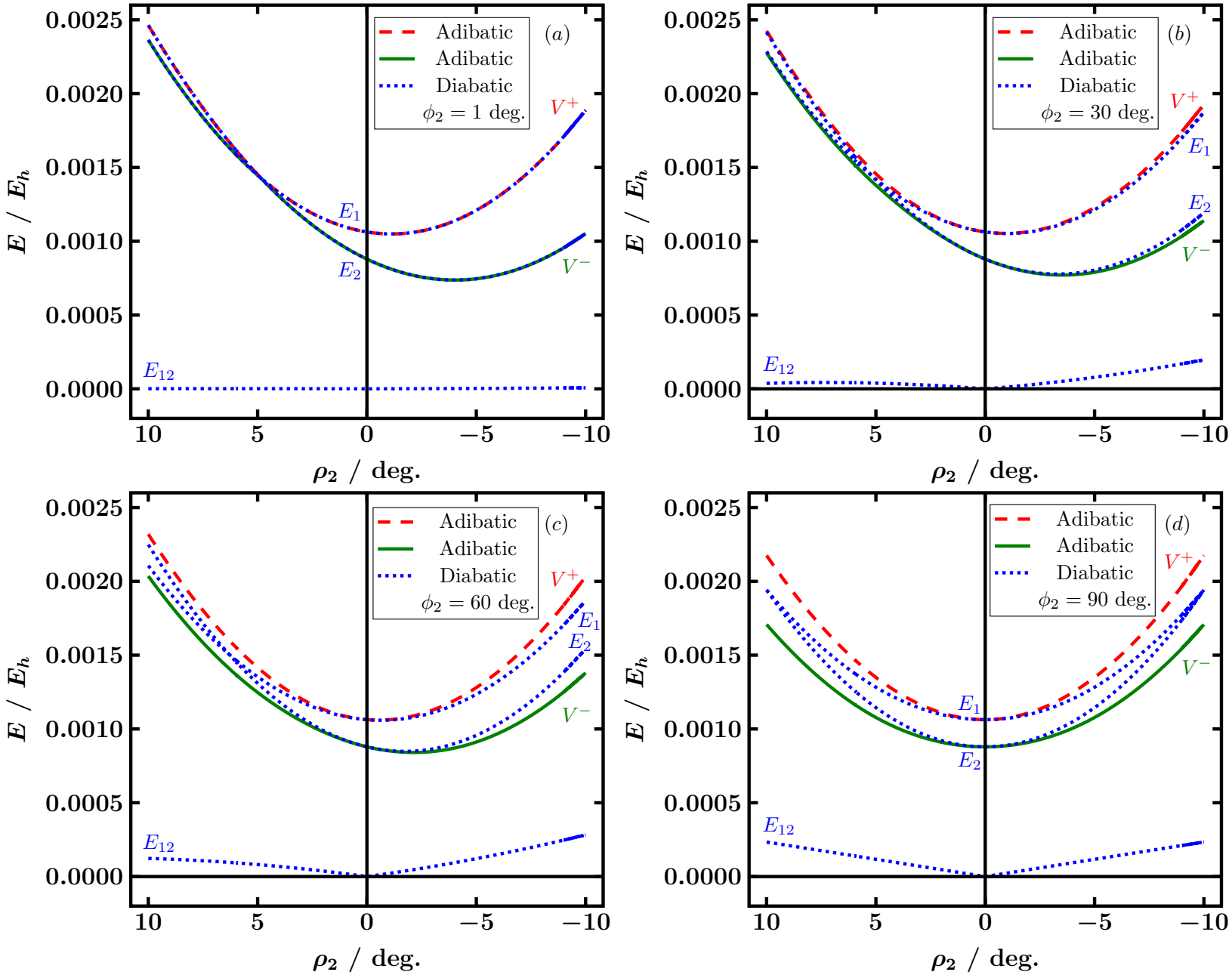

Model Ab initio ϕ_2 / deg.
1
30
60
90
1
30
60
90
E / E_h
ρ_2 / deg.


Model Ab initio ρ_1/ρ_2
10/9.999
10/7.5
10/5
10/2.5
10/0.001
B_1/A''
A_1/A'
B
A
A'/B_u
A''/A_u
E / E_h
ϕ_2 / deg.


$\frac{\partial\tau}{\partial\rho_2}$ / rad^{-1}
0
−2
−4
−6
−8
−10
−12
−14
−16
−18
10 8 6 4 2 0 −2 −4 −6 −8 −10
ρ_2 / deg.
Model *Ab initio* ϕ_2 / deg.
0.01
1
30
60
90


$\frac{\partial\tau}{\partial\phi_2}$
0.6
0.5
0.4
0.3
0.2
0.1
0.0
−0.1
−0.2
−0.3
10 8 6 4 2 0 −2 −4 −6 −8 −10
ρ_2 / deg.
Model *Ab initio* ϕ_2 / deg.
0.01
1
30
60
90


τ / deg.
ρ2 / deg.
Model Ab initio ϕ2 / deg.
0.01
1
30
60
90
τ / deg.
ϕ2 / deg.
Model ρ1/ρ2
10/9.999
10/7.5
10/5
10/2.5
10/0.001


Adibatic
Adibatic
Diabatic
(a)
$\phi_2 = 1$ deg.
(b)
$\phi_2 = 30$ deg.
(c)
$\phi_2 = 60$ deg.
(d)
$\phi_2 = 90$ deg.
V^+
V^-
E_1
E_2
E_{12}
E / E_h
ρ_2 / deg.
0.0025
0.0020
0.0015
0.0010
0.0005
0.0000
10
5
0
−5
−10

Vibronski spektar $C_2H_2^+$

TABLE III. Low-lying vibronic levels (in cm^{-1}) of the $X^2\Pi_u$ electronic state of $C_2H_2^+$. The set of parameters used in calculations of entries from columns Pert. and Var. is $\omega_T \equiv \omega_4 = 692.32$ cm^{-1}, $\omega_C \equiv \omega_5 = 704.05$ cm^{-1}, $\varepsilon_4 = 0.2923$, $\varepsilon_5 = 0.0219$ (the parameters $\varepsilon_4, \varepsilon_5$ are dimensionless), and $A_{SO} = -31.42$ cm^{-1}. The numbers in parentheses are differences between the values from the corresponding column and those from column Expt.

v_T, v_C	State	Expt.[a]	Pert.[b]	Var.[b]
0, 0	$\Pi_{3/2u}$	0	0(0)	0(0)
	$\Pi_{1/2u}$	29.8	31.4(+2)	30.7(+1)
1, 0	Σ_u^-	499.5	505.1(+6)	502.7(+3)
	Σ_u^-	501.7	505.1(+3)	502.7(+1)
	$\Delta_{5/2u}$	672.9	662.7(−10)	662.3(−10)
	$\Delta_{3/2u}$	701.4	694.2(−7)	691.6(−10)
	Σ_u^+	909.9	911.0(+1)	913.0(+3)
	Σ_u^+	912.1	911.0(−1)	913.0(+1)
0, 1	Σ_g^+	694.9	697.7(+3)	697.8(+3)
	Σ_g^+	696.5	697.7(+1)	697.8(+1)
	$\Delta_{5/2g}$	713.4	703.9(−9)	703.9(−9)
	$\Delta_{3/2g}$	743.0	735.3(−8)	734.6(−8)
	Σ_g^-	738.2	741.8(+4)	741.0(+3)
	Σ_g^-	739.8	741.8(+2)	741.0(+1)
2, 0	$\Pi_{3/2u}$	1108.3	1105.1(−3)	1102.2(−6)
	$\Pi_{1/2u}$	1110.0	1107.6(−2)	1104.5(−5)
	$\Phi_{7/2u}$	1316.0	1310.7(−5)	1310.4(−6)
	$\Phi_{5/2u}$	1342.7	1342.1(−1)	1337.9(−5)
	$\Pi_{1/2u}$	1683.5	1678.4(−5)	1679.3(−4)
	$\Pi_{3/2u}$	1685.3	1680.8(−4)	1682.6(−3)
1, 1	$\Pi_{3/2g}$	1210.2	1208.3(−2)	1206.0(−4)
	$\Pi_{1/2g}$	1209.9	1208.4(−1)	1206.0(−4)
	$\Phi_{7/2g}$	1370.4	1366.6(−4)	1366.2(−4)
	$\Phi_{5/2g}$	1398.9	1398.0(−1)	1395.5(−3)
	$\Pi_{3/2g}$	1373.1	1367.0(−6)	1366.5(−7)
	$\Pi_{1/2g}$	1401.6	1398.4(−3)	1395.8(−5)
	$\Pi_{1/2g}$	1620.6	1615.5(−5)	1617.4(−4)
	$\Pi_{3/2g}$	1620.4	1615.5(−5)	1617.4(−3)
0, 2	$\Pi_{3/2u}$	1404.8	1396.8(−8)	1396.9(−8)
	$\Pi_{1/2u}$	1399.9	1397.0(−3)	1397.0(−3)
	$\Phi_{7/2u}$	1410.7	1407.7(−3)	1407.7(−3)
	$\Phi_{5/2u}$	1440.5	1439.1(−1)	1438.4(−2)
	$\Pi_{1/2u}$	1451.2	1450.6(−1)	1449.8(−1)
	$\Pi_{3/2u}$	1449.3	1450.7(+1)	1449.9(+1)

Sadržaj izlaganja

Model za molekule sa proizvoljnim brojem jezgara

$$\hat{H} = \hat{H}_e + \hat{T}_n + \hat{H}_{SO}$$
$$= \hat{H}_e - \frac{1}{2}\sum_{i=1}^{S-2}\left(\frac{\partial^2}{\partial q_i^2} + \frac{1}{q_i}\frac{\partial}{\partial q_i} + \frac{1}{q_i^2}\frac{\partial^2}{\partial \phi_i^2}\right)\omega_i + A_{SO}\hat{L}_z\hat{S}_z$$

$$\tau = -\frac{1}{2}\arctan\left\{\frac{\sum_{i=1}^{S-2}\sum_{j=1}^{S-2}\varepsilon_{ij}\sqrt{\omega_i\omega_j}q_iq_j\sin\left(\phi_i+\phi_j\right)}{\sum_{i=1}^{S-2}\sum_{j=1}^{S-2}\varepsilon_{ij}\sqrt{\omega_i\omega_j}q_iq_j\sin\left(\phi_i+\phi_j\right)}\right\}$$

- Izbegnuta presecanja i pri planarnim i pri neplanarnim geometrijama
- Model testiran na primeru $X\ ^2\Pi_u$ stanja molekula C_5^-

Vibronski spektar C_5^-

Table 1
Low-lying $K = 0$ and $K = 2$ vibronic energy levels (in cm^{-1}) in the $X\ ^2\Pi_u$ electronic state of C_5^-.

v_T, v_{C1}, v_{C2}	$E^{(0)}$	$K = 0$				$K = 2$			
		Pert.[a]		Var.[b]		Pert.[a]		Var.[b]	
		$\Sigma = -1/2$	$\Sigma = 1/2$	$\Sigma = -1/2$	$\Sigma = 1/2$	$\Sigma = -1/2$	$\Sigma = 1/2$	$\Sigma = -1/2$	$\Sigma = 1/2$
0,0,1	1171	1098	1098	1091	1091	1112	1134	1108	1127
		1123	1123	1117	1117				
1,0,0	1347	1219	1219	1218	1218	1290	1312	1288	1307
		1409	1409	1402	1402				
0,0,3	1487	1369	1369	1358	1358	1380	1360	1364	1356
		1399	1399	1396	1396	1389	1408	1392	1402
0,1,0	1534	1373	1373	1385	1385	1452	1474	1446	1464
		1684	1684	1677	1677				
1,0,2	1663			1493	1493	1495	1491	1493	1492
				1547	1547	1564	1586	1559	1575
				1561	1561	1682	1686	1659	1664
				1663	1663				
0,0,5	1803	1639	1639	1632	1632	1647	1632	1634	1630
		1677	1677	1677	1677	1669	1684	1674	1681
0,1,2	1850			1660	1660	1690	1687	1681	1692
				1670	1670	1684	1706	1704	1705
				1704	1704	1998	2002	2039	2037
			2051	2051					
1,0,4	1979		1770	1770			1770	1770	
				1820	1820			1829	1815
				1843	1843			1839	1815
				1939	1939			1929	1935
3,0,0	2015	1786	1786	1785	1785	1809	1813	1809	1811
		2165	2165	2147	2147	2141	2138	2132	2138
1,1,1	2026	1820[c]		1813	1813	1844[d]	1844[d]	1821	1828
		1820[c]		1919	1919	2015[d]	2037[d]	1870	1882
		1926[c]		1930	1930	2015[d]	2037[d]	1945	1954
		1926[c]		2064	2064	2208[d]	2208[d]	2175	2179
		2182[c]		2173	2173				
		2182[c]		2194	2194				

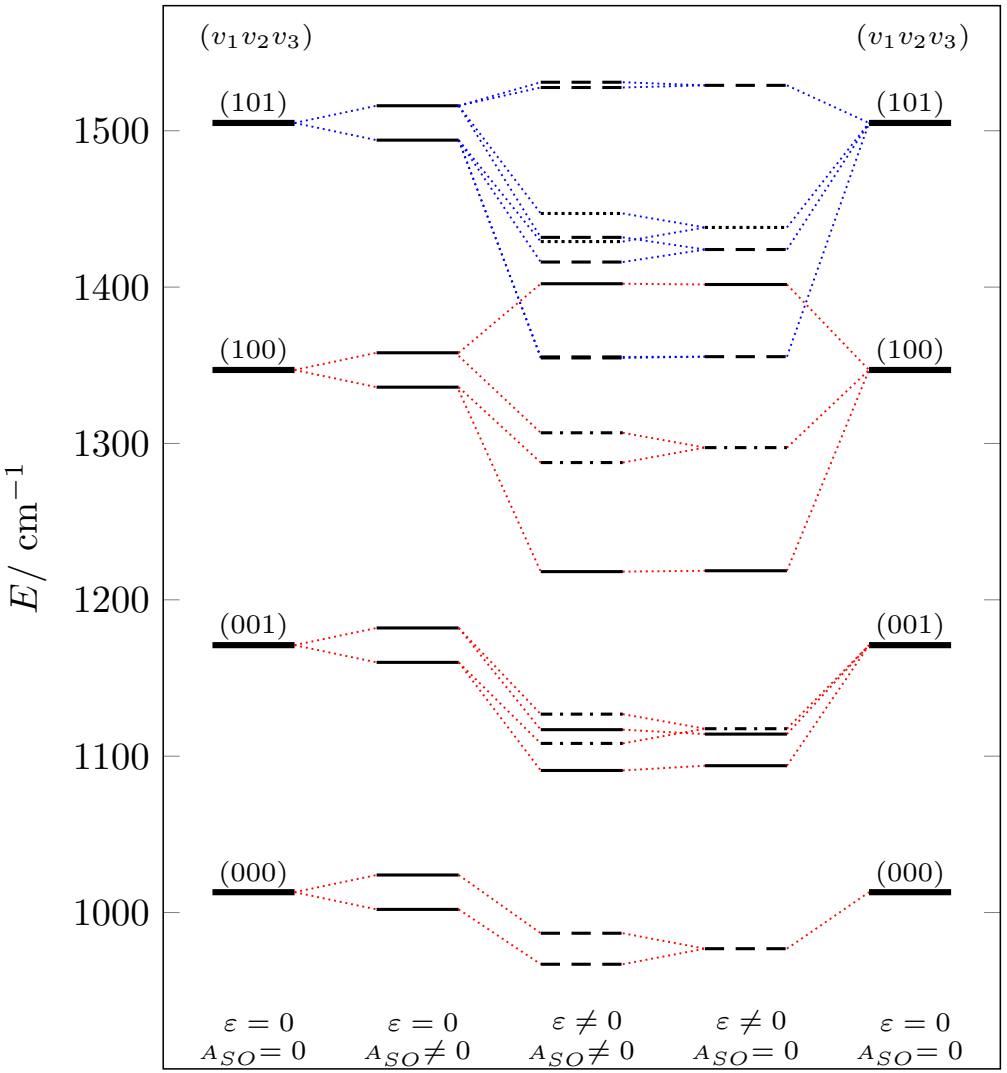
Vibronski spektar C_5^-

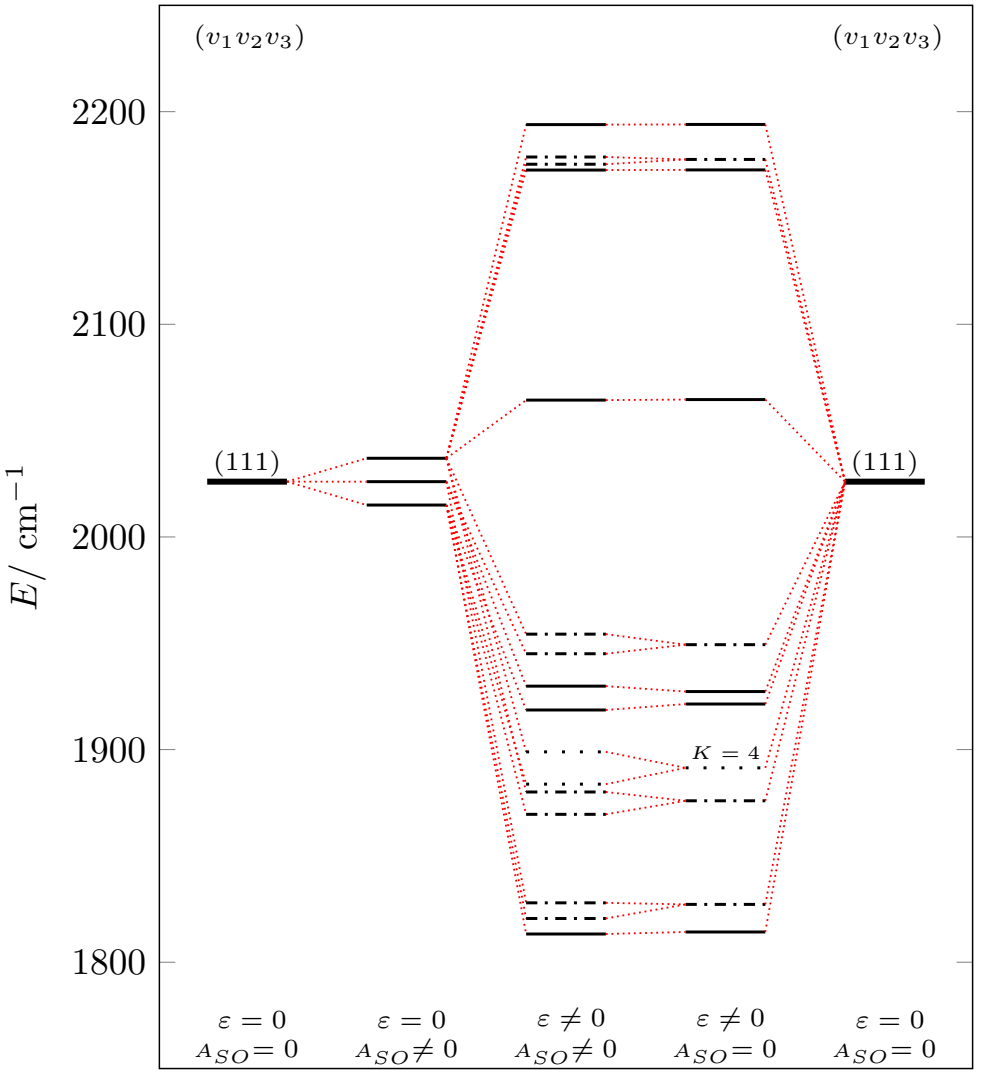
Table 2
Low-lying $K = 1$ and $K = 3$ vibronic energy levels in the $X\ ^2\Pi_u$ electronic state of C_5^-.

v_T, v_{C1}, v_{C2}	$E^{(0)}$	$K = 1$				$K = 3$			
		Pert.[a]		Var.[b]		Pert.[a]		Var.[b]	
		$\Sigma = -1/2$	$\Sigma = 1/2$	$\Sigma = -1/2$	$\Sigma = 1/2$	$\Sigma = -1/2$	$\Sigma = 1/2$	$\Sigma = -1/2$	$\Sigma = 1/2$
0,0,0	1013	969	991	967	987	-	-	-	-
0,0,2	1329	1240 1255	1229 1266	1228 1253	1222 1260	1255	1277	1250	1267
1,0,1	1505	1357 1420 1545	1354 1442 1548	1355 1416 1528	1355 1432 1531	1433	1455	1429	1447
0,0,4	1645	1509 1534	1500 1542	1496 1534	1494 1537	1520 1523	1492 1550	1499 1532	1492 1544
2,0,0	1681	1510 1780	1511 1778	1509 1767	1510 1765	1604	1626	1605	1624
0,1,1	1692	1532 1555 1840	1529 1577 1844	1542 1554 1875	1544 1564 1880	1581	1603	1569	1585
1,0,3	1821			1631 1692 1695 1794	1631 1682 1707 1798	1633 1707 1816	1625 1729 1824	1632 1703 1792	1631 1718 1798
1,1,0	1868	1665 1800 2033	1668 1822 2029	1674 1803 2017		1773	1795	1767	1768
0,0,6	1961	1777 1813	1771 1819	1771 1817		1786 1804	1765 1825	1773 1818	1784 1828
0,1,3	2008			1791 1793 1794 1803		1813 1851 2153	1835 1841 2163	1813 1855 2198	1823 1854 2199
0,2,0	2055	1828 2272	1832 2268	1875 2263	1880 2267	1924	1946	1917	1933

(a) [Perić *et al.* 2008]
(b) [Mitić *et al.* 2016]

Vibronski spektar C_5^-





Zaključak

- Born-Openhajmerova aproksimacija
- *Ab initio* metode
- Mali molekuli
- Rener-Telerov efekat
- Model za tretiranje vibronske sprege kod četvoroatomskih molekula
- Ključan korak - dijabatizacija
- Kombinacija neke vrste J-T efekta i R-T efekta
- Model za molekule sa proizvoljnim brojem jezgara

Radovi

M. Perić, S. Jerosimić, M. Mitić, M. Milovanović, R. Ranković, "Underlying theory of a model for the Renner–Teller effect in tetra-atomic molecules: $X\ ^2\Pi_u$ electronic state of $C_2H_2^+$", *The Journal of Chemical Physics*, **142**, 174306 (2015), doi: 10.1063/1.4919285.

M. Mitić, R. Ranković, M. Milovanović, S. Jerosimić, M. Perić, "Underlying theory of a model for the Renner-Teller effect in any-atomic linear molecules on example of the $X\ ^2\Pi_u$ electronic state of C_5^-", *Chemical Physics*, **464**, 55 (2016), doi: 10.1016/j.chemphys.2015.11.002.

Hvala na pažnji!