

MULTI KONFIGURACIJSKI OPIS ATOMA

①

Opis lastnih stanj in energij \hat{H}_{NR} izboljšamo, če presčemo omejitve, da so elektroni v atomu gibljejo neodvisno, naš v povprečnem efektivnem iregelnem simetričnem potencialu. Upoštevati moramo KORELACIJE MED ELEKTRONI.

POGOJNA VERJETNOSTNA GOSTOTA, da najdemo elektron na danem položaju ni več neodvisna od položaja drugih elektronov.

$$P(\vec{r}_1, \dots, \vec{r}_N) = |\Psi(\vec{r}_1, \dots, \vec{r}_N)|^2 \quad \int P(\vec{r}_1, \dots, \vec{r}_N) d\vec{r}_1 \dots d\vec{r}_N = 1$$

VERJETNOSTNA GOSTOTA, DA SO e^- NA POZICIJAH $\vec{r}_1, \dots, \vec{r}_N$.

$$P(\vec{r}_1) = \int P(\vec{r}_1, \dots, \vec{r}_N) d\vec{r}_2 \dots d\vec{r}_N \leftarrow (\text{brezpogojna}) \text{ VERJETNOSTNA GOSTOTA, DA SE } e^- \text{ NAHAJA NA POZICIJI } \vec{r}_1, \text{ NE GLEDE NA TO, KJE SO DRUGI } e^-.$$

$$P(\vec{r}_1 | \vec{R}_2, \vec{R}_3, \dots, \vec{R}_N) = \frac{P(\vec{r}_1, \vec{R}_2, \dots, \vec{R}_N)}{\int P(\vec{r}_1, \vec{R}_2, \dots, \vec{R}_N) d\vec{r}_1} \leftarrow \text{POGOJNA VERJETNOSTNA GOSTOTA, DA SE } e^- \text{ NAHAJA NA POZICIJI } \vec{r}_1, \text{ \u010cE SO DRUGI } e^- \text{ NA POZICIJAH } \vec{R}_2, \dots, \vec{R}_N.$$

ELEKTRON NI KORELIRAN Z DRUGIMI e^- , \u010cE VELJA

$$P(\vec{r}_1 | \vec{R}_2, \dots, \vec{R}_N) = P(\vec{r}_1)$$

- Konfiguracija:

$$\Psi(\vec{r}_1, \dots, \vec{r}_N) = \psi_a(\vec{r}_1) \psi_b(\vec{r}_2) \dots \psi_m(\vec{r}_N) \equiv \psi_a(\vec{r}_1) \Theta(\vec{r}_2, \dots, \vec{r}_N)$$

$$P(\vec{r}_1 | \vec{R}_2, \dots, \vec{R}_N) = \frac{\psi_a^2(\vec{r}_1) \Theta^2(\vec{R}_2, \dots, \vec{R}_N)}{\Theta^2(\vec{R}_2, \dots, \vec{R}_N)} = \psi_a^2(\vec{r}_1) = P(\vec{r}_1) \quad \text{NI KORELACIJE}$$

- (dve) konfiguraciji z eno zamenjavo:

$$\Psi = c_1 \psi_a(\vec{r}_1) \Theta(\vec{r}_2, \dots, \vec{r}_N) + c_2 \psi_b(\vec{r}_1) \Theta(\vec{r}_2, \dots, \vec{r}_N)$$

NI KORELACIJE

$$P(\vec{r}_1 | \vec{R}_2, \dots, \vec{R}_N) = \frac{[c_1^2 \psi_a^2(\vec{r}_1) + 2c_1 c_2 \psi_a(\vec{r}_1) \psi_b(\vec{r}_1) + c_2^2 \psi_b^2(\vec{r}_1)] \Theta^2(\vec{R}_2, \dots, \vec{R}_N)}{(c_1^2 + c_2^2) \Theta^2(\vec{R}_2, \dots, \vec{R}_N)} = P(\vec{r}_1)$$

- (dve) konfiguraciji z drzajno zamenjavo:

$$\Psi = c_1 \psi_a(\vec{r}_1) \psi_{a'}(\vec{r}_2) \Theta(\vec{r}_3, \dots, \vec{r}_N) + c_2 \psi_b(\vec{r}_1) \psi_{b'}(\vec{r}_2) \Theta(\vec{r}_3, \dots, \vec{r}_N)$$

$$P(\vec{r}_1, \vec{r}_2 | \vec{R}_3, \dots, \vec{R}_N) = \frac{c_1^2 \psi_a^2(\vec{r}_1) \psi_{a'}^2(\vec{r}_2) + 2c_1 c_2 \psi_a(\vec{r}_1) \psi_b(\vec{r}_1) \psi_{a'}(\vec{r}_2) \psi_{b'}(\vec{r}_2) + c_2^2 \psi_b^2(\vec{r}_1) \psi_{b'}^2(\vec{r}_2)}{c_1^2 \psi_{a'}^2(\vec{R}_2) + c_2^2 \psi_{b'}^2(\vec{R}_2)} \neq P(\vec{r}_1)$$

$$P(\vec{r}_1) = c_1^2 \psi_a^2(\vec{r}_1) + c_2^2 \psi_b^2(\vec{r}_1)$$

KORELACIJA JE

DODAJANJE KONFIGURACIJ Z DVOSNO ZAMENJAVO UVEDE KORELACIJE V VALOVNO FUNKCIJO. ENOELEKTROMSKI DEL NE SME BITI SEPARABILEN:

$$\Psi(\vec{r}_1, \dots, \vec{r}_N) \neq \Psi(\vec{r}_i) \Phi(\vec{r}_1, \dots, \vec{r}_{i-1}, \vec{r}_{i+1}, \dots, \vec{r}_N)$$

DELNO VPELJE KORELACIJO ŽE OPIS VALOVNE FUNKCIJE S SLATERJEVO DETERMINANTO, KER JE TAM VERJETNOST, DA SE e^- NAMAJA NA TOČNO ISTEM MESTU KOT NEK DRUGI e^- Z ISTO PROJEKCIJO SPINA ENAKA 0. 3
 SISTEMATIČNO VPELJEMO KORELACIJE MED e^- TAKO DA DOVOLIMO MULTIKONFIGURACIJSKI OPIS ATOMSKIM STANJ.

$$E = E^{HF} + E^c$$

\uparrow PRAVA ENERGIJA AT. STANJA (TOČNA REŠITEV \hat{H}_{NR} !)
 \uparrow ENERGIJA V PRIBLIŽKU HARTREE-FOCK
 \leftarrow KORELACIJSKA ENERGIJA

Recimo He ($1s^2$):

$$E^{HF} = -2'861 \text{ a.u.}$$

$$E = -2'9037234... \text{ a.u.}$$

MCHF – MULTICONFIGURATION HARTREE-FOCK

$$\Psi_{MCHF}(\chi LS) = \sum_i c_i \phi(\chi_i LS) \quad \sum_i c_i^2 = 1$$

NEZNANKE SO UTEŽI KONFIGURACIJ c_i TER NAČELOMA, NABOR RADIALNIH ORBITAL $p_{m_i l_i}(r)$, KI OPISUJE KONFIGURACIJE.

ČE SO RADIALNE ORBITALE PRIBITE (recimo HF račun za vsako konfigur. posebej), LAHKO IZBOLJŠAMO OPIS STANJ Z DIAGONALIZACIJO \hat{H}_{NR}

ISTI LS

$$\begin{bmatrix} (\chi_1) \\ (\chi_2) \\ \dots \end{bmatrix} \rightarrow \begin{bmatrix} 0 & \emptyset \\ \emptyset & 0 \\ & & \emptyset & 0 \end{bmatrix} \quad E(\chi LS) = \sum_{i,j} c_i c_j \langle \phi(\chi_i LS) | H | \phi(\chi_j LS) \rangle = \mathbf{c}^T \mathbf{H} \mathbf{c}$$

$$H_{ij} = \langle \phi(\chi_i LS) | H | \phi(\chi_j LS) \rangle$$

SPLOŠEN MCHF PROBLEM:

IŠČEMO VEKTOR UTEŽI $\vec{c} = \{c_i\}$ TER VEKTOR ORBITAL $\vec{P} = \{P_{m_a a}, P_{m_b b}, \dots\}$

TAKO DA BO IMEL FUNKCIONAL STACIONARNO VREDNOST (glede na majhne spremembe \vec{c} in \vec{P})

$$F(\vec{P}, \vec{c}) = E(\chi LS) + \underbrace{\sum_a \lambda_a \langle a|a \rangle + \sum_{a \neq b} \delta_{m_a m_b} \lambda_{ab} \langle a|b \rangle}_{\text{VEZI}} - \lambda \sum_i c_i^2$$

(4)

ŽAMTEVA PRIVEDE DO INTEGRO-DIFERENCIALNIH ENAČB TIPA HF, KJER SO ŠE UTEŽI c_i (VARIACIJA \vec{P}) TER DO SEKULARNE ENAČBE (VARIACIJA \vec{c})

$$H\vec{c} = \lambda\vec{c}$$

KJER JE $\lambda = E$ LASTNA ENERGIJA (ENERGIJE) TER JE MATRIKA H ODVISNA OD OBLIKE RADIALNIH ORBITAL \vec{P} .

PRIMER: OPIS OSNOVNEGA STANJA He $1s^2$ ŽELIM IZBOLJŠATI S PRIMESJO KONFIGURACIJE $2s^2$

$$\Psi_{\text{MCHF}}(1s^2, 2s^2; ^1S) = c_1 \Psi(\{1s\}^2 ^1S) + c_2 \Psi(\{2s\}^2 ^1S)$$

$$E(1s^2, 2s^2; ^1S) = \langle \Psi_{\text{MCHF}} | H | \Psi_{\text{MCHF}} \rangle = c_1^2 [2I_{1s} + F^0(1s, 1s)] + 2c_1 c_2 G^0(1s, 2s) + c_2^2 [2I_{2s} + F^0(2s, 2s)]$$

$$\delta(F(P_{1s}, P_{2s}, c_1, c_2)) = \delta(E + \lambda_{1s} \langle 1s|1s \rangle + \lambda_{2s} \langle 2s|2s \rangle + \lambda_{1s 2s} \langle 1s|2s \rangle - \lambda(c_1^2 + c_2^2)) = 0$$

$$\hat{Q}_n = -\frac{1}{2} \frac{d^2}{dr_n^2} + \frac{l_n(l_n+1)}{2r_n^2} - \frac{Z}{r_n}$$

5

$$\delta P_{1s} \rightarrow \hat{Q}_{1s} P_{1s}(r) - \frac{2}{r} [Y^0(1s1s,r) P_{1s}(r) + \overset{\text{NOVO}}{\frac{c_2}{c_1} Y^0(1s2s,r) P_{2s}(r)}] = \epsilon_{1s} P_{1s}(r) + \overset{\text{NOVO}}{\epsilon_{1s2s} P_{2s}(r)}$$

$$\delta P_{2s} \rightarrow \hat{Q}_{2s} P_{2s}(r) - \frac{2}{r} [Y^0(2s2s,r) P_{2s}(r) + \frac{c_1}{c_2} Y^0(1s2s,r) P_{1s}(r)] = \epsilon_{2s1s} P_{1s}(r) + \epsilon_{2s} P_{2s}(r)$$

$$\epsilon_{ms} = \frac{\lambda_{ms}}{c_m^2} \quad m=1,2 \quad \epsilon_{1s2s} = \frac{\lambda_{1s2s}}{2c_1^2} = \left(\frac{c_2}{c_1}\right)^2 \epsilon_{2s1s} \quad \epsilon_{2s1s} = \frac{\lambda_{2s1s}}{2c_2^2}$$

$\delta c_1, \delta c_2$ sekularna enačba:

$$\begin{bmatrix} H_{11} - \lambda & H_{12} \\ H_{21} & H_{22} - \lambda \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$H_{mm} = 2I_{ms} + F^0(m_s, m_s) \quad n=1,2$$

$$H_{12} = H_{21} = G^0(1s, 2s)$$

Če približno $c_1 = 1, c_2 = 0$ DOBIMO HF enačbo za konfigur. $1s^2$ $E_{\text{CHF}}(0s, s)$
 $c_1 = 0, c_2 = 1$ $2s^2$ $\approx 2.903476 \text{ a.u.}$

ZAKAJ SAMO DVOJNE ZAMENJAVE v HF KONFIGURACIJAH?

UTEŽI: c_{1s^2} $2s^2$ $3s^2$ $4s^2$ $2p^2$ $3p^2$ $4p^2$ $3d^2$ $4d^2$ $4f^2$ $5g^2$

0.995967	-0.061750	-0.001707	0.011044	-0.012793	0.004103	UTEŽI KONFIG. V ZADNJEM PRIBLJ. KU)
	-0.007847	0.062046	0.002691	-0.003467	-0.001894	

E : -2.86168 -2.87791 -2.87887 -2.87899 -2.89855 -2.90039 -2.90015 -2.90217 -2.90252 -2.90290 -2.90303

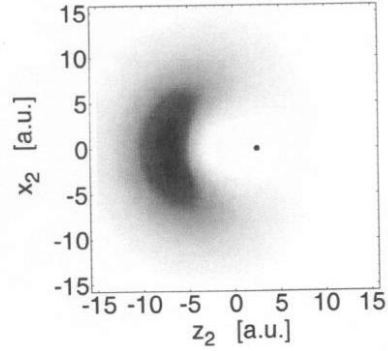
ZAPOREDNI PRIBLJIKI

$E = -62.77 \text{ eV}, (1,0)^-$

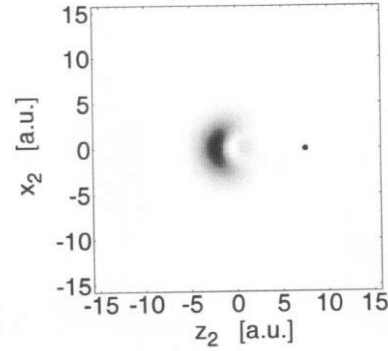
$$\psi \approx \frac{1}{\sqrt{2}}(2p_{3n} - 2s_{3p})$$

3^-

$\Gamma = 185 \text{ ns}^{-1}$



$\gamma = 5.2 \text{ ns}^{-1}$

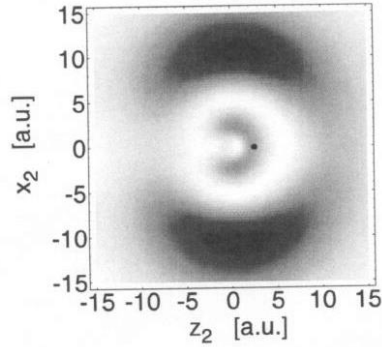


$E = -63.68 \text{ eV}, (0,1)^+$

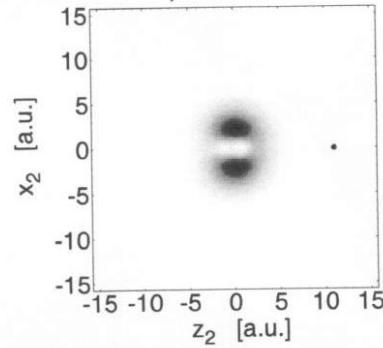
$$\psi \approx \frac{1}{\sqrt{2}}(2p_{3n} + 2s_{3p})$$

3^+

$\Gamma = 10000 \text{ ns}^{-1}$



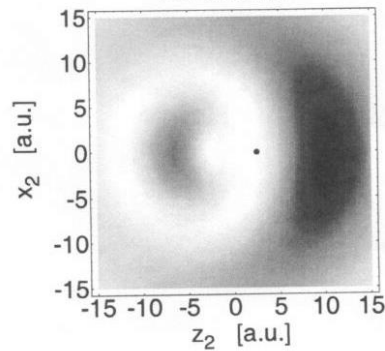
$\gamma = 7.2 \text{ ns}^{-1}$



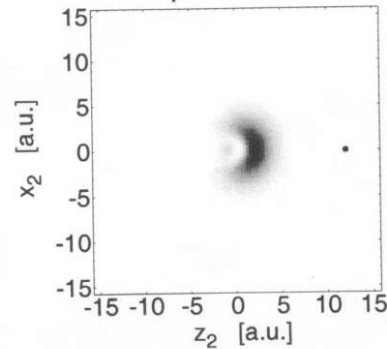
$E = -64.12 \text{ eV}, (-1,0)^0$

$2p_{3d}$

$\Gamma = 0.18 \text{ ns}^{-1}$



$\gamma = 4.9 \text{ ns}^{-1}$



ONSTRAN COULOMBSKE INTERAKCIJE — FINA STRUKTURA ATOMA

6

"NERELATIVISTIČNI" HAMILTONOV OPERATOR \hat{H}_{NR} JE TREBA DOPOLNITI S PRISPEVKI, KI JIH ZAMTEVA RELATIVISTIČNO KOREKTEN OPIS ATOMA Z DIRACOVO ENAČBO.

ČE VBEREMO RELATIVISTIČNE POPRAVKE NAJNIŽJEGA REDA ($\frac{1}{c^2}$), DOBIMO NERELATIVISTIČNO SCHRÖDINGERJEVO ENAČBO Z RELATIVISTIČNIMI POPRAVKI:

BREIT-PAULIJEV HAMILTONIAN: \hat{H}_{BP}

VODIKOV ATOM:

$$E = E' + mc^2$$

$$E = \frac{mc^2}{\sqrt{1 + \left(\frac{\alpha Z}{m} \left(j + \frac{1}{2} + \sqrt{(j + \frac{1}{2})^2 - d^2 Z^2} \right) \right)^2}} \quad \begin{array}{l} \text{TOČNA REŠITEV} \\ \text{DIRACOVE} \\ \text{ENAČBE} \end{array}$$

$$E' \xi(\vec{r}) = c(i\hbar \vec{\sigma} \cdot \nabla) \eta(\vec{r}) + V(r) \xi(\vec{r})$$

$$(E' + 2mc^2) \eta(\vec{r}) = c(-i\hbar \vec{\sigma} \cdot \nabla) \xi(\vec{r}) + V(r) \eta(\vec{r})$$

$$\Psi(\vec{r}) = \begin{pmatrix} \xi(\vec{r}) \\ \eta(\vec{r}) \end{pmatrix} = \frac{1}{r} \begin{pmatrix} P(r) \Omega_{esj m_j}(\theta, \varphi) \\ i Q(r) \Omega_{esj m_j}(\theta, \varphi) \end{pmatrix}$$

$$\Omega_{esj m_j} = \sum_{m_l m_s} \langle l m_l \frac{1}{2} m_s | l \frac{1}{2} j m_j \rangle \times Y_{l m_l}(\theta, \varphi) \chi_{\frac{1}{2} m_s}$$

SPINSKE FUNKCIJE $\chi_{\frac{1}{2} \frac{1}{2}} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\chi_{\frac{1}{2} -\frac{1}{2}} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

$$\beta(\vec{r}) = |\Psi(\vec{r})|^2 \rightarrow \Psi \approx \left(1 - \frac{\hbar^2}{8m^2 c^2} \nabla^2 \right) \xi(\vec{r})$$

Za majhne Z : $E' = E - mc^2 \approx \frac{mc^2}{2} \frac{\alpha^2 Z^2}{m^2} \rightarrow \frac{Z^2}{2n^2} \text{ a.u.}$

$$\hat{H}_{BP} = \underbrace{-\frac{\hbar^2}{2m} \nabla^2 + U}_{\text{KINETIČNA ENERGIJA \& REL. KOREKCIJO}} - \frac{\hbar^4}{8m^3c^2} \nabla^4 + \underbrace{\frac{e_0 \hbar^2}{2m^2c^2} \frac{1}{r} \frac{dV}{dr} \vec{l} \cdot \vec{s}}_{\text{INTERAKCIJA SPIN-TIR}} + \frac{\hbar^2}{8m^2c^2} \nabla^2 V$$

(7) BREIT-PAULIJEV HAMILTONIAN

Coulomb² POT. $\frac{ze^2}{4\pi\epsilon_0} \delta(\vec{r})$

• enodelčni DARWINOV ČLEN $\frac{\pi^2 \hbar^2}{2m^2c^2} \left(\frac{ze^2}{4\pi\epsilon_0} \right) \delta(\vec{r})$

$$E = c \sqrt{p^2 + m^2c^2} \approx mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2}$$

$$\begin{aligned} H_{so} &= -\vec{\mu}_s \cdot \vec{B} = 2\mu_B \vec{s} \cdot \vec{B} \\ &= 2\mu_B \vec{s} \cdot \left(\frac{\vec{v} \times \vec{E}}{c^2} \right) = 2\mu_B \vec{s} \cdot \left(\frac{\vec{v}}{c^2} \times \left(-\frac{\vec{r}}{r} \frac{\partial V}{\partial r} \right) \right) \\ &= \frac{2\mu_B}{mc^2} \left(\frac{1}{r} \frac{\partial V}{\partial r} \right) \vec{l} \cdot \vec{s} = \frac{2e\hbar^2}{2m^2c^2} \left(\frac{1}{r} \frac{\partial V}{\partial r} \right) \vec{l} \cdot \vec{s} \\ &\rightarrow \alpha^2 \left(\frac{1}{r} \frac{\partial V}{\partial r} \right) \vec{l} \cdot \vec{s} \text{ (a.u.)} \end{aligned}$$

MANJKA 2 → THOMASOVA PRECESIJA V IMENOVANCU!

- KVANTNE FLUKTUACIJE e^- NE ČUTI POTENCIALA NA TISTEM MESTU KJER JE ZARADI TVORBE VIRTUALNIH PAROV ELEKTRON-POZITRON.

$$U(\vec{r} + \vec{\xi}) = U(\vec{r}) + \vec{\xi} \cdot \nabla U(\vec{r}) + \frac{1}{2} \sum_{ij} \xi_i \xi_j \partial_i \partial_j U(\vec{r}) \leftarrow \text{TAYLORJEV RAZVOJ}$$

$\delta U = \frac{\hbar^2}{6m^2c^2} \nabla^2 U$

možhen premik $\vec{\xi} \approx c \Delta t \approx \frac{\hbar}{mc^2} c \leftarrow \text{Comptonova valovna dolžina } \lambda_c$

$$\overline{U(\vec{r} + \vec{\xi})} = U(\vec{r}) + \frac{1}{6} \overline{\xi^2} \nabla^2 U(\vec{r}) \quad \overline{\xi} = 0 \quad \overline{\xi_i \xi_j} = \frac{1}{3} \overline{\xi^2} \delta_{ij} \leftarrow \text{POVPREČJE ČEZ FLUKTUACIJE}$$

$$\delta U \approx \frac{1}{6} \lambda_c^2 \nabla^2 U = \frac{\hbar^2}{6m^2c^2} \nabla^2 U, \quad \nabla^2 U = -\nabla^2 \frac{ze^2}{4\pi\epsilon_0 r} = 4\pi \left(\frac{ze^2}{4\pi\epsilon_0} \right) \delta(\vec{r}), \quad \nabla^2 \left(\frac{1}{r} \right) = -4\pi \delta(\vec{r})$$

IZRAČUN ENERGIJE SPIN-TIR ZA VODIK:

8

$$E_{so} = \frac{\alpha^2}{2} \left\langle \frac{1}{r} \frac{dV}{dr} \vec{\ell} \cdot \vec{s} \right\rangle = \frac{\alpha^2}{2} \left\langle \frac{1}{r} \frac{dV}{dr} \right\rangle \langle \vec{\ell} \cdot \vec{s} \rangle \leftarrow$$

$$\left\langle \frac{1}{2} (\hat{j}^2 - \hat{\ell}^2 - \hat{s}^2) \right\rangle = \frac{1}{2} (j(j+1) - \ell(\ell+1) - s(s+1))$$

$$\int_0^\infty |P_{m\ell}(r)|^2 \left(\frac{1}{r} \frac{dV}{dr} \right) dr \propto \left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{m^3 \ell(\ell + \frac{1}{2})(\ell + 1)}$$

$$E_{so} = -\frac{\alpha^2}{2} \frac{Z^2}{m^2} E_m \frac{m(j(j+1) - \ell(\ell+1) - s(s+1))}{\ell(\ell + \frac{1}{2})(\ell + 1)} \propto \frac{Z^4 \alpha^2}{m^3} \quad E_{so} = 0 \text{ } \bar{a} \text{ } j = s \text{ } (l = 0)$$

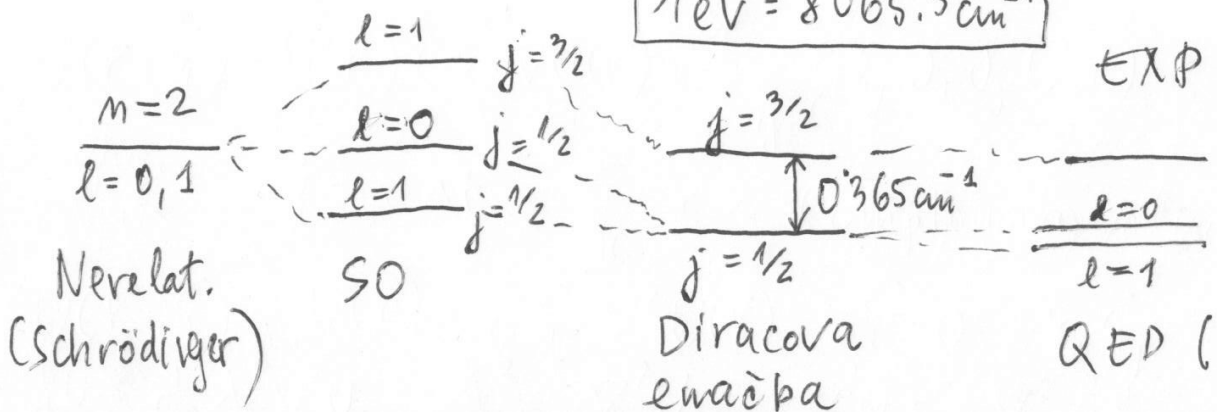
$$-\frac{Z^2}{2n^2} \quad \frac{E_{so}}{E_m} \propto \frac{\alpha^2 Z^2}{m} \xrightarrow{\substack{Z=1 \\ m=1}} \alpha^2$$

KONSTANTA FINE STRUKTURE

Za dano orbitalo je $j = l \pm \frac{1}{2}$, razen za $l=0$ ($j = \frac{1}{2}$).

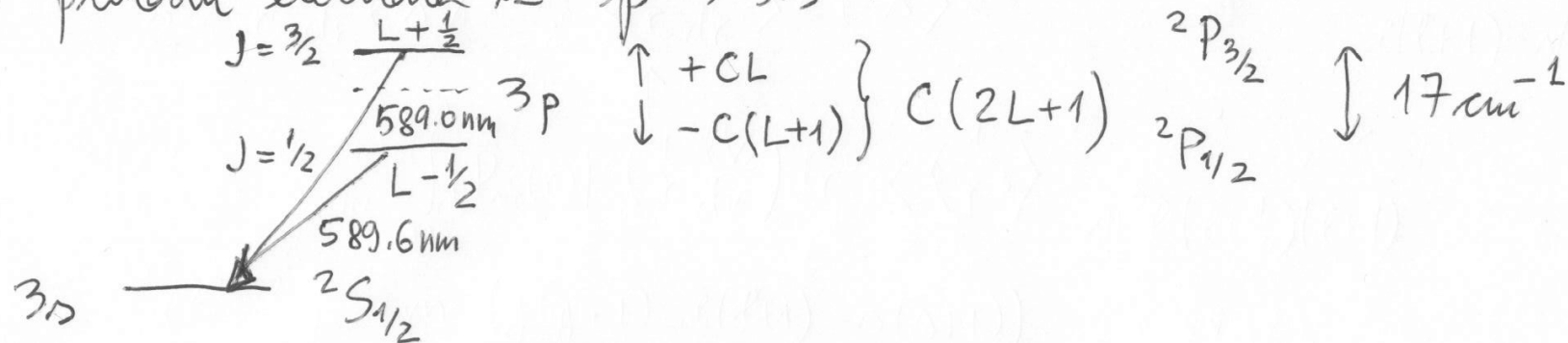
$$\sim \frac{1}{137}$$

$$1 \text{ eV} = 8065.5 \text{ cm}^{-1}$$



PRIBLIŽEK BP DELA BOLJE ZA ATOME BREZ DEGENERACIJE POL (USI ALKALNI ELEMENTI (RAZEN H!) Z E⁻ ZUNAJ POLNIM LUPIN

- Na: V spektru Na svetilke vidimo močan dublet črt, pri pripadate (9)
($Z=11$) prehodu elektrona iz $3p \rightarrow 3s$



- Pri Cs ($Z=55$) je razcep $6p \rightarrow 6s$ črte
glede na $6p \rightarrow 6s$ že okrog 554 cm^{-1}

RELATIVISTIČNI EFEKTI V VEČELEKTRONSKIH ATOMIH

$$H_{BP} = H_{NR} + H_{RS} + H_{FS} \quad \leftarrow \text{OPERATOR FINE STRUKTURE (NE KOMUTIRA z } \hat{L}, \hat{S})$$

\uparrow običajni nerelativ. H
 \uparrow OPERATOR RELATIVISTIČNEGA PREMENA (KOMUTIRA z \hat{L} in \hat{S})

$$-\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_i \frac{Z}{r_i} + \sum_{i>j} \frac{1}{r_{ij}}$$