# MULTIKONFIGURACIJSKI OPIS ATOMA



Opis lastnih stanj in energij $\hat{H}_{NR}$ izboljšamo, če presežemo omejitev, da se elektroni v atomu gibljejo neodvisno, vsak v povprečnem efektivnem izregelno simetričnem potencialu. Upoštevati moramo KORELACIJE MED ELEKTRONI. $\boxed{\text{POGOJNA VERJETNOSTNA GOSTOTA}}$, da najdemo elektron na danem položaju ni več neodvisna od položaja drugih elektronov.

$$\rho(\vec{r}_1, \ldots \vec{r}_N) = |\Psi(\vec{r}_1, \ldots \vec{r}_N)|^2 \qquad \int \rho(\vec{r}_1, \ldots \vec{r}_N)\, d\vec{r}_1 \ldots d\vec{r}_N = 1$$

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

$$\rho(\vec{r}_1) = \int \rho(\vec{r}_1, \ldots \vec{r}_N)\, d\vec{r}_2 \ldots d\vec{r}_N$$

← (brezpogojna) VERJETNOSTNA GOSTOTA, DA SE $e^-$ NAHAJA NA POZICIJI $\vec{r}_1$, NE GLEDE NA TO, KJE SO DRUGI $e^-$.

$$\rho(\vec{r}_1 | \vec{R}_2, \vec{R}_3, \ldots \vec{R}_N) = \frac{\rho(\vec{r}_1, R_2, \ldots R_N)}{\int \rho(\vec{r}_1, \vec{R}_2, \ldots \vec{R}_N)\, d\vec{r}_1}$$

← POGOJNA VERJETNOSTNA GOSTOTA, DA SE $e^-$ NAHAJA NA POZICIJI $\vec{r}_1$, ČE SO DRUGI $e^-$ NA POZICIJAH $\vec{R}_2, \ldots \vec{R}_N$.

ELEKTRON NI KORELIRAN Z DRUGIMI $e^-$, ČE VELJA

$$\rho(\vec{r}_1 | \vec{R}_2, \ldots \vec{R}_N) = \rho(\vec{r}_1)$$

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– Konfiguracija:

$$\Psi(\vec{r}_1,\ldots\vec{r}_N)=\varphi_a(\vec{r}_1)\varphi_b(\vec{r}_2)\ldots\varphi_m(\vec{r}_N)\equiv\varphi_a(\vec{r}_1)\Theta(\vec{r}_1,\ldots\vec{r}_N)$$

$$\rho(\vec{r}_1|\vec{R}_2,\ldots\vec{R}_N)=\frac{\varphi_a^2(\vec{r}_1)\Theta^2(\vec{R}_2,\ldots\vec{R}_N)}{\Theta^2(\vec{R}_2,\ldots\vec{R}_N)}=\varphi_a^2(\vec{r}_1)=\rho(\vec{r}_1)$$ NI KORELACIJE

– (dve) konfiguraciji z eno zamenjavo:

$$\Psi=c_1\varphi_a(\vec{r}_1)\Theta(\vec{r}_2,\ldots\vec{r}_N)+c_2\varphi_b(\vec{r}_1)\Theta(\vec{r}_2,\ldots\vec{r}_N)$$ NI KORELACIJE

$$\rho(\vec{r}_1|\vec{R}_2,\ldots\vec{R}_N)=\frac{[c_1^2\varphi_a^2(\vec{r}_1)+2c_1c_2\varphi_a(\vec{r}_1)\varphi_b(\vec{r}_1)+c_2^2\varphi_b^2(\vec{r}_1)]\Theta^2(\vec{R}_2,\ldots\vec{R}_N)}{\underbrace{(c_1^2+c_2^2)}_{1}\Theta^2(\vec{R}_2,\ldots\vec{R}_N)}=\rho(\vec{r}_1)$$

– (dve) konfiguraciji z dvojno zamenjavo:

$$\Psi=c_1\varphi_a(\vec{r}_1)\varphi_{a'}(\vec{r}_2)\Theta(\vec{r}_3,\ldots\vec{r}_N)+c_2\varphi_b(\vec{r}_1)\varphi_{b'}(\vec{r}_2)\Theta(\vec{r}_3,\ldots\vec{r}_N)$$

$$\rho(\vec{r}_1|\vec{R}_2,\ldots\vec{R}_N)=\frac{c_1^2\varphi_a^2(\vec{r}_1)\varphi_{a'}^2(\vec{R}_2)+2c_1c_2\varphi_a(\vec{r}_1)\varphi_b(\vec{r}_1)\varphi_{a'}(\vec{R}_2)\varphi_{b'}(\vec{R}_2)+c_2^2\varphi_b^2(\vec{r}_1)\varphi_{b'}^2(\vec{R}_2)}{c_1^2\varphi_{a'}^2(\vec{R}_2)+c_2^2\varphi_{b'}^2(\vec{R}_2)}\neq\rho(\vec{r}_1)$$

$$\rho(\vec{r}_1)=c_1^2\varphi_a^2(\vec{r}_1)+c_2^2\varphi_b^2(\vec{r}_1)$$ KORELACIJA JE

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

$$\Psi(\vec{r}_1,\ldots\vec{r}_N)\neq\varphi(\vec{r}_i)\phi(\vec{r}_1,\ldots\vec{r}_{i-1},\vec{r}_{i+1},\ldots\vec{r}_N)$$

DELNO VPELJE KORELACIJO ŽE OPIS VALOVNE FUNKCIJE S SLATERJEVO DETERMINANTO, KER JE TAM VERJETNOST, DA SE $e^-$ NAHAJA NA TOČNO ISTEM MESTU KOT NEK DRUGI $e^-$ Z ISTO PROJEKCIJO SPINA ENAKA 0. (3)

SISTEMATIČNO VPELJEMO KORELACIJE MED $e^-$ TAKO DA DOVOLIMO <u>MULTIKONFIGURACIJSKI OPIS</u> ATOMSKIM STANJ.

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

PRAVA ENERGIJA AT. STANJA (TOČNA REŠITEV $\hat{H}_{NR}$!)

ENERGIJA V PRIBLIŽKU HARTREE-FOCK

KORELACIJSKA ENERGIJA

Recimo He$(1s^2)$:

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

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

MCHF – MULTICONFIGURATION HARTREE-FOCK

$$\Psi_{MCHF}(\gamma LS) = \sum_i c_i \phi(\gamma_i LS) \qquad \sum_i c_i^2 = 1$$

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

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

ISTI LS $\begin{bmatrix} (\gamma_1) & \bullet & \\ \bullet & (\gamma_2) & \\ & & \ddots \end{bmatrix} \rightarrow \begin{bmatrix} 0 & \emptyset & \\ \emptyset & 0 & \\ & & 0 \end{bmatrix}$

$$E(\gamma LS) = \sum_{i,j} c_i c_j \langle \phi(\gamma_i LS) | H | \phi(\gamma_j LS) \rangle = \tilde{c} H c$$

$$H_{ij} = \langle \phi(\gamma_i LS) | H | \phi_j LS \rangle$$

## SPLOŠEN MCHF PROBLEM:

IŠČEMO VEKTOR UTEŽI $\vec{c} = \{c_i\}$ ter VEKTOR ORBITAL $\vec{P} = \{P_{n_a l_a}, P_{n_b l_b}, \ldots\}$ TAKO DA BO IMEL FUNKCIONAL STACIONARNO VREDNOST (glede na majhne spremembe $\vec{c}$ in $\vec{P}$)

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

ZAHTEVA 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 ENERIJA (ENERGIJE) TER JE MATRIKA $H$ ODVISNA OD OBLIKE RADIALNIH ORBITAL $\vec{P}$.

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

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

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

$$!!\quad \delta(F(P_{1s}, P_{2s}, c_1, c_2)) = \delta(E + \lambda_{1s}\langle 1s|1s\rangle + \lambda_{2s}\langle 2s|2s\rangle + \lambda_{1s2s}\langle 1s|2s\rangle - \lambda(c_1^2 + c_2^2)) = 0$$

(5)

$$\hat{\mathcal{L}}_n \equiv -\frac{1}{2}\frac{d^2}{dr_n^2} + \frac{l_n(l_n+1)}{2r_n^2} - \frac{Z}{r_n}$$

NOVO                      NOVO

$$\delta P_{1s} \rightarrow \quad \hat{\mathcal{L}}_{1s}P_{1s}(r) - \frac{2}{r}\left[Y^0(1s1s,r)P_{1s}(r) + \frac{c_2}{c_1}Y^0(1s2s,r)P_{2s}(r)\right] = \varepsilon_{1s}P_{1s}(r) + \varepsilon_{1s2s}P_{2s}(r)$$

$$\delta P_{2s} \rightarrow \quad \hat{\mathcal{L}}_{2s}P_{2s}(r) - \frac{2}{r}\left[Y^0(2s2s,r)P_{2s}(r) + \frac{c_1}{c_2}Y^0(1s2s,r)P_{1s}(r)\right] = \varepsilon_{2s1s}P_{1s}(r) + \varepsilon_{2s}P_{2s}(r)$$

$$\varepsilon_{ns} = \frac{\lambda_{ns}}{c_n^2} \quad n=1,2 \qquad \varepsilon_{1s2s} = \frac{\lambda_{1s2s}}{2c_1^2} = \left(\frac{c_2}{c_1}\right)^2\varepsilon_{2s1s} \qquad \varepsilon_{2s1s} = \frac{\lambda_{1s2s}}{2c_2^2}$$

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

$$\begin{bmatrix} H_{11}-\lambda & H_{12} \\ H_{21} & H_{22}-\lambda \end{bmatrix}\begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix} \qquad \begin{aligned} H_{nn} &= 2I_{ns} + F^0(ns,ns) \quad n=1,2 \\ H_{12} &= H_{21} = G^0(1s,2s) \end{aligned}$$

Če približno $c_1 = 1,\ c_2 = 0$ DOBIMO HF enačbo za konfig. $1s^2$    $E_{MCHF}$ (os.st)
$c_1 = 0,\ c_2 = 1$                                  $2s^2$    $= -2.903476$ 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 | -0.007847 | -0.001707 | 0.062046 | 0.011044 | 0.002691 | -0.012793 | -0.003467 | 0.004103 | -0.001894 |

(UTEŽI KONFIG. V ZADNJEM PRIBLIŽKU)

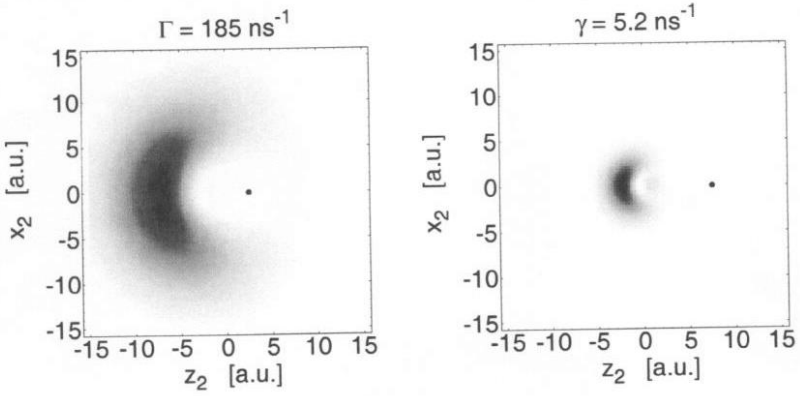
$\boxed{E}$: -2.86168   -2.87791   -2.87887   -2.87899   -2.89855   -2.90015   -2.90039   -2.90217   -2.90252   -2.90290   -2.90303

ZAPOREDNI PRIBLIŽKI

**E = -62.77 eV, $(1,0)^-$**

$$\Psi \approx \frac{1}{\sqrt{2}}(2p3s - 2s3p)$$

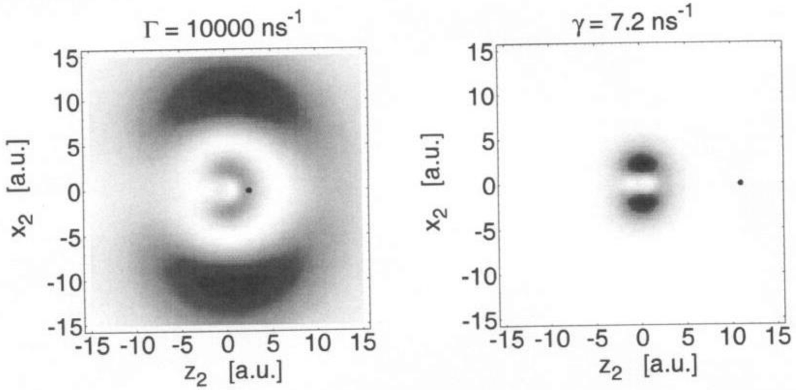
$3^-$




**E = -63.68 eV, $(0,1)^+$**

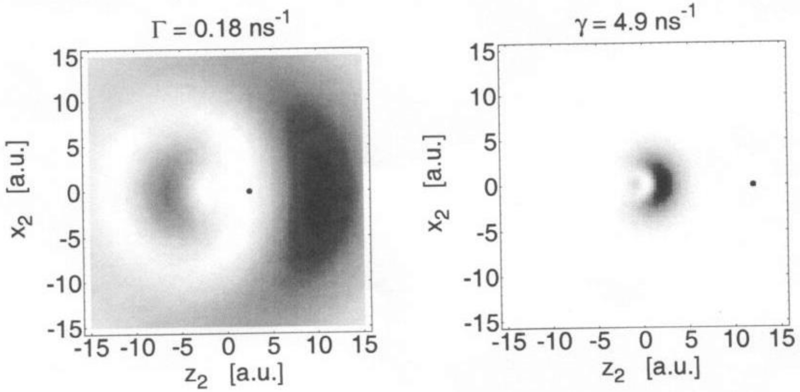
$$\Psi \approx \frac{1}{\sqrt{2}}(2p3s + 2s3p)$$

$3^+$




**E = -64.12 eV, $(-1,0)^0$**

2p 3d



# ONSTRAN COULOMBSKE INTERAKCIJE — FINA STRUKTURA ATOMA

"NERELATIVISTIČNI" HAMILTONOV OPERATOR $\hat{H}_{NR}$ JE TREBA DOPOLNITI S PRISPEVKI, KI JIH ZAHTEVA RELATIVISTIČNO KOREKTEN OPIS ATOMA Z DIRACOVO ENAČBO. ČE ZBEREMO RELATIVISTIČNE POPRAVKE NAJNIŽJEGA REDA $\left(\frac{1}{c^2}\right)$, DOBIMO NERELATIVISTIČNO SCHRÖDINGERJEVO ENAČBO Z RELATIVISTIČNIMI POPRAVKI: BREIT–PAULIJEV HAMILTONIAN: $\hat{H}_{BP}$

VODIKOV ATOM:

$$E = E' + mc^2 \qquad E = \frac{mc^2}{\sqrt{1 + \left(\dfrac{\alpha Z}{n - j - \frac{1}{2} + \sqrt{(j+\frac{1}{2})^2 - \alpha^2 Z^2}}\right)^2}}$$

TOČNA REŠITEV DIRACOVE ENAČBE

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

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

$$\psi(\vec{r}) = \begin{pmatrix} \xi(\vec{r}) \\ \eta(\vec{r}) \end{pmatrix} = \frac{1}{r}\begin{pmatrix} P(r)\,\Omega_{lsjm_j}(\theta,\varphi) \\ iQ(r)\,\Omega_{lsjm_j}(\theta,\varphi) \end{pmatrix} \qquad \Omega_{lsjm_j} = \sum_{m_l m_s} \langle l m_l \tfrac{1}{2} m_s | l \tfrac{1}{2} j m_j \rangle \times Y_{lm_l}(\theta,\varphi)\,\chi_{\frac{1}{2}m_s}$$

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

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

Za majhne Z: $E' = E - mc^2 \approx \dfrac{mc^2}{2}\dfrac{\alpha^2 Z^2}{n^2} \longrightarrow \dfrac{Z^2}{2n^2}$ a.u.

POTENCIAL

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

BREIT-PAULIJEV HAMILTONIAN

Coulomb pot. $l=0$

$$\frac{\pi^2\hbar^2}{2m^2c^2}\left(\frac{Ze_0^2}{4\pi\varepsilon_0}\right)\delta(\vec{r})$$

KINETIČNA ENERGIJA Z REL. KOREKCIJO

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

$$H_{SO} = -\vec{\mu}_s\cdot\vec{B} = 2\mu_B\vec{s}\cdot\vec{B}$$
$$= 2\mu_B\vec{s}\cdot\left(\frac{\vec{v}\times\vec{E}}{c^2}\right) = 2\mu_B\vec{s}\cdot\left(\frac{\vec{v}}{c^2}\times\left(-\frac{\vec{r}}{r}\frac{\partial V}{\partial r}\right)\right)$$
$$= \frac{2\mu_B}{mc^2}\left(\frac{1}{r}\frac{\partial V}{\partial r}\right)\vec{l}\cdot\vec{s} = \frac{2e_0\hbar^2}{2m^2c^2}\left(\frac{1}{r}\frac{\partial V}{\partial r}\right)\vec{l}\cdot\vec{s}$$
$$\rightarrow \alpha^2\left(\frac{1}{r}\frac{\partial V}{\partial r}\right)\vec{l}\cdot\vec{s} \quad (\text{a.u.})$$

MANJKA 2 → THOMASOVA PRECESIJA V IMENOVALCU!

- KVANTNE FLUKTUACIJE

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

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

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

majhen premik

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

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

$$\delta U \approx \frac{1}{6}\lambda_C^2\nabla^2 U = \frac{\hbar^2}{6m^2c^2}\nabla^2 U, \quad \nabla^2 U = -\nabla^2\frac{Ze^2}{4\pi\varepsilon_0 r} = 4\pi\left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\delta(\vec{r}), \quad \nabla^2\left(\frac{1}{r}\right) = -4\pi\delta(\vec{r})$$

## IZRAČUN ENERGIJE SPIN-TIR ZA VODIK!

(8)

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

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

$$\uparrow$$

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

$$E_{so} = -\frac{\alpha^2}{2}\frac{Z^2}{n^2}E_n\frac{n\,\big(j(j+1)-l(l+1)-s(s+1)\big)}{l(l+\frac{1}{2})(l+1)} \propto \frac{Z^4\alpha^2}{n^3}$$

$$E_n \downarrow -\frac{Z^2}{2n^2}$$

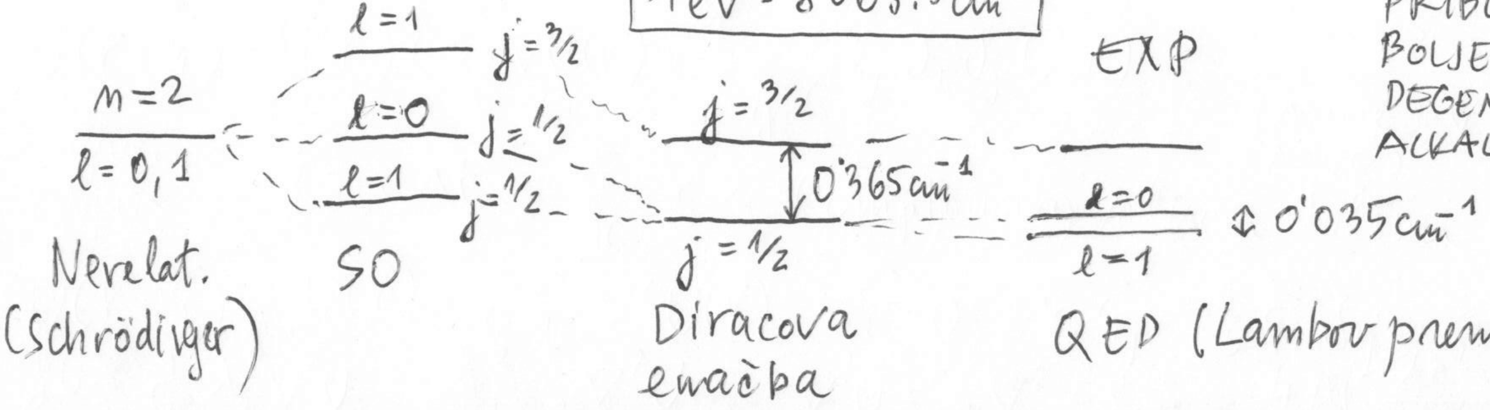
$E_{so} = 0$
če $j = s$
$(l = 0)$

$$\frac{E_{so}}{E_n} \propto \frac{\alpha^2 Z^2}{n} \xrightarrow[n=1]{Z=1} \alpha^2$$

KONSTANTA FINE STRUKTURE $\sim \frac{1}{137}$

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

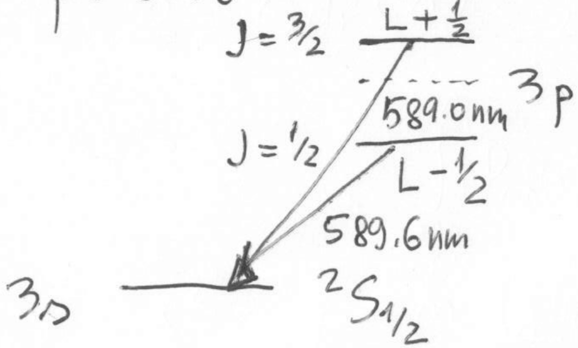
$\boxed{1\,\text{eV} = 8065.5\,\text{cm}^{-1}}$




PRIBLIŽEK BP DELA BOLJE ZA ATOME BREZ DEGENERACIJE PO $l$ (VSI ALKALNI ELEMENTI (RAZEN H!) Z $e^-$ ZUNAJ POLNIH LUPIN

(9)

- Na: V spektru Na svetilke vidimo močan dublet črt, ki pripadata
($Z=11$) prehodu elektrona iz $3p \to 3s$




$$\left.\begin{matrix}\uparrow +CL \\ \downarrow -C(L+1)\end{matrix}\right\} C(2L+1) \qquad \begin{matrix}{}^2P_{3/2} \\ {}^2P_{1/2}\end{matrix} \updownarrow 17\,\mathrm{cm}^{-1}$$

- Pri Cs ($Z=55$) je razcep $6p\,{}^2P_{3/2} \to 6s\,{}^2S_{1/2}$ črte glede na $6p\,{}^2P_{1/2} \to 6s\,{}^2S_{1/2}$ že okrog $554\,\mathrm{cm}^{-1}$

## RELATIVISTIČNI EFEKTI V VEČELEKTRONSKIH ATOMIH

$$H_{BP} = H_{NR} + H_{RS} + H_{FS}$$

$\longleftarrow$ OPERATOR FINE STRUKTURE (NE KOMUTIRA Z $\vec{L}, \vec{S}$)

$H_{NR}$: običajen nerelativ. H

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

$H_{RS}$: OPERATOR RELATIVISTIČNEGA PREMIKA (KOMUTIRA Z $\vec{L}$ in $\vec{S}$)

RAZCEP IN PREMIK ENERGIJSKIH NIVOJEV ZARADI DODATNIH INTERAKCIJ DOBIMO Z DIAGONALIZACIJO

$$H_{ij} = \langle \gamma_i L_i S_i JM | \hat{H}_{BP} | \gamma_j L_j S_j JM \rangle$$

ZA VSAK J.