3. The Helium Atom & the Periodic table

SS 2024

AQM

Lorenzo

Tomasi

As non-trivial application of these ideas, we describe how QM can be used to make predictions about **Atoms with $Z > 1$**

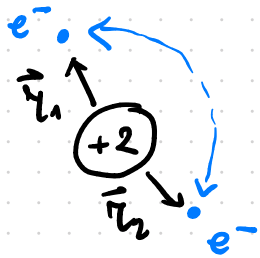
Atoms with more than one electron are much more complicated than Hydrogen. New "physics" due to

- repulsion between electrons
- Pauli exclusion Principle

Both effects can be seen on the simplest example HELIUM ($Z = 2$) $\Rightarrow \sim \frac{1}{4}$ MATTER UNIVERSE (excluding DM!)

In the exercises you will consider also atoms with $Z > 2$ [regularities & structure of the PERIODIC TABLE]

HELIUM



e^- & nucleus interact only through EM.

Putting nucleus @ ORIGIN, hamiltonian reads

$$\mathcal{H} = \frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

We are ignoring many (subleading) effects

- motion of nucleus
- spin-orbit couplings
- effect of electric current generated by one electron on the other one

$\Longrightarrow$ only interactions are Coulomb-like

So we write

$$H = \underset{\substack{\uparrow \\ \text{First electron}}}{H_1} + \underset{\substack{\uparrow \\ \text{Second electron}}}{H_2} + \underset{\substack{\uparrow \\ e^-e^- \text{ interaction}}}{V_{12}}$$

Clearly, if $V_{12} = 0$, then we could obtain full solution for H by using solutions for Hydrogen-like Atoms (1 electron, general Z)

As first attempt, we can try to use PERTURBATION THEORY with $\underline{H_1 + H_2 = H_0}$ & $\underline{V_{12} = \lambda H1}$

From your study of the Hydrogen Atom

$$H_i \, \phi_{n_i l_i m_i}(\vec{r}_i) = E_{n_i} \, \phi_{n_i l_i m_i} \qquad \underline{i = 1,2}$$

$$\phi_{n_i l_i m_i}(\vec{r}_i) = \mathcal{U}_{n_i}^{l_i}(r_i)\, Y_{l_i}^{m_i}(\theta_i, \varphi_i)$$

depends only on $r_i = |\vec{r}_i|$

spherical Harmonics

So we can write

$$u(\vec{r}_1, \vec{r}_2) = \phi_{n_1 l_1 m_1}(\vec{r}_1)\, \phi_{n_2 l_2 m_2}(\vec{r}_2)$$ with

$$H_0 u(\vec{r}_1, \vec{r}_2) = E_{n_1 n_2} u(\vec{r}_1, \vec{r}_2) = [E_{n_1} + E_{n_2}]\, u$$

with $E_n = -\frac{1}{2} mc^2 (Z\alpha)^2 \frac{1}{n^2}$ Nucleus charge = Z

and $\underline{E_{n_1, n_2} = -\frac{1}{2} mc^2 [Z\alpha]^2 \left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)}$

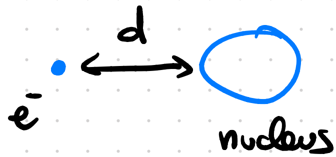
For Ground State $E_{1,1} = -mc^2[2\alpha]^2$

$\underline{mc^2 = 0{,}511\ \text{MeV}}$

$$= 8\, E_1^{\text{Hydrogen}} \quad (2 \cdot Z^2 = 8)$$

$$= -108.8\ \text{eV}$$

to see if it makes sense to try perturb theory, we can try to estimate effect of V_{12}



for each electron in ground state of one-el. atom we can take $d \sim \frac{a_0}{Z}$

$$a_0 = \frac{\hbar}{\alpha m c} \sim 0.53\ \mathring{A} \sim 0.5 \cdot 10^{-10}\ m$$ **BOHR RADIUS**

the energy is lowest when electrons are as far away as possible $D = 2d = 2\frac{a_0}{Z} \sim f\frac{a_0}{Z}$

with $f < 2$!

$$\Delta E \sim \frac{e^2}{4\pi\varepsilon_0 D} = \frac{e^2}{4\pi\varepsilon_0 a_0}\left(\frac{Z}{f}\right) \sim (27.2\,eV)\cdot\frac{Z}{f}$$

$\Delta E < 108.8\ eV$ so pert theory is reasonable !

Even before switching on the perturbation, we notice something interesting

- Ionization Energy $E_{ioniz} = 54.4\ eV$

(remove one $e^- \to r = \infty$)

In this "state", Atom has $E^{ioniz}_{He} = -54.4\ eV$

- First excited states give

$$E_1 = -\frac{5}{8} mc(2\alpha)^2 = -68,1\ eV$$

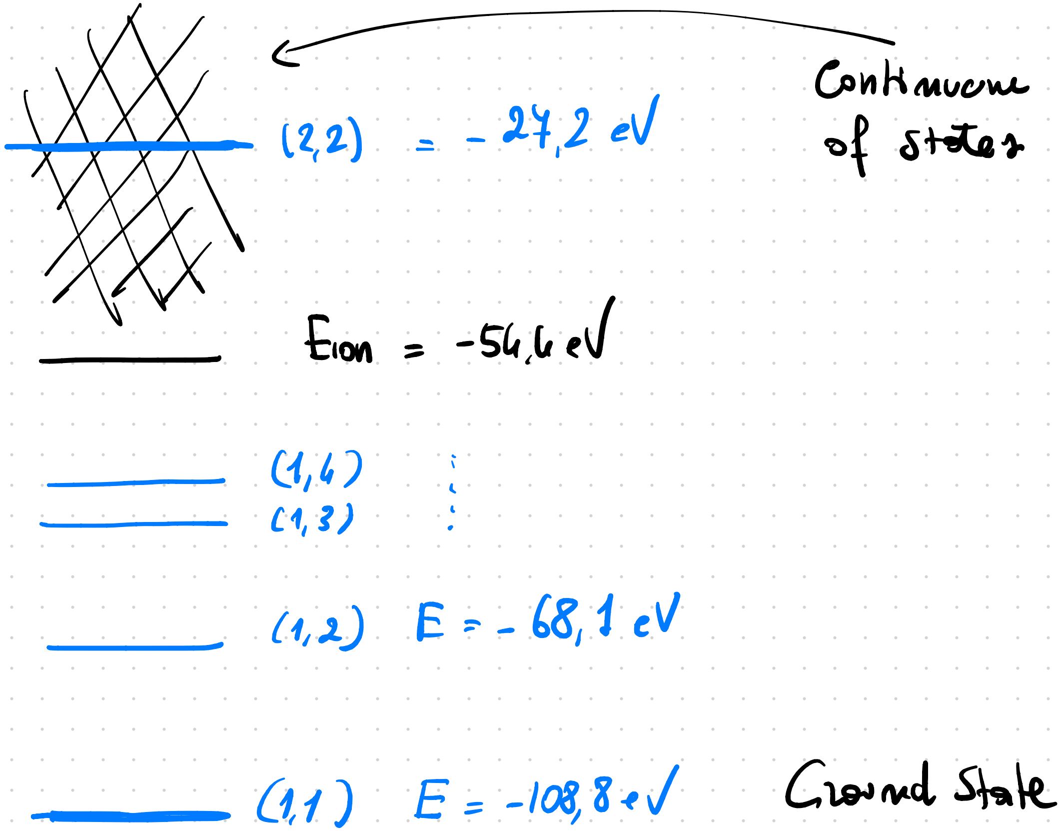
$n_1 = 1,\ n_2 = 2$ or viceversa

$\vdots$

$$E_X = -\frac{1}{4} mc^2 [2\alpha]^2 = -27,2\ eV$$

$n_1 = 2$
$n_2 = 2$

is ABOVE Ionization energy ⇒ Discrete state in Continuum!



New phenomenon of AUTOIONIZATION

$$He^{[2,2]} \longrightarrow He^{+} + e^{-}$$

it can decay into singly ionized Helium !

We'll talk more about how atoms go through these decays later in the course !

Our picture of Helium still very primitive, let's add some more effects

* PAULI EXCLUSION PRINCIPLE

two electrons are IDENTICAL FERMIONS, total wave function must be ANTISYMMETRIC

Ground state (1, 1)

$$u_0(\vec{r}_1, \vec{r}_2) = \underbrace{\phi_{100}(\vec{r}_1)\,\phi_{100}(\vec{r}_2)}_{\text{symmetric}}\ \chi_{\text{singl.}}$$

SINGLET Antisymm.

$$\chi_{\text{singl}} = \frac{1}{\sqrt{2}}\left[\chi_+^{(1)}\chi_-^{(2)} - \chi_-^{(1)}\chi_+^{(2)}\right]$$

First excited state $(1,2) \sim (2,1)$ } we can either antisymm spin or coordinate part explicitly $n=2$, $\ell = \{0,1\}$; $m = \{-1, 0, 1\}$

$$u_1^{singl} = \left[\phi_{100}(\vec{r}_1)\, \phi_{2\ell m}(\vec{r}_2) + \phi_{2\ell m}(\vec{r}_1)\, \phi_{100}(\vec{r}_2) \right] \chi_{singl}$$

$$u_1^{tripl} = \left[\phi_{100}(\vec{r}_1)\, \phi_{2\ell m}(\vec{r}_2) - \phi_{2\ell m}(\vec{r}_1)\, \phi_{100}(\vec{r}_2) \right] \chi_{tripl}$$

$$\chi_{tripl} = \begin{cases} \chi_+^{(1)} \chi_+^{(2)} \\ \dfrac{\chi_+^{(1)} \chi_-^{(2)} + \chi_-^{(1)} \chi_+^{(2)}}{\sqrt{2}} \\ \chi_-^{(1)} \chi_-^{(2)} \end{cases}$$

$\to$ $\forall$ value of $\{\ell, m\}$!

4 different states which, in current picture, are all <u>DEGENERATE IN ENERGY</u>

Still we have ignored important effect,

V_{12} = interaction among two electrons

$\Rightarrow$ let's try to estimate it with pert. th.

FIRST ORD PERT. THEORY

first ord pert

- Ground State $\quad E_0^{(1)} = E_0 + \Delta E_0$

$$\Delta E_0 = \langle 100;100 \mid V_{12} \mid 100;100 \rangle$$

$$= \int d^3\vec{r}_1 \, d^3\vec{r}_2 \; u_0^*(\vec{r}_1,\vec{r}_2) \; V_{12}(\vec{r}_1,\vec{r}_2) \; u_0(\vec{r}_1,\vec{r}_2)$$

spin indep

$$= \int d^3\vec{r}_1 \, d^3\vec{r}_2 \; |\phi_{100}(\vec{r}_1)|^2 \, |\phi_{100}(\vec{r}_2)|^2 \, \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|}$$

NOTICE THAT:

$$\Rightarrow \int d^3\vec{r}_1 \, \frac{\overbrace{e|\phi_{100}(\vec{r}_1)|^2}^{\text{charge density for first } e^-}}{|\vec{r}_1 - \vec{r}_2|} = U(\vec{r}_2)$$

potential generated by first e^- @ $\vec{r} = \vec{r}_2$

$$\Delta E_0 = -\frac{1}{4\pi\varepsilon_0}\int d^3r_2 \; e\,|\phi_{100}(\vec{r}_2)|^2 \quad U(\vec{r}_2)$$

is electrostatic energy of e^- number 2 in $U(r)$

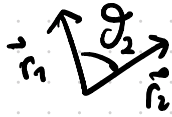
this integral is "standard"

$$\phi_{100}(\vec{r}) = \frac{2}{\sqrt{4\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-\frac{Zr}{a_0}}$$

$$\Delta E_0 = \frac{1}{\pi^2}\left(\frac{Z}{a_0}\right)^6 \frac{e^2}{4\pi\varepsilon_0}\int_0^\infty dr_1\, r_1^2\, e^{-\frac{2Zr_1}{a_0}}\int_0^\infty dr_2\, r_2^2\, e^{-\frac{2Zr_1}{a_0}}$$

$$\times \int d\Omega_1\, d\Omega_2 \underbrace{\frac{1}{|\vec{r}_1-\vec{r}_2|}}_{\Downarrow}$$

$$\int_0^{2\pi} d\varphi_2 \int_{-1}^{1} \frac{d\cos\vartheta_2}{\sqrt{\vec{r}_1^{\,2}+\vec{r}_2^{\,2}-2r_1r_2\cos\vartheta_2}} =$$



$$= \frac{2\pi}{r_1 r_2} \left\{ \underbrace{\sqrt{r_1^2 + r_2^2 + 2 r_1 r_2}}_{\sqrt{(r_1+r_2)^2}} - \sqrt{r_1^2 + r_2^2 - 2 r_1 r_2} \right\}$$

$$\sqrt{(r_1+r_2)^2} - \sqrt{(r_1 - r_2)^2}$$

$$= \frac{2\pi}{r_1 r_2} \left[r_1 + r_2 - | r_1 - r_2 | \right]$$

↑ depends on whether $r_1 \lessgtr r_2$

and $\int d\Omega_1 = 4\pi$, so putting all together

$$\Delta E_0 = \frac{8e^2}{4\pi\varepsilon_0} \left(\frac{Z}{a_0}\right)^6 \int_0^\infty dr_1 \, r_1 \, e^{-\frac{2Zr_1}{a_0}} \times$$

$$\times \left\{ 2 \int_0^{r_1} dr_2 \, r_2^2 \, e^{-\frac{2Zr_2}{a_0}} + 2 r_1 \int_{r_1}^\infty dr_2 \, r_2 \, e^{-\frac{2Zr_2}{a_0}} \right\}$$

$$= \frac{5}{8} \frac{Ze^2}{4\pi\varepsilon_0 a_0} = \frac{5}{4} Z \left[\frac{1}{2} mc^2 \alpha^2 \right] > 0$$

if $Z = 2$ $\qquad \Delta E_{11} = +34 \, eV$

remember that very roughly we had estimated

$$\Delta E_0 \sim (27.2\ eV) \cdot \frac{Z}{f}$$

some factor "$f \leq 2$"

Indeed this value corresponds to $f \sim 1.6$

& we get

$$E_0^{(1)} = (-108.8 + 34)\ eV = -74.8\ eV$$

EXPERIMENTALLY one finds $\boxed{E_{exp} = -78.975\ eV}$

first order perturbation theory

not bad, but makes mistake

$O(5\%)$

NOTE: integrals can be done by parts

$$\int_a^b \frac{d}{dx}\left[x^n e^{-Ax}\right] dx = b^n e^{-Ab} - a^n e^{-A \cdot a}$$

$$\parallel$$

$$n \int_a^b x^{n-1} e^{-Ax}\, dx - A \int_a^b x^n e^{-Ax}\, dx$$

$$\Rightarrow \int_a^b x^n e^{-Ax}\, dx = \frac{n}{A} \int_a^b x^{n-1} e^{-Ax}\, dx$$

$$+ \frac{b^n e^{-Ab} - a^n e^{-Aa}}{A}$$

Can be used to reduce them all to $\underline{\int e^{-Ax} dx}$

So as far as GROUND STATE goes, PAULI principle and spin play no role. What about excited states ?

$n = 2$, $\ell = \{0, 1\}$ & $m = \{0, -1, 1\}$

consider only $m = 0$ since V_{12} commutes with L_z

which means it cannot change spin along that axis !

So consider generic ℓ , $m = 0$ & $\left\{ \begin{matrix} \text{SINGLET} \\ \text{TRIPLET} \end{matrix} \right\}$

$$\Delta E_1^{(s,t)} = \frac{1}{2} \frac{e^2}{4\pi\varepsilon_0} \int d^3\vec{r}_1 \, d^3\vec{r}_2 \, \frac{\left[\phi_{100}(\vec{r}_1)\phi_{2\ell 0}(\vec{r}_2) \pm \phi_{100}(\vec{r}_2)\phi_{2\ell 0}(\vec{r}_1) \right]^2}{|\vec{r}_1 - \vec{r}_2|}$$

where $+ \Rightarrow$ singlet spin

$- \Rightarrow$ triplet spin

opening the square and using V_{12} ($r_1 \leftrightarrow r_2$) symm to rename the int variables, we write

$$\Delta E_1^{(s)} = J + K$$

$$\Delta E_1^{(t)} = J - k$$

where

$$J = \frac{e^2}{4\pi\varepsilon_0} \int d^3\vec{r}_1 \, d^3\vec{r}_2 \, \frac{|\phi_{100}(\vec{r}_1)|^2 |\phi_{2\ell 0}(\vec{r}_2)|^2}{|\vec{r}_1 - \vec{r}_2|}$$

$$k = \frac{e^2}{4\pi\varepsilon_0} \int d^3\vec{r}_1 \, d^3\vec{r}_2 \, \frac{\phi_{100}^*(\vec{r}_1)\,\phi_{100}(\vec{r}_2)\,\phi_{2\ell 0}^*(\vec{r}_1)\,\phi_{2\ell 0}(\vec{r}_2)}{|\vec{r}_1 - \vec{r}_2|}$$

NOTE $J > 0$ manifestly

$k > 0$ less obvious for general ℓ

(see exercises !)

the same can be derived for $u \sim \phi_{100}\,\phi_{n\ell 0}$
$\uparrow$ general n!

this means $\underline{\Delta E^{(t)}_{n,\ell} < \Delta E^{(s)}_{n,\ell}}$

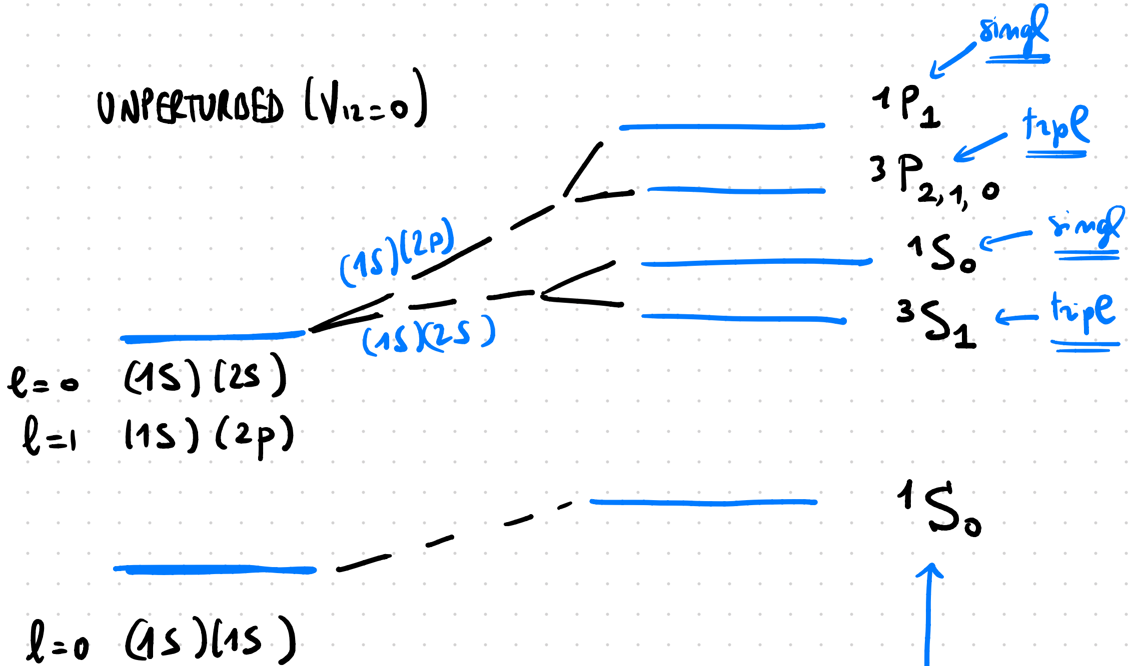
so PAULI PRINCIPLE implies that degeneration of states with different arrangement of spins is lifted

$\Rightarrow$ even if V is SPIN INDEPENDENT, symmetry requirements on wave function make its effects spin dependent

$\Rightarrow$ "EXCHANGE INTERACTION"

through this effect, spin-dependent forces can be generated which are NOT SUPPRESSED compared to electrical interactions [typically spin ~ magnetic suppressed $O\left(\left(\frac{v}{c}\right)^2\right) \sim O(\alpha^2)$]

so thanks to this effect we predict He spectrum



spectroscopic notation

TOT SPIN $\longrightarrow$ $^{2S+1}L_J$

J: TOT ANG MOMENTUM OF ELECTRONS

$L=0 \to S$

$L=1 \to P$

$L=2 \to D$

$L=3 \to F$

We can improve on our estimate for energy of ground state of Helium using VARIATIONAL PRINCIPLE

Consider some Hamiltonian $\mathcal{H}$ & a state $|\psi\rangle$ with $\langle\psi|\psi\rangle = 1$

$H|k\rangle = E_k|k\rangle$ complete set of eigenstates

then $|\psi\rangle = \sum_k C_k|k\rangle$

normalization implies $\sum_k |C_k|^2 = 1$

also we have

$$\langle\psi|H|\psi\rangle = \sum_k |C_k|^2 E_k$$

$$\geq E_0 \sum_k |C_k|^2 = E_0$$

because $E_k \geq E_0$ ground state

$$\Rightarrow \quad E_0 \leq \langle \psi | H | \psi \rangle \quad !$$

we can use this choosing some $|\psi\rangle = |\psi(\alpha_1 \dots \alpha_n)\rangle$

parameters

computing $\langle \psi | H | \psi \rangle = \Delta(\alpha_1, \dots, \alpha_n)$

and finally minimizing Δ wrt α_j

$\Rightarrow$ if we choose $|\psi\rangle$ "wisely", this procedure can give very good estimate of ground state $\underline{\underline{E_0}}$.

how we apply this to HELIUM ?

$$|\psi\rangle = \psi_{100}(\vec{r}_1, Z^*)\, \psi_{100}(\vec{r}_1, Z^*)$$

Hydrogen like but with ARBITRARY Z^*

this is like $\phi_{100}(\vec{r})$ used before, but with $Z \to Z^*$; we call it ψ_{100} not to confuse it!

$\Rightarrow$ physical intuition : in using simple perturbation theory, we neglect SCREENING EFFECT : e^- see smaller $Z^* < Z \, (=2)$ because part of it is screened by other electron!

So we have

suppress dependence on Z^*

$$\left(\frac{\vec{p}^{\,2}}{2m} - \frac{Z^* e^2}{4\pi\varepsilon_0 r} \right) \psi_{100}(\vec{r}) = E^* \, \psi_{100}(\vec{r})$$

$$\langle \psi | H | \psi \rangle = \int d^3\vec{r}_1 \, d^3\vec{r}_2 \left[\frac{\vec{p}_1^{\,2}}{2m} + \frac{\vec{p}_2^{\,2}}{2m} - \frac{Z e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_1} + \frac{1}{r_2}\right) + \frac{e^2}{4\pi\varepsilon_0 |\vec{r}_1 - \vec{r}_2|} \right] |\psi_{100}(\vec{r}_1)|^2 \, |\psi_{100}(\vec{r}_2)|^2$$

Hamiltonian evaluated for correct Z, not Z^*!

$$\langle\psi|H|\psi\rangle = 2\int d^3\vec{r}_1\, d^3\vec{r}_2\; |\psi_{100}(\vec{r}_1)|^2 |\psi_{100}(\vec{r}_2)|^2 \times$$

$$\times\left[\underbrace{\frac{p_1^2}{2m} - \frac{Z^* e^2}{4\pi\varepsilon_0 r_1}}_{\text{standard Coulomb problem}} - \frac{e^2(Z-Z^*)}{4\pi\varepsilon_0 r_1}\right]$$

using $r_1 \leftrightarrow r_2$ symmetry

extra $\frac{1}{r}$ term

$$+\int d^3\vec{r}_1\, d^3\vec{r}_2\; |\psi_{100}(\vec{r}_1)|^2 |\psi_{100}(\vec{r}_2)|^2 \times\left[\frac{e^2}{4\pi\varepsilon_0|\vec{r}_1-\vec{r}_2|}\right]$$

computed before ΔE_0

with Z^*

$$= 2E^* - 2\frac{e^2(Z-Z^*)}{4\pi\varepsilon_0}\underbrace{\left\langle 100\left|\frac{1}{r}\right|100\right\rangle}_{\frac{Z^*}{a_0}} + \underbrace{\frac{5}{8}\frac{Z^* e^2}{4\pi\varepsilon_0 a_0}}_{\frac{5}{4}Z^*\left(\frac{1}{2}mc^2\alpha^2\right)}$$

$$2E^* = -\frac{1}{2}mc^2(Z^*\alpha)^2\times 2$$

$$= -\frac{1}{2}mc^2\alpha^2\left[2Z^{*2} + 4Z^*(Z-Z^*) - \frac{5}{4}Z^*\right]$$

$$= -\frac{1}{2} mc^2\alpha^2 \left[-2Z^{*2} + 4 ZZ^* - \frac{5}{4} Z^* \right] = F(Z^*)$$

$$\frac{\partial}{\partial Z^*} F(Z^*) = 0 \Rightarrow Z^* = Z - \frac{5}{16}$$

$$\frac{\partial^2}{\partial Z^{*2}} F(Z^*) = 2\alpha^2 mc^2 > 0 \quad \text{minimum!}$$

$$E_0 \leq -\frac{1}{2} mc^2\alpha^2 \left[2 \left(Z - \frac{5}{16} \right)^2 \right] = -77{,}4 \text{ eV}$$

VERY CLOSE to Eexp!

remember $\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} = \frac{1}{137}$ fine structure constant

$$a_0 = \frac{1}{\alpha} \frac{\hbar}{mc} = \frac{\hbar c}{\alpha mc^2}$$

$$\frac{Z^* e^2}{4\pi\varepsilon_0 a_0} = Z^*\alpha \cancel{\hbar c} \frac{Z^*\alpha}{\cancel{\hbar c}} mc^2$$

$$= (Z^*\alpha)^2 mc^2$$