Ground state wf of He

Mittwoch, 1. Dezember 2021 16:24

$1s^2$ $\uparrow\downarrow$ He both e^- in 1s $n = 1$
1 2 $\ell = 0$
$m_\ell = 0$

anti-symmetric total wf.
spatial only symmetric
spin antisymmetric $S = 0$, $m_s = 0$

$$\psi = \frac{1}{2}\left(u_{1,0,0}(1)\,u_{1,0,0}(2) + u_{100}(2)\,u_{100}(1)\right)\cdot\frac{1}{\sqrt{2}}\left(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2\right)$$

$$H = \boxed{\frac{p_1^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r_1}} + \boxed{\frac{p_2^2}{2m} - \frac{Ze^2}{4\pi\varepsilon_0}\frac{1}{r_2}} + \boxed{\frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_1 - \vec{r}_2|}}$$

perturbation
→ later

For each e^-
and $Z = 2$

$$\boxed{E_i = -13.6\,\text{eV}\cdot\frac{Z^2}{n^2} = -54.4\,\text{eV}}$$

$$E_{total}^{bare} = -108.8\,\text{eV}$$

Reminder: perturbation theory

Suppose we have a Hamiltonian $\underline{\underline{H_0}}$ ⇐ the green stuff above

for which we know $|\psi_0\rangle$ wave functions

E_0 eigen energies

To this we add a perturbation

$$H = H_0 + H_{pert}$$

This obviously leads to an energy correction

$$E = E_0 + \Delta E$$

We use the original (unperturbed) wave functions Ψ_0 to calculate ΔE

$$\Delta E = \langle H_{pert} \rangle = \langle \Psi_0 | H_{pert} | \Psi_0 \rangle$$

↪ 1st order energy correction caused by the perturbing Hamiltonian

$e^- - e^-$ interaction in the g.s.

pert. $H_{e-e} = \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|}$ $\quad \Delta E = \langle \Psi | H_{ee} | \Psi \rangle$

singlet $S=0$ state

$$\Psi = \frac{1}{2}\left(u_{1,0,0}(1)\, u_{1,0,0}(2) + u_{100}(2)\, u_{1,0,0}(1)\right) \frac{1}{\sqrt{2}}\left(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2\right)$$

$$\Delta E = \int d^3r_1\, d^3r_2\, u^*_{100}(1)\, u^*_{100}(2) \frac{e^2}{4\pi\varepsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} u_{100}(1)\, u_{100}(2)$$

$$= \int d^3r_1\, e\, |u_{100}(1)|^2 \boxed{\int d^3r_2 \frac{e}{4\pi\varepsilon_0} \frac{1}{|\vec{r}_1 - \vec{r}_2|} |u_{100}(2)|^2}$$

potential produced by 2nd e^- as seen by 1st e^-

screening → reduces the binding

$= \dots = 34\,eV$

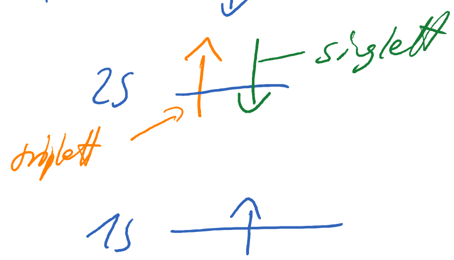
$E_{tot} = -108.8\,eV + 34\,eV = -74.8\,eV$

expt'l value: $E_{tot} = -78.9\,eV$

g.s. He: 1s $\uparrow\downarrow$ $\quad 1s^2$ Singulett $\quad {}^1S \quad -78.9\,eV$

1st. excited state in He:

One e^- in 2s state, 2 possibilities



The excited e^- can be

- singlet state
  ↳ antisymmetric spin w.f.
  symmetric spatial w.f. for $n=1$ and $n=2$
- triplet state
  ↳ symmetric spin w.f.
  antisymmetric spatial w.f.

$$\psi_{s/t} = \frac{1}{\sqrt{2}}\left(u_{100}(1)\,u_{200}(2) \pm u_{100}(2)\,u_{200}(1)\right)\cdot \chi_{a/s}$$

$\Delta E = \dots\dots$

$$= \underbrace{\frac{e^2}{4\pi\varepsilon_0}\int d^3r_1\, d^3r_2\, |u_{100}(1)|^2\, |u_{200}(2)|^2\, \frac{1}{|\vec{r}_1-\vec{r}_2|}}_{}$$

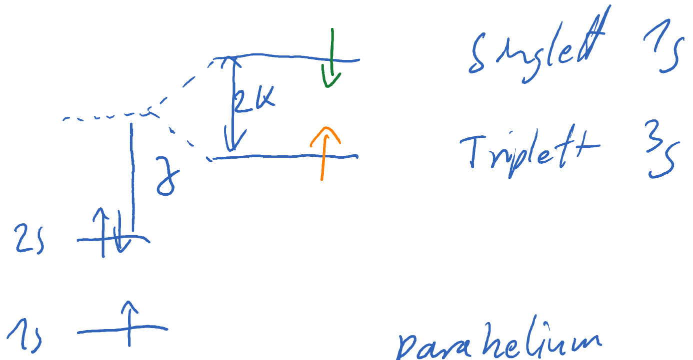
$$\underbrace{\frac{\quad}{4\pi\varepsilon_0} \int \ldots \frac{\quad}{\ldots r_2|}}_{=:J}$$

$$\pm \underbrace{\frac{e^2}{4\pi\varepsilon_0} \int d^3r_1\, d^3r_2\, u^*_{100}(2)\, u^*_{200}(1)\, \frac{1}{|\vec{r}_1 - \vec{r}_2|}\, u_{100}(1)\, u_{200}(2)}_{=:K}$$

J: direct integral, repulsion of 2 spherically symmetric charge distributions

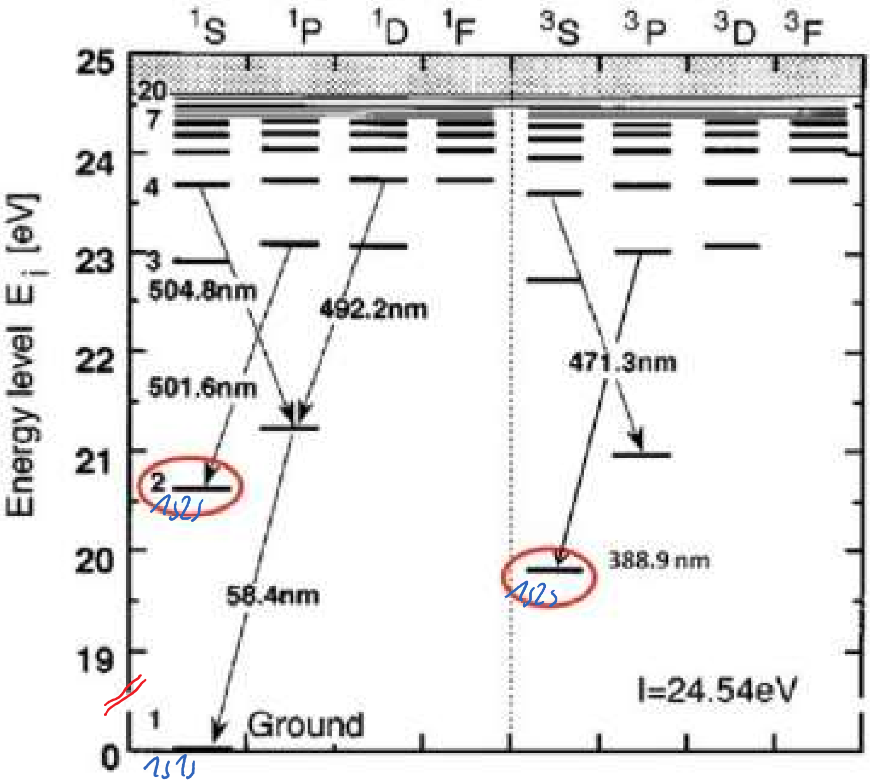
K: exchange integral, interference term

$$\Delta E = J \pm K = 0.971\,\text{eV} \pm 0.399\,\text{eV}$$



parahelium   orthohelium

singlett   triplett


^1S ^1P ^1D ^1F ^3S ^3P ^3D ^3F
Energy level E_i [eV]
25
24
23
22
21
20
19
0
20
7
4
3
2
1
504.8nm
492.2nm
501.6nm
471.3nm
388.9 nm
58.4nm
Ground
I=24.54eV
1s2s
1s2s
1s1s