Chapter 3 - Helium

In this chapter, we will mainly worry about the electronic states of He. Because there is no solution to the two electron state, much of the discussion will be qualitative. As much as possible, I'll focus on what is known.

The non relativistic, ∞ mass nucleus Hamiltonian is

$$H = -\frac{\hbar^2}{2m_e}\nabla_1^2 - \frac{\hbar^2}{2m_e}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0|\vec{r}_1 - \vec{r}_2|}$$

$Z = 2$ for He
$= 3$ for Li^+

Where are spin operators? Why is there 0.8 eV energy difference between $1s2s\ ^3S$ and $1s2s\ ^1S$?

The Hamiltonian commutes with the swap operator, A
$$A F(1,2) = F(2,1)$$
Can simultaneously find eigenstates of H, A
Even stricter, H commutes with swapping <u>only</u> space part, S
$$S F(\vec{r}_1, \vec{r}_2) = F(\vec{r}_2, \vec{r}_1)$$

The eigenvalues of the swap operators are ± 1. This means can find

symmetric
$$\psi^S_{space}(\vec{r}_1, \vec{r}_2) = \psi^S_{space}(\vec{r}_2, \vec{r}_1)$$

antisymmetric
$$\psi^A_{space}(\vec{r}_1, \vec{r}_2) = -\psi^A_{space}(\vec{r}_2, \vec{r}_1)$$

Spin ½ are Fermions $\Rightarrow$ the wave function of both space and spin (χ) must be antisymmetric
$$\psi(\vec{r}_1\chi_1, \vec{r}_2\chi_2) = -\psi(\vec{r}_2\chi_2, \vec{r}_1\chi_1)$$
There are two ways to make this happen:
$$\psi(\vec{r}_1\chi_1, \vec{r}_2\chi_2) = \psi^S_{space}(\vec{r}_1, \vec{r}_2)\,\psi^A_{spin}(\chi_1, \chi_2) \quad \text{or} \quad \psi^A_{space}(\vec{r}_1, \vec{r}_2)\,\psi^S_{spin}(\chi_1, \chi_2)$$

The spin functions are
$$\psi^A_{spin} = \frac{1}{\sqrt{2}}(|\uparrow_1,\downarrow_2\rangle - |\downarrow_1,\uparrow_2\rangle) \qquad S=0, M_S=0 \qquad \text{singlet}$$
$$\psi^S_{spin} = |\uparrow_1,\uparrow_2\rangle \quad \text{or} \quad \frac{1}{\sqrt{2}}(|\uparrow_1,\downarrow_2\rangle + |\downarrow_1,\uparrow_2\rangle) \quad \text{or} \quad |\downarrow_1,\downarrow_2\rangle \qquad S=1;\ M_S=1,0,-1$$
triplet

The spatial ground state for 2 electrons has zero nodes $\Rightarrow \psi^S_{space} \Rightarrow \psi^A_{spin}$
This is why ground state has $S=0$

The ground state is often written as $1s^2$ to indicate it is approximately

$$\Psi_{g.s.}(\vec{r}_1, \vec{r}_2) \simeq R_{10}(r_1) R_{10}(r_2) Y_{00}(\Omega_1) Y_{00}(\Omega_2)$$

The actual wave function is much more complicated.

$$\Psi_{g.s.}(\vec{r}_1, \vec{r}_2) = C_0 R_{00}(r_1, r_2)(Y_0 Y_0)_{m=0}^{L=0} + C_1 R_{11}(r_1, r_2)(Y_1 Y_1)_{m=0}^{L=0} + C_2 R_{22}(r_1, r_2)(Y_2 Y_2)_{m=0}^{L=0} + \dots$$

why all have $L=0$, $M=0$? What is radial correlation? Angular correlation?

Calculations are done using the variational principle:

$$E_{gs} \leq \frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle} \qquad \text{Why?}$$

Write Ψ as a function of parameters. Find the parameters that give the smallest $\langle \Psi | H | \Psi \rangle / \langle \Psi | \Psi \rangle$. That is your best guess at the ground state energy.

Example $\qquad \Psi = \frac{\tilde{Z}^3}{\pi a^3} e^{-\tilde{Z}(r_1 + r_2)/a}$

$$E_{gs} \leq -\left(-2\tilde{Z}^2 + \frac{27}{4}\tilde{Z}\right) 13.6 \text{eV} \qquad \text{How to choose } \tilde{Z}?$$

$$\frac{d}{d\tilde{Z}}\left(-2\tilde{Z}^2 + \frac{27}{4}\tilde{Z}\right) 13.6 \text{eV} = 0 \Rightarrow \tilde{Z} = \frac{27}{16}$$

$$E_{gs} \leq -\frac{1}{2}\left(\frac{3}{2}\right)^6 13.6 \text{eV} \simeq -77.5 \text{eV} \qquad \sim 2\% \text{ error}$$

He requires 24.59 eV to ionize⎤ Total binding energy = 79.01 eV
He^+ " 54.42 eV " " ⎦

The He nonrelativistic, ∞ mass ground state can be found to huge number of digits

In general for He nonrelativistic, ∞ mass, the $\vec{L}^2$, L_z where $\vec{L} = \vec{L}_1 + \vec{L}_2$ is a conserved quantum number. This means it commutes with the Hamiltonian. Neither $\vec{L}_1$ nor $\vec{L}_2$ are conserved. This is because θ_1, ϕ_1 (or θ_2, ϕ_2) are in $e^2/(4\pi\epsilon_0 |\vec{r}_1 - \vec{r}_2|)$

The states are labeled $nl\, n'l'\ ^{2S+1}L_J$ but are, at best, approximate.
Examples $\quad 1s2p\ ^1P_1$, $\quad 1s2p\ ^3P_0$, $\quad 1s3d\ ^1D_2$

Trends in excited state energy. The He states can be very complicated. The states where one electron is in the $1s$ and the other is in $n\ell$ has an OK approximation using

$$\Psi^\pm_{1sn\ell}(\vec{r}_1, \vec{r}_2) = \frac{1}{\sqrt{2}}\left[R_{10}^{z=2}(r_1) Y_{00}(\Omega_1) R_{n\ell}^{z=1} Y_{\ell m}(\Omega_2) \pm R_{n\ell}^{z=1}(r_1) Y_{\ell m}(\Omega_1) R_{10}^{z=2} Y_{00}(\Omega_2) \right]$$

Why is this reasonable?

These are not eigenstates though. Use $E_1 = -13.6\,eV$

$$H\,① = \left(\frac{P_1^2}{2m} - \frac{2e^2}{4\pi\epsilon_0 r_1} + \frac{P_2^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r_2} \right)① + \left(\frac{e^2}{4\pi\epsilon_0 r_{12}} - \frac{e^2}{4\pi\epsilon_0 r_2} \right)①$$

$$= \left(4E_1 + \frac{E_1}{n^2} \right)① + \left(\frac{e^2}{4\pi\epsilon_0 r_{12}} - \frac{e^2}{4\pi\epsilon_0 r_2} \right)①$$

$$H\,② = \left(4E_1 + \frac{E_1}{n^2} \right)② + \left(\frac{e^2}{4\pi\epsilon_0 r_{12}} - \frac{e^2}{4\pi\epsilon_0 r_1} \right)②$$

If $\ell \geq 1$, then the two orbitals are orthogonal. For $\ell = 0$, the orbitals are **not** orthogonal and you need to account for the overlap.

$$\langle \Psi^\pm | H | \Psi^\pm \rangle = \left(4E_1 + \frac{E_1}{n^2} \right) + \frac{1}{2}\frac{e^2}{4\pi\epsilon_0}\left[\langle ① | \tfrac{1}{r_{12}} - \tfrac{1}{r_2} | ① \rangle + \langle ② | \tfrac{1}{r_{12}} - \tfrac{1}{r_1} | ② \rangle \right.$$

$$\left. \pm \langle ② | \tfrac{1}{r_{12}} - \tfrac{1}{r_2} | ① \rangle \pm \langle ① | \tfrac{1}{r_{12}} - \tfrac{1}{r_1} | ② \rangle \right]$$

(same — arrows connecting terms)

$$J_{1sn\ell} = \frac{e^2}{4\pi\epsilon_0} \iint \left(\frac{1}{r_{12}} - \frac{1}{r_2} \right) | R_{10}^{z=2}(r_1) Y_{00}(\Omega_1) |^2 | R_{n\ell}^{z=1}(r_2) Y_{\ell m}(\Omega_2) |^2 d^3r_1 \, d^3r_2 \qquad \text{Direct}$$

$$K_{1sn\ell} = \frac{e^2}{4\pi\epsilon_0} \iint \left(\frac{1}{r_{12}} - \frac{1}{r_2} \right) \left(R_{10}^{z=2}(r_1) Y_{00}(\Omega_1) R_{n\ell}^{z=1}(r_2) Y_{\ell m}(\Omega_2) \right)\left(R_{10}^{z=2}(r_2) Y_{00}^*(\Omega_2) R_{n\ell}^{z=1}(r_1) Y_{\ell m}^*(\Omega_1) \right) d^3r_1 \, d^3r_2$$

Exchange

The 6-dimensional integrals can be simplified by using the expansion

$$\frac{1}{r_{12}} = \sum_{k=0}^{\infty} \frac{r_<^k}{r_>^{k+1}} \frac{4\pi}{2k+1} \sum_{q=-k}^{k} Y_{kq}^*(\Omega_1) Y_{kq}(\Omega_2) \qquad \text{Can put the }^* \text{ on either one!}$$

For the $J_{1sn\ell}$, the $|Y_{00}(\Omega_1)|^2$ means only the $k=0, q=0$ term is nonzero. This means $1/r_{12} \to 1/r_>$

$$J_{1sn\ell} = \frac{e^2}{4\pi\epsilon_0} \int_0^\infty \left[\int_{r_2}^\infty \left(\frac{1}{r_1} - \frac{1}{r_2} \right) \left(R_{10}^{z=2}(r_1) \right)^2 r_1^2 \, dr_1 \right] \left(R_{n\ell}^{z=1}(r_2) \right)^2 r_2^2 \, dr_2$$

$$= \frac{e^2}{4\pi\epsilon_0} \int_0^\infty \alpha(r_2) \left(R_{n\ell}^{z=1}(r_2) \right)^2 r_2^2 \, dr_2 \qquad \alpha(r_2) \to -1/r_2 \text{ as } r_2 \to 0$$

$$\to -()r_2 e^{-4r_2/a_0} \text{ as } r_2 \to \infty$$

$\alpha(r_2)$ is negative for all r_2 Why?

Because the integrand is nonzero for a region $r_2 < \sim a_0$
the $J_{1sn\ell} \sim -(\ )/n^3$

Now do the exchange integral $\beta_{1sn\ell}(r) = R_{10}^{z=2}(r)\, R_{n\ell}^{z=1}(r)\, r^2$

$$K_{1sn\ell} = \frac{e^2}{4\pi\varepsilon_0} \frac{1}{2\ell+1} \int_0^\infty \int_0^\infty \left(\frac{r_<^\ell}{r_>^{\ell+1}} - \frac{\delta_{\ell,0}}{r_2} \right) \underset{1sn\ell}{\beta(r_1)}\ \underset{1sn\ell}{\beta(r_2)}\ dr_1\, dr_2$$

$$= \frac{e^2}{4\pi\varepsilon_0} \frac{1}{2\ell+1} \int_0^\infty \left[\int_0^{r_2} \left(\frac{r_1^\ell}{r_2^{\ell+1}} - \frac{\delta_{\ell,0}}{r_2} \right) \beta_{1sn\ell}(r_1)\, dr_1 + \int_{r_2}^\infty \left(\frac{r_2^\ell}{r_1^{\ell+1}} - \frac{\delta_{\ell,0}}{r_2} \right) \beta_{1sn\ell}(r_1)\, dr_1 \right] \beta_{1sn\ell}(r_2)\, dr_2$$

For $\ell > 0$, the $\underset{1sn\ell}{\beta(r)} \sim (\ )\, e^{-2r/a_0}\, r^\ell / n^{3/2}$, This gives
$K_{1sn\ell} \sim (\text{positive}) / n^3$
This means the singlet states, which have symmetric spatial
functions, are at higher energy. Physical reason why??

$$E_{n\ell}^{\pm} = \underbrace{\left(4E_1 + \frac{E_1}{n^2} \right)}_{\text{hydrogenic + He}^+ \text{BE}} + J_{1sn\ell} \pm K_{1sn\ell}$$

How does energy depend on n? $\quad E_{n\ell}^{\pm} = E_{Th} + \frac{E_1}{n^2} + E_1 \frac{2\mu_\ell^{\pm}}{n^3}$

$\mu_\ell^{\pm} = \frac{n^3}{2E_1} (J_{1sn\ell} \pm K_{1sn\ell})$

A more standard form $\quad E_{n\ell}^{\pm} = E_{Th} + \frac{E_1}{(n-\mu_\ell^{\pm})^2} \qquad \mu = \text{quantum defect}$

Why?? $\quad \frac{1}{(n-\mu_\ell^{\pm})^2} = \frac{1}{n^2(1-\frac{\mu_\ell^{\pm}}{n})^2} = \frac{1}{n^2} + \frac{2\mu_\ell^{\pm}}{n^3} \ldots$

Often, the splittings and shifts are proportional to the
hydrogenic energy spacing between successive n

$$\Delta E = \frac{E_1}{n^2} - \frac{E_1}{(n+1)^2} = \frac{E_1}{n^2}\left(1 - \frac{1}{(1+1/n)^2} \right) = \frac{E_1}{n^2}\left(1 - \left(1 - \frac{2}{n} \ldots \right) \right) = \underline{E_1 / n^3}$$

The quantum defects μ_ℓ decrease rapidly with ℓ once
centrifugal potential pushes outer electron outside of core electrons.
$\Delta E_{1s4s} = 0.08\,eV$, $\quad \Delta E_{1s4p} \sim 0.034\,eV$, $\quad \Delta E_{1s4d} \sim 0.0002\,eV$, $\quad \Delta E_{1s4f} \sim 0.00001\,eV$

Schematic of energies

singlet   triplet
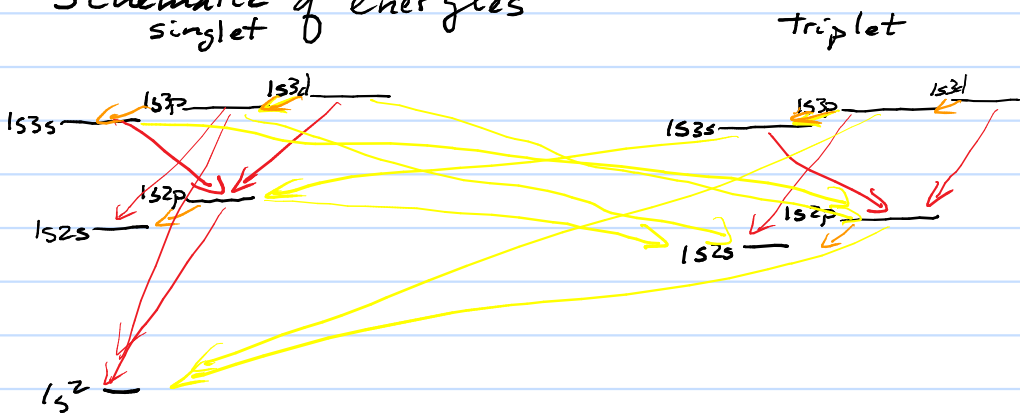
$^3P_{J=1}$ can decay to $^1S_0$ by spin orbit mixing with $^1P_1$

$^3P_{J=0}$ can not decay into $^1S_0$ unless there is nonzero nuclear spin.

Similar processes for other $^{2S+1}L_J$

$1s3p \ ^3P_0 \xrightarrow{\text{emit photon}} 1s2p \ ^3P_1$ can happen if external E-field mixes some $1s3s \ ^3S_1$ or $1s3d \ ^3D_{1,2}$ into the $1s3p \ ^3P_1$ Also, Parity non conservation effects (PNC larger for heavier atoms)

The lifetime of $1s2s \ ^3S_1$ is ~ 2 hours. Can be used in many experiments (BEC, cold gas) like ground state atoms.

The $1s2s \ ^3S - 1s2p \ ^3P$ transition wavelength is $\lambda = 1.08 \mu m$

One big difference is inelastic collisions

$He(1s2s \ ^3S) + He(1s2s \ ^3S) \longrightarrow He(1s^2) + He^+(1s) + e^-(15eV)$
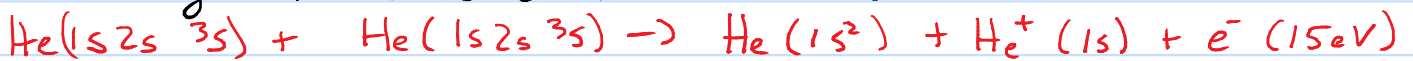
Why?

Helium is the simplest system to understand autoionization. Exchange of energy between electrons in same atom can lead to one (or more) electrons ejected.

2s4ℓ ═══ ══ ═══ ── Excited ionization threshold ($He^+(2s)$, $He^+(2p)$)
2s3ℓ ──
$2s^2$ ── 2s2p ──

1s4ℓ ═══ ══ ══ ── Ionization threshold ($He^+(1s)$)
1s3ℓ ──
1s2s── 1s2p ──

See the NIST data tables for neutral He

$1s^2$ ──

$He(2s2p (^1P)) \longrightarrow He^+(1s) + e^- (\ell=1, \sim 34eV)$
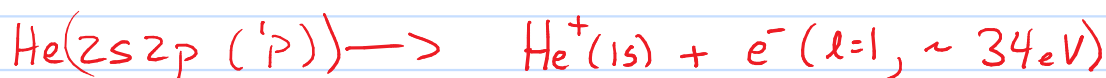
Energy width $0.042\,eV = \hbar\Gamma$

$\Gamma = 0.042 \times 1.6\times10^{-19} / 1.054\times10^{-34} \; s^{-1} = 6.4\times10^{13}\; s^{-1}$

Life time $\sim 1/\Gamma = 15.7 \times10^{-15}\, s \approx 16\, fs$
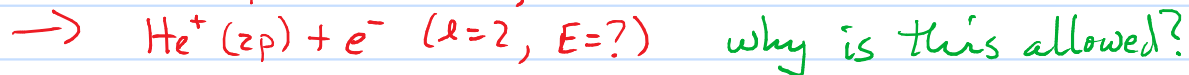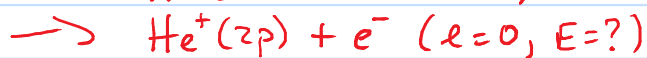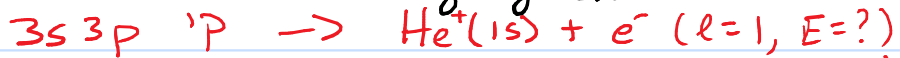
For He there is a special symmetry because
$E_{2s} \cong E_{2p}$ of He^+
$(2s\,np \pm 2p\,ns)$
with decay rates $\Gamma^{\pm} \sim (\;)^{\pm}/n^3$

For even more highly excited can leave the ion excited
$3s3p\; ^1P \rightarrow He^+(1s) + e^- (\ell=1, E=?)$
$\rightarrow He^+(2s) + e^- (\ell=1, E=?)$
$\rightarrow He^+(2p) + e^- (\ell=0, E=?)$
$\rightarrow He^+(2p) + e^- (\ell=2, E=?)$ why is this allowed?

These above states above the ionization threshold are an example of **Feshbach** resonances. Feshbach resonances occurs in any quantum system that has 2+ degrees of freedom and energy above break-up threshold.

Why does He have funny shaped resonance lines?