P423 — Lecture 12: Atoms and the periodic table

→ mention that the Hamiltonian does not depend on spin ⇒ can prove that eigenstates are either singlets or triplets.

Atoms with atomic number Z have Z electrons:

$$H = \sum_{j=1}^{Z} \left\{ -\frac{\hbar^2}{2m} D_j^2 - \frac{1}{4\pi\varepsilon_0} \frac{Ze^2}{r_j} \right\} + \frac{1}{4\pi\varepsilon_0} \sum_{j<k} \frac{e^2}{|\vec{r}_j - \vec{r}_k|}$$

$\underbrace{\qquad}$
Coulomb repulsion
Can not be solved exactly

while we can not solve for eigenenergies and eigenstates exactly, we can say a lot about

the qualitative behavior of electronic structure of atoms.

1) Helium

The two electrons, $Z = 2$. Let's ignore the Coulomb repulsion for now. The eigenstates would

be $\quad \Upsilon(\vec{r}_1, \vec{r}_2) = \Upsilon_{n\ell m}(\vec{r}_1) \, \Upsilon_{n'\ell'm'}(\vec{r}_2)$

with effective Bohr radius

$$a = \frac{1}{2} a_B \qquad (a_B = 0.5\text{Å}), \text{ and}$$

$$E = 4(E_n + E_{n'}). \qquad (\text{Because } e^2 \to 2e^2 \text{ in H-atom's solution!})$$

write down ground state:

$$\Upsilon_0 = \frac{e^{-\frac{r_1}{a}}}{\sqrt{\pi a^3}} \frac{e^{-\frac{r_2}{a}}}{\sqrt{\pi a^3}} = \frac{1}{\pi \frac{a_B^3}{8}} e^{-\frac{2(r_1 + r_2)}{a_B}} \quad /\!/$$

$$E_0 = -4(13.6\text{ eV} + 13.6\text{ eV}) = -108.8\text{ eV} \quad /\!/.$$

Excited states: The bound states are only given by

$$\Psi_{nlm} \Psi_{100}$$

i.e., excite one electron and keep the other in ground state. Why?

Suppose we excite both electrons, say consider $\Psi_{200} \Psi_{200}$ which would give rise to the lowest excited energy for 2 electrons:

$$E = 4\left(-\frac{13.6\,eV}{4} - \frac{13.6\,eV}{4}\right) = -27.2\,eV$$

Compare this to the energy of one free electron with zero energy + Ψ_{100}:

$$\Psi_{n=\infty,\,l,\,m} \Psi_{100} \quad \text{has energy} \quad E = 4(-13.6\,eV) = -54.4\,eV$$

Lower than $\Psi_{200}\Psi_{200}$! Hence, if we create $\Psi_{200}\Psi_{200}$, one electron will fly with kinetic energy $-27.2\,eV - (-54.4\,eV) = 27.2\,eV$ away and the other will go down to Ψ_{100}! i.e., all energies above $-54.4\,eV$ are in the "continuum" of propagating modes.
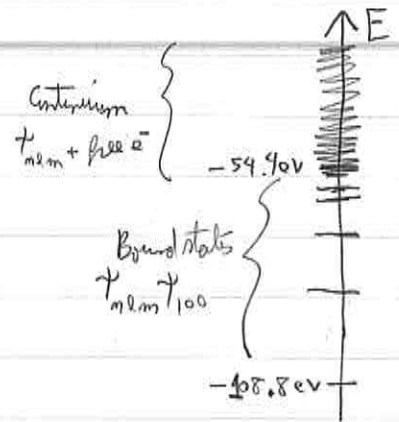
Need to add spin to ground state:

$$\Psi_o(\vec{r}_1, \vec{r}_2) = \Psi_{100}(r_1)\Psi_{100}(r_2)\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

Has to be singlet to satisfy antisymmetry!

In reality, Helium ground state has energy equal to $-78.975\,eV$, that is $\approx 30\,eV$ higher than our estimate $\Rightarrow$ Coulomb repulsion is important.

But ground state is indeed a singlet.

Excited states can be singlets or triplets:

$$\Psi_{2S}^{(Parahelium)} = \frac{1}{\sqrt{2}}\left[\Psi_{200}(1)\Psi_{100}(2) + \Psi_{100}(1)\Psi_{200}(2)\right]\frac{1}{\sqrt{2}}\left(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle\right)$$

$$\Psi_{2S}^{Orthohelium} = \frac{1}{\sqrt{2}}\left[\Psi_{200}(1)\Psi_{100}(2) - \Psi_{100}(1)\Psi_{200}(2)\right]\begin{cases}|\uparrow\uparrow\rangle \\ \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ |\downarrow\downarrow\rangle\end{cases} \text{(3 states!)}$$

The orthohelium states have lower energies! Why?

Because $\Psi^{orthohelium}(\vec{r}_1 = \vec{r}_2) = 0$ while $\Psi^{Para}(\vec{r}_1 = \vec{r}_2) \neq 0$ —

Antisymmetric orbital wave fnc <u>minimizes</u> Coulomb repulsion.

$$E_{2S}^{Para} \approx -4eV - 54.4eV$$

$$E_{2S}^{ortho} \approx -5eV - 54.4eV$$

| Show slide with energies of para and ortho |

<u>Electronic structure of atoms</u>: <u>Periodic table</u>.

<u>First Guess</u> = Guess the electronic structure of atoms with a simple qualitative idea:

That electrons fill the shells with <u>lower</u> single electron energy —

⇒ Degeneracy $2n^2$

↑ spin   # of states with principal quantum number n

⇒ Would predict that

Periodic table has 2 , 8 , 18 , 32 , ... · elements in each row —

↓ ↓ ↓ ↓
n=1 n=2 n=3 n=3

actually this is not the Case. The periodic table has
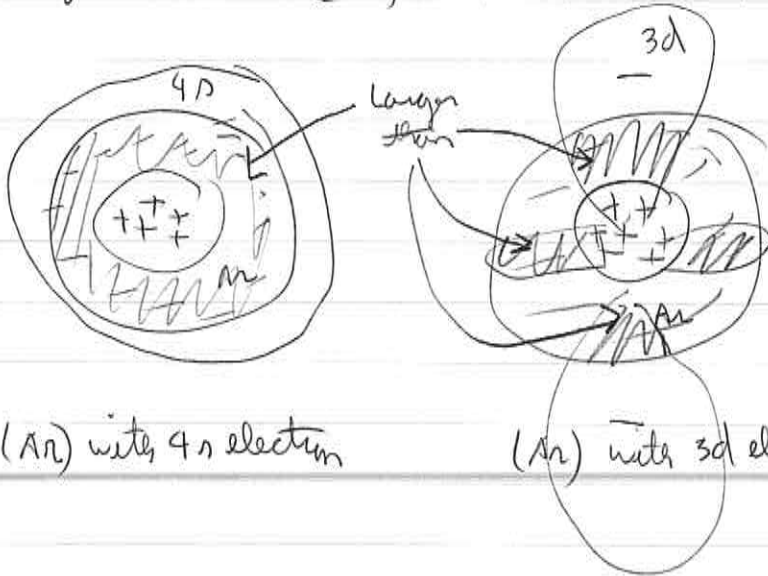
$$2, 8, 8, 18, 18, \ldots$$

why ? What throws the counting off starting from $n=3$?

why? V_{e-e} interaction!

The largest energy shift of $e-e$ interaction is <u>screening</u>. Consider Potassium:

$$K = (Ar)(4s) \qquad \text{where} \quad (Ar) = (1s)^2 (2s)^2 (2p)^6 (3s)^2 (3p)^6$$

why not $(Ar)(3d)^1$? Shouldn't it have lower energy?

(Ar) with 4s electron   (Ar) with 3d electron

Note how most of the $4s$ wave fnc is <u>closer</u> to the positively charged nucleus.

The $3d$ wave fnc, although it has smaller radius, has two lobes sticking out. These lobes

"see" the $+$ nucleus as if it has charge $Q \approx +Ze - (Z-1)e = +e$.

                                                    Ar electrons

instead of $Q = +Ze$.   "screening"

$\Rightarrow$ Lower ℓ has less screening $\Rightarrow$ more attraction, lower energy.

That's why we add electrons to the shell like:

Sc , $Z = 21$:

$(1s)^2$

$(2s)^2 (2p)^6$

$(3s)^2 (3p)^6 (3d)$

$(4s)^2$

add additional electron diagonally.