Systems involving many electrons

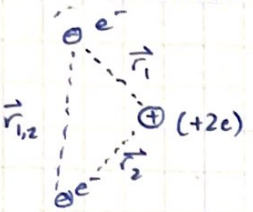
So far, we have discussed only the system of Hydrogen, with one proton and one electron. What about for helium, lithium, or the other atoms? First, we should consider just isotopes of hydrogen, to simplify matters a little.

- Consideration of Com and μ (reduced mass):

Isotopes of Hydrogen:

^1H	p^+	1 amu	The larger the mass, the better the estimation for Com at the nucleus & $\mu \approx e^-$. Therefore, the same exact equations may be used.
^2H	$p^+ + n^0$	2 amu	
^3H	$p^+ + 2n^0$	3 amu	

Let us consider Helium:



- Having more than one mass at the center of this atom is not a problem, as shown in the previous analyses of Com and μ equations.
- The forces acting between the two electrons, however, are an issue. If we try and solve the Schrödinger's equation analytically for this system, we would get:

$$\left(-\frac{\hbar^2}{2m_e}\nabla_{e1}^2 - \frac{\hbar^2}{2m_e}\nabla_{e2}^2 - \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)\psi(r_1, r_2) = E\psi(r_1, r_2).$$

where

$$\nabla_{e_1}^2 = \frac{1}{r_1^2}\frac{\partial}{\partial r_1}\left(r_1^2\frac{\partial}{\partial r_1}\right) + \frac{1}{r_1^2\sin^2\theta_1}\frac{\partial^2}{\partial\phi_1^2} + \frac{1}{r_1^2\sin\theta_1}\left(\frac{\partial}{\partial\theta_1}\right)\left(\sin\theta_1\frac{\partial}{\partial\theta_1}\right)$$

This is just for a 2 e^- system. If we expand this to a system like Argon, the eigenfunction of energy would depend simultaneously on the coordinates of (18 electrons)!.

- The kinetic energy, $K = \frac{p^2}{2m_e}$ will not change depending on the charge. However,
- The potential energy, $U_H = -\frac{1}{4\pi\varepsilon_0}\left(\frac{e \cdot e}{r}\right)$ would depend on charge: Instead, $U = -\frac{1}{4\pi\varepsilon_0}\frac{ze^2}{r}$, where z depends on how many protons / electrons there are (for He, $z = 2$)

$$E_n = -\frac{\hbar^2}{2m_e a_0^2}\frac{1}{n^2}, \text{ where } a_0 = \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}.$$

It follows, then, that for multiple electron systems, $a_0' = \frac{4\pi\varepsilon_0\hbar^2}{m_e z e^2} = \frac{a_0}{z}$. Putting this into consideration, for any multi-electron system,

$$E_n = -\frac{\hbar^2}{2m_e(a_0')^2}\frac{1}{n^2} = -\frac{\hbar^2}{2ma_0^2}\left(\frac{1}{n^2}\right)z^2.$$

Let us assume that the two electrons in helium have no interaction with each other, in a sort of "dream scenario." That is, we assume $\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}_2 - \vec{r}_1|} = 0$.

$$\left.\begin{aligned}\Sigma K &= K_{e_1} + K_{e_2} + K_{nuc} \\ \Sigma U &= -\frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_1} - \frac{1}{4\pi\varepsilon_0}\frac{2e^2}{r_2} + \overset{0}{\cancel{\frac{1}{4\pi\varepsilon_0}\frac{e^2}{|\vec{r}_2 - \vec{r}_1|}}}\end{aligned}\right\} \Sigma E = \overbrace{K_{e_1} + U_{e_1}}^{=E_{e_1}} + \overbrace{K_{e_2} + U_{e_2}}^{=E_{e_2}}$$

Essentially, multiplicative wave functions, ψ_1 for H.

$$E_n = -\frac{\hbar^2}{2ma_0^2}\left(\frac{1}{n^2}\right), \text{ and } \psi = \psi_{n,l,m_l}(r_1, \theta_1, \phi_1) \cdot \psi_{n,l,m_l}(r_2, \theta_2, \phi_2)$$

Since the wave functions multiply.

For the case $U(e_1) = -\frac{1}{4\pi\epsilon_0}\left(\frac{2e^2}{r_1}\right) + \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\vec{r_2}-\vec{r_1}|}$, we must also consider that e^- exists as a cloud: the electron is everywhere, and as such we should multiply by the probability density.

$$U_{e_1} = -\frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1} + \frac{e^2}{4\pi\epsilon_0}\frac{1}{|\vec{r_2}-\vec{r_1}|}$$
. Where does the second e_1^- come from?

$$\int \frac{1}{|\vec{r_2}-\vec{r_1}|} P(\vec{r_2})\, r_2^2\, dr_2 \sin\theta_2\, d\theta_2\, d\phi_2 \rightarrow$$
After this integration, we are simply left with a function of r, $f(r_1)$, since r_2 has already been averaged out in the probability density consideration. Calling upon Gauss' Law, we rewrite as $\frac{1}{4\pi\epsilon_0}\frac{eQ}{r}$

When $\zeta = 1$, no shielding
when $\zeta \approx 0$, heavy shielding

The effective potential can be calculated as:

$$U_{e_1}^{eff} = -\frac{1}{4\pi\epsilon_0}\frac{1}{r_1}(2e^2 - Qe), \text{ or } -\frac{e^2}{4\pi\epsilon_0}\left(\frac{2-Q/e}{r_1}\right), \text{ where } \boxed{(2-Q/e) = \zeta} \text{ shielding effect.}$$

→ This shielding effect, ζ, depends on the atom of interest:

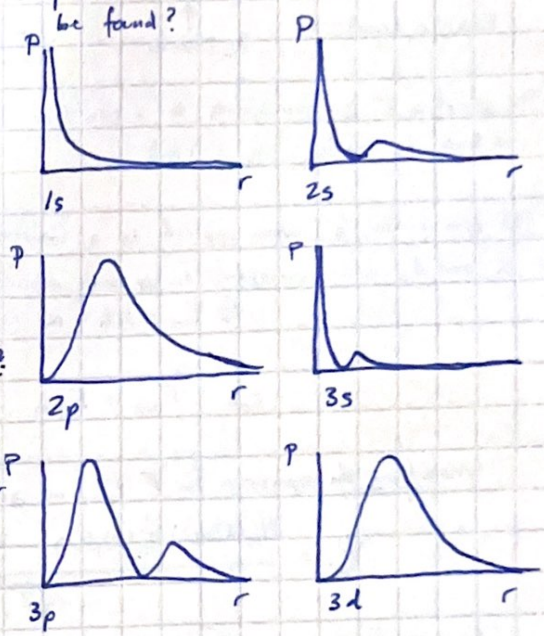
	Z	ζ
H	1	1
He	2	1.69
Li	3	1s = 2.69 2s = 1.28

Since the 2s orbital is more shielded than the 1s orbital.

Recall that in Gauss' Law, the e_1^- is only influenced by the ■ part and not ▨, what is outside.

Generally,
$\zeta_s > \zeta_p > \zeta_d$

Considering probability: What is the most/least probable distance from the nucleus which the e^- will be found?



To find the radial probability, that is, the probability a particle will be within the volume of a sphere with radius r_1, the probability density function cannot simply be $|\Psi(r,\theta,\phi)|^2$:
→ The jacobian must also be considered:

$$P_{n,\ell}(r)dr = \left\{\int_0^{2\pi} d\phi \int_0^{\pi} [Y_\ell^{m_\ell}(\theta,\phi)]^* [Y_\ell^{m_\ell}(\theta,\phi)] \sin\theta\, d\theta\right\} r^2 R_{n,\ell}^2(r)\, dr$$
$$= r^2 R_{n,\ell}^2(r)\, dr$$

So far, we can classify atoms based on their e^- configuration:

- H = 1s
- He = $1s^2$
- Li = $1s^2, 2s$ = [He] 2s
- Be = [He] $2s^2$
- ... etc

→ ~~So far~~ Why is this term not $1s^3$ instead of $1s^2$? Pauli's exclusion principle is one part of the answer, but the most basic explanation is the fundamental principle of symmetry: we should not be able to tell the 2 particles apart.

If there are 2 particles in 2 states:
#1 = $\Psi_A(1)$ and #2 = $\Psi_B(2)$,
Pauli's exclusion principle states that
#1' = $\Psi_A(2)$ and #2' = $\Psi_B(1)$
should be indiscernable. That is:
$$|\Psi(1,2)|^2 = |\Psi_A(1)\Psi_B(2)|^2 = |\Psi_B(1)\Psi_A(2)|^2 = |\Psi(2,1)|^2$$
The probability density of the two should be equivalent.

Pauli postulated that electrons are antisymmetric (which was true):

$\Psi(1,2) = \Psi(2,1)$ Symmetric Case (Bosons)
$\Psi(1,2) = -\Psi(2,1)$ Asymmetric Case (Fermions)

If there are $2e^-$ in the same orbital, the proper form of the wave function should be Ψ_{anti}.