① **Helium**

Estimating shift of helium ground state $(1s^2)$ energy due to electron-electron interactions.

$$\Delta E = \frac{e^2}{4\pi\varepsilon_0} \left\langle 1s^2 \left| \frac{1}{r_{12}} \right| 1s^2 \right\rangle = \frac{1}{4\pi\varepsilon_0} \int\!\!\int |\Psi_{1s}(\vec{r_1})|^2 \frac{e^2}{r_{12}} |\Psi_{1s}(\vec{r_2})|^2 \, d^3r_1 \, d^3r_2$$

$$\longrightarrow \quad \Delta E \approx \Delta E_1^{\#2} + \Delta E_2^{\#1}$$

$\underbrace{\qquad\qquad}_{\text{approximation}}$

Approach taken in the book (and the approach we'll take for alka...

Consider the effective Coulomb potential felt by electron #2 due to the average density distribution of electron #1. Add the energy shift due to this to the corresponding term for electron #2's influence on electron #1.

Note: This "mean-field" approach ignores correlations between the electrons induced by interactions.

For the general case, this approach of adding an effective "potential" to the $-\dfrac{Ze^2}{4\pi\varepsilon_0 r_2}$ term generalizes to the Hartree method.

For our ground state, it's simpler (symmetric spatial w.f., s-orbitals)

Due to symmetry of the s-orbitals, the total effective potential felt by electron #2 at a distance r_2 away from the nucleus looks like:

$$\left[\text{full potential due to nuclear charge @ } r_2=0\right]$$
$\qquad \hat{}$ attractive

$+\left[\text{partial repulsive potential due to an effective charge } Q_1(r_2) \text{ centered @ r...}\right.$
relating to the net charge of electron #1 expected to be
found with $r_1 < r_2$

$$Q_1(r_2) = -e \int_0^{r_2} |\Psi_{1s}(r_1)|^2 \, 4\pi r_1^2 \, dr_1$$

limits $\begin{cases} Q_1(r_2=0) = 0 \\ \rightarrow \text{ electron #2 sees full Coulo...} \\ \qquad \text{potential at small } r_2 \text{ value...} \\[4pt] Q_1(r_2 \to \infty) = -e \\ \rightarrow \text{ electron #2 sees Coulomb p...} \\ \qquad \text{w/ } Z' = (Z-1) \text{ at large } r_2 \text{ val...} \end{cases}$

② <u>Excited states</u>   Let's again construct 2-particle states from the single-electron orbitals, considering solutions of the form:

$$\psi_{1s}(1) = \frac{R_{1s}(r_1)}{\sqrt{4\pi}}$$

$$\psi_{n\ell}(2) = R_{n\ell}(r_2) Y_{\ell m}(\theta_2, \varphi_2)$$

We already know that, given the required antisymmetrization of ψ_{TOT} where $\psi_{TOTAL} = \psi_{spatial} \otimes \psi_{spin}$, we'll be able to have 2-electron wave funct of the forms:

$$\psi_{TOTAL} = \psi_{spatial}^{S} \otimes \psi_{spin}^{A} \qquad or \qquad \psi_{TOTAL} = \psi_{spatial}^{A} \otimes \psi_{spin}^{S}$$

symmetric ↗   antisymmetric ↗

where we have

$$\psi_{spin}^{A} = \frac{1}{\sqrt{2}}\left(\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2\right) \quad , \quad \psi_{spin}^{S} = \begin{cases} \uparrow_1 \uparrow_2 \\ \frac{1}{\sqrt{2}}\left(\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2\right) \\ \downarrow_1 \downarrow_2 \end{cases}$$

and the allowed spatial states are

$$\psi_{spatial}^{A} = \frac{1}{\sqrt{2}}\left[\psi_{1s}(1)\,\psi_{n\ell}(2) - \psi_{1s}(2)\,\psi_{n\ell}(1)\right]$$

and

$$\psi_{spatial}^{S} = \frac{1}{\sqrt{2}}\left[\psi_{1s}(1)\,\psi_{n\ell}(2) + \psi_{1s}(2)\,\psi_{n\ell}(1)\right]$$

With only the "Hartree" term, these two spatial wave functions would relate to the same energy. We'll see however that this is not the case, and we need to consider an exchange energy as well.

③ Corrections to the excited state energies

$$H_0 = H_{0,1} + H_{0,2} = -\frac{\hbar^2}{2m}\vec{\nabla}_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{\hbar^2}{2m}\vec{\nabla}_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2}$$

$$H_{int} = \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

$$(H_0 + H_{int})\Psi = E\Psi$$

$$H_0\Psi = E^{(0)}\Psi$$

correction due
to interactions

$$\Delta E = E - E^{(0)} \implies \boxed{H_{int}\Psi = \Delta E\Psi}$$

we know our $\overset{\text{excited}}{\wedge}$ spatial wave functions should be of the form

$$\Psi = \alpha \underbrace{\Psi_{1s}(1)\Psi_{n\ell}(2)}_{\Psi_{space}^a} + \beta \underbrace{\Psi_{1s}(2)\Psi_{n\ell}(1)}_{\Psi_{space}^b}$$

__Let's do the following__: multiply the right + left sides of
$$H_{int}\Psi = \Delta E\Psi \quad \sout{\text{and integrate}}$$
$\sout{\text{these by}}$ by $\left(\Psi_{space}^a\right)^*$ or $\left(\Psi_{space}^b\right)^*$ and integrate.

RHS

~~$\iint \Psi_{1s}^*(1)\Psi_{n\ell}^*(2)\Delta E\Psi = \alpha\Delta E$~~

$$\iint \Psi_{1s}^*(1)\Psi_{n\ell}^*(2)\Delta E\Psi \, d^3r_1 \, d^3r_2 = \alpha\Delta E$$

$$\iint \Psi_{1s}^*(2)\Psi_{n\ell}^*(1)\Delta E\Psi \, d^3r_1 \, d^3r_2 = \beta\Delta E$$

LHS

$$\iint \psi_{1s}^*(1)\, \psi_{ne}^*(2) \frac{e^2}{4\pi\varepsilon_0 r_{12}} \psi\, d^3r_1\, d^3r_2$$

$$= \alpha \underbrace{\frac{e^2}{4\pi\varepsilon_0} \iint \frac{|\psi_{1s}(1)|^2\, |\psi_{ne}(2)|^2}{r_{12}}\, d^3r_1\, d^3r_2}_{J_d}$$

$$+ \beta \underbrace{\frac{e^2}{4\pi\varepsilon_0} \iint \psi_{1s}^*(1)\, \psi_{ne}^*(2) \frac{1}{r_{12}} \psi_{1s}(2)\, \psi_{ne}(1)\, d^3r_1\, d^3r}_{J_e}$$

$$\iint \psi_{1s}^*(2)\, \psi_{ne}^*(1) \frac{e^2}{4\pi\varepsilon_0 r_{12}} \psi\, d^3r_1\, d^3r_2 = \alpha J_e^* + \beta J_d$$

$J_d \to$ the "direct" ene
due to the "effecti
potential

$J_e \to$ an "exchange" e
term, mixing term

recast as

$$\begin{pmatrix} J_d & J_e \\ J_e^* & J_d \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = \Delta E \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

arrive @ 2 solutions using 1st order deg. pert. Theory

$$\Delta E_\pm = J_d \pm J_e \implies \text{the "+" solution relates to}$$

the spatial w.f. $\psi_{spatial}^S = \frac{1}{\sqrt{2}}\left[\psi_{1s}(1)\psi_{ne}(2) + \psi_{1s}(2)\psi_{ne}(1)\right]$. This

state has an antisymmetric spin wave function ψ_{spin}^A, and

a higher energy.

$\Rightarrow$ the "$-$" solution relates to

$$\Psi_{spatial}^{A} = \frac{1}{\sqrt{2}} \left[\Psi_{1s}(1)\Psi_{ne}(2) - \Psi_{1s}(2)\Psi_{ne}(1) \right], \text{ which}$$

has 3 possible related spin configurations (the triplet states).

These triplet states have a _lower_ energy. The electrons in this state are anticorrelated, and less likely to be found near each other, resulting in a _smaller_ positive correction due to $\bar{e}-\bar{e}$ interactions and a lower energy.

This effect relates to _Hund's Rule #1_

$\Rightarrow$ spin states w/ larger multiplicity will have a lower energy (due to correlations of the spatial w.f.)

Note: The two contributions to the energy corrections that we saw here (direct + exchange terms) are central to the Hartree-Fock method for determining w.f.'s and energies in multi-electron atoms.