Recap of what we learned from a first-order approach to Helium. (ignoring spin-orbit, nuclear interactions etc.)

Electrostatic repulsion between electrons gives rise to.

- Screening of nuclear charge, in 1st order characterized by the integral $J = \int \frac{|u_a^{(1)}|^2 \, |u_b^{(2)}|^2}{4\pi\epsilon_0 r_{12}} \, d^3r_1 \, d^3r_2$

  → lifts $\vec{L}$ degeneracy

- exchange energy shifts, in 1st order characterized by integral

$$K = \int \frac{u_a^*(1)\, u_a(2)\, u_b^*(2)\, u_b(1)}{4\pi\epsilon_0 \, r_{12}} \, d^3r_1 \, d^3r_2$$

→ parity dependent, therefore lifts the spin state degeneracy. But Note: the spin degeneracy is lifted by electrostatic interactions + Pauli symmetrization, not by magnetic spin-spin interactions.

terminology: ^{2S+1}L,

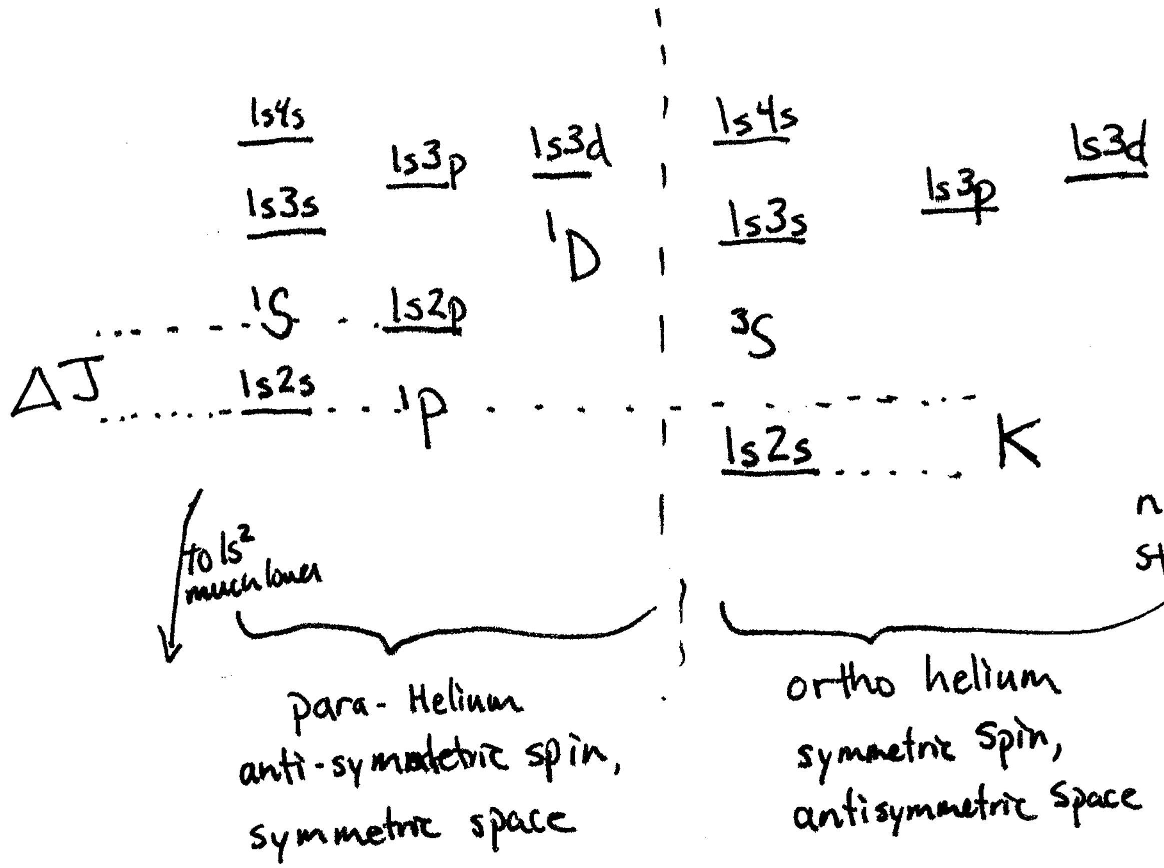
$L = s, p, d$

$S = \frac{1}{2} + \frac{1}{2} = 1$ or

$= \frac{1}{2} - \frac{1}{2} = 0$

For He

This gives energies that look like



note: no $1s^2\ {}^3S$ state exists due to Paulli exclusion!

note: if you ignored spin altogether, the only state you'd get wrong is the missing $1s^2$

When calculating the integrals, a better zero-order approximation to the single particle states was made by considering the screening when writing the single-particle Hamiltonian:

$$H_0 = \sum_{i=1,2} \frac{p_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{r_1} + \frac{1}{r_1}\right)$$

"residual electrostatic interaction" →

$$H_I = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{12}} - \frac{1}{r_1}\right)$$

← move $\frac{1}{2}$ of the nuclear repulsion (which is screened) to the interaction part.

Now → extend to multi-electron atoms.

An aside:

for Alkali atoms which have one electron outside of a closed shell, we expect this to be a pretty good description. → obviously its a better description for larger + larger l (due to the cetrifugal barrier $+\frac{l(l+1)}{r^2}$)

it turns out that the l-dependence is very well parameterized in a simple way for alkali's

$$E_H = -E_0 \frac{1}{n^2}$$

$$E_0 = +\frac{e^2}{4\pi\epsilon_0}\frac{1}{2a_0} = \left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{m}{2\hbar^2}$$

$$E_{Alkali} = -E_0 \frac{1}{(n-\delta_l)^2}$$

} the effectively reduced principle quantum #,
→ goes to hydrogenic as $l \to$ large.
acts like it is in a lower energy state for lower l.

eg. for Na
$n \gtrsim 5$
$\delta_s = 1.35$
$\delta_p = 0.86$
$\delta_d = 0.01$
$\delta_l \simeq 0.$

Now go back to the general problem

Extend this to multi-electron atoms:

$$H_{CF} = \sum_i \frac{p_i^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r_i} + S(r_i) \leftarrow$$

Add and subtract a potential $S(r)$

CF for central field

$$H_{re} = \sum_i \left(\sum_{j<i} \left(\frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}} \right) - S(r_i) \right) \swarrow$$

re for residual electrostatic

First consider only H_0:

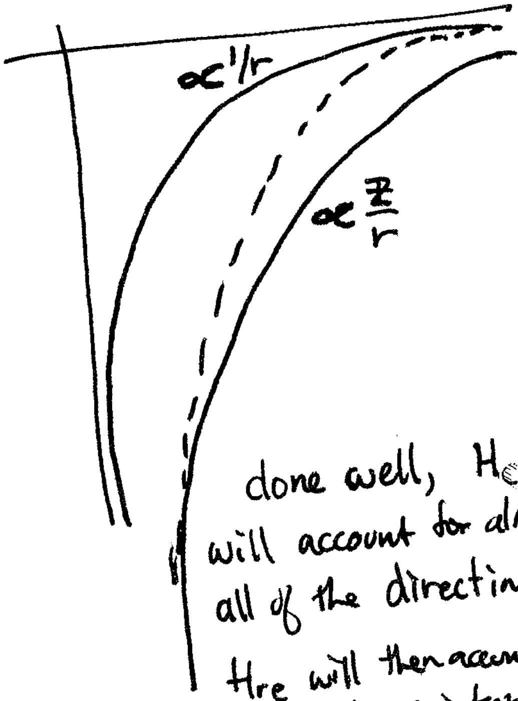
$S(r)$ is spherically symmetric, and depends only on the single particle distance to the nucleus: it can be viewed as averaging the potential due to all electrons in the atom. It should be chosen to minimize H_I contributions.

One can also parameterize $S(r)$ as

$$S(r) = -\frac{Z(r)\, e^2}{4\pi\epsilon_0\, r}, \quad \text{where} \quad Z(r) = \begin{cases} Z & r \ll a_0 \\ 1 & r \gg a_0 \end{cases}$$

In practice, the solution for $S(r)$ and $\psi_i(r)$ are done self consistently: pick a good guess for $S(r)$, solve for $\psi_i(r_i)$, calculate the average potential created by $\psi_1(r_1)\psi_2(r_2)\dots\psi_N(r_N)$, $S'(r)$, solve for $\psi_i(r_i)$ etc.

Called the Hartree-technique.



done well, H_{CF} will account for almost all of the direct integral

H_{re} will then account for exchange integral.

~~[illegible] about Symmetrization~~

Very similar to Hydrogen → radially symmetric potential!

for example:

$$S(r_i) = -\frac{Ze^2}{4\pi\epsilon_0 r_i} + \left\langle \sum_{j\neq i} \int \frac{e^2}{4\pi\epsilon_0 r_{ij}} \psi_j^* \psi_j \, d^3 r_j \right\rangle$$

→ average over angles.

What about Symmetrization?

The Hartree method gives solutions of the form

$$\psi = \prod_i \psi_i(r_i) \rightarrow \text{not symmetrized.}$$

a way to symmetrize N electron wavefunctions is given by the slater determinant:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_a(1) & \psi_a(2) & \cdots & \psi_a(N) \\ \psi_b(1) & \psi_b(2) & \cdots & \psi_b(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_x(1) & \psi_x(2) & \cdots & \psi_x(N) \end{vmatrix}$$

Since the determinant changes sign when two columns (electrons) are interchanged, this is an antisymmetric wave function:

$$\Psi = \frac{1}{\sqrt{N!}} \sum_P (-1)^P \prod_{i=1}^{N} \psi_i(P r_i)$$

, where p are permutations of N objects.

Using Ψ in the self-consistent solution is called the Hartree - Fock method.

Can be <u>very</u> good!

Since $[H_{re}, \hat{P}] = 0$, ↗ Parity operator

we can find simultaneous eigenfcts of H + Parity

What about the other, ignored terms in the Hamiltonian?

a rough list of Contributions to H_A, in roughly decreasing orders of magnitude

H contribution	Degeneracy	Good quantum #'s	state labels
spherically symmetric electrostatic. (single particle) $H_{CF} = \sum_i \left(\frac{p_i^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_i} + S(r_i) \right)$	accounts for most of the "direct" integral, or screening. Lifts the degeneracy of states within a configuration that have different l.	$[H_{CF}, \vec{A}^2] = 0$ $\vec{A} = \vec{l}_i, \vec{s}_i, \vec{L}, \vec{S}$ so $l_i, s_i, m_{l_i}, m_{s_i}, L, M_L$ $S\ M_S \rightarrow$ all good	"Configuration" examples: B: $1s^2 2s^2 2p$ Mg: $1s^2 2s^2 2p^6 3s^2$ list of H-like single particle functions
residual electrostatic $H_{re} = \sum_i \left(\sum_{j>i} \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{ij}} - S(r_i) \right)$	lifts the degeneracy due to symmetry: lifts the S degeneracy	$[H_{re}, \vec{l}_i^2] \neq 0$ $L, S, M_L, M_S \rightarrow$ good	"Term" examples B: $1s^2 2s^2 2p \quad {}^2P$ Mg: $1s^2 2s^2 2p^6 3s^2 \quad {}^1S$
Spin Orbit: $H_{SO} = \sum_i \beta_i \vec{s}_i \cdot \vec{l}_i$ $= \beta_{SO} \vec{S} \cdot \vec{L}$	lifts degeneracy between states with different J when $L \neq 0$ and $S \neq 0$ $\vec{J} = \vec{L} + \vec{S}$	$[H_{SO}, \vec{L}^2] \neq 0$ $[H_{SO}, \vec{S}^2] \neq 0$ $[H_{SO}, \vec{J}^2] = 0 \quad \overset{\text{good}}{J, M_J}$	"Level" examples B: $1s^2 2s^2 2p \quad {}^2P_{1/2}, {}^2P_{3/2}$ Mg: $1s^2 2s^2 2p^6 3s^2 \quad {}^1S_0$ Mg*: $1s^2 2s^2 2p^6 3s 3p$ ${}^3P_0 \ {}^3P_1 \ {}^3P_2$
Hyperfine $H_{HFS} = A \vec{I} \cdot \vec{J}$ $\vec{I}$ = nuclear moment	Splits the degeneracy of J states with different I	$[H_{HFS}, \vec{J}^2] \neq 0$ $F, M_F \rightarrow$ good $\vec{F} = \vec{J} + \vec{I}$	Hyperfine state $\vert \beta F, M_F \rangle$ $\beta = 1s^2 2s^2 2p \quad {}^2P_{1/2}$ etc.

Look at spin-orbit interaction in Hydrogen (simplest case) this is also the first correction to the simple Hydrogen spectrum, because there are no other electrons.

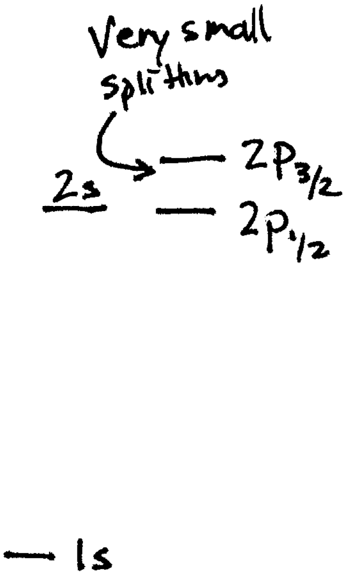
$$H_{so} = \beta \vec{S}\cdot\vec{l} \quad , \quad \beta = \frac{e^2}{2m^2c^2}\frac{1}{4\pi\epsilon_0}\left\langle \frac{1}{r^3}\right\rangle$$

$$[H_{so}, l^2] \neq 0 \quad [H_{so}, S^2] \neq 0 \quad [H_{so}, J^2] = 0 \quad \rightarrow J \text{ \& } m_j \text{ are good quantum \#'s}$$

$$\hat{\vec{J}} = \hat{\vec{l}} + \hat{\vec{S}} \qquad \hat{\vec{J}}^2 = \hat{\vec{l}}^2 + \hat{\vec{S}}^2 + 2\hat{\vec{l}}\cdot\hat{\vec{S}}$$

$$\vec{S}\cdot\vec{l} = \frac{1}{2}\left(\hat{\vec{J}}^2 - \hat{\vec{l}}^2 - \hat{\vec{S}}^2\right)$$

So $$H_{so} = \frac{\beta}{2}\left(\hat{\vec{J}}^2 - \hat{\vec{l}}^2 - \hat{\vec{S}}^2\right)$$



if H_{so} is very small, then l ans S are almost good quantum #s, use perturbation theory to calculate the energy shift.

example: $|J;ls\rangle$ states for 2p levels

$$|J=3/2; l=1, s=1/2\rangle , \quad |J=1/2; l=1, s=1/2\rangle$$

$$\langle 3/2; 1, 1/2 | H_{so} | 3/2; 1, 1/2\rangle = \frac{\beta\hbar^2}{2}\left(J(J+1) - l(l+1) - S(S+1)\right) = \frac{\beta\hbar^2}{2}$$

$$\langle 1/2; 1, 1/2 | H_{so} | 1/2; 1, 1/2\rangle = \frac{\beta\hbar^2}{2} \quad \text{''} \quad = -\beta\hbar^2$$

$$\Bigg\} \Delta E_{so} = \frac{3}{2}\beta\hbar^2 = J\beta\hbar^2$$

evaluating $\beta = \frac{e^2}{2m^2c^2} \frac{1}{4\pi\epsilon_0} \langle \frac{1}{r^3} \rangle$

for $n\ell$ states → $\beta = \frac{e^2}{2m^2c^2} \frac{1}{4\pi\epsilon_0} \left[\frac{1}{(na_0)^3} \frac{1}{\ell(\ell+\frac{1}{2})(\ell+1)} \right]$

for $s = 1/2$

$j = \ell \pm 1/2$ $\quad \Delta E_{so} = E_{so}(\ell + 1/2) - E_{so}(\ell - 1/2) = \beta\hbar^2 j_{max} = \beta\hbar^2(\ell + 1/2)$

$$\Delta E_{so} = E_0 \frac{\alpha^2}{n^3 \ell(\ell+1)} \qquad E_0 = 13.6\text{eV} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{2a_0}$$

$$E_{\text{Hydrogen}}(n) = \frac{-13.6\text{eV}}{n^2}$$

$$= \frac{\alpha^2}{n\,\ell(\ell+1)} |E_H(n)| \quad (\ell \neq 0)$$

→ spin orbit or fine structure is smaller than the gross Hydrogen structure by α^2, and the 2p states have the largest splitting.

What about systems with more than 1 electron?

→ the calculation depends on whether

Most common case → $H_{re} \gg H_{so}$. → L, S are pretty good quantum #s.

or

less common, usually at high Z → $H_{re} \ll H_{so}$ → $\vec{J}_1, \vec{J}_2 \cdots \vec{J}_n$ are pretty good quantum #s.