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
  \[ J = \int \frac{|U_a(1)^2| |U_b(2)^2|}{4\pi\epsilon_0 R_{12}} \, d^3r_1 \, d^3r_2 \]
  \[ \rightarrow \text{lifts} \ \mathcal{L} \ \text{degeneracy} \]

- Exchange energy shifts, in 1st order characterized by integral
  \[ K = \int \frac{U_a^*(1) U_a(2) U_b^*(2) U_b(1)}{4\pi\epsilon_0 R_{12}} \, d^3r_1 \, d^3r_2 \]
  \[ \rightarrow \text{parity dependent, therefore lifts the spin state degeneracy. But Note: the spin degeneracy is lifted by electrostatic interactions and Pauli symmetrization, not by magnetic spin-spin interactions.} \]
This gives energies that look like

\[
\begin{align*}
  &\frac{1s}{1s} \quad \frac{1s}{1s} \quad \frac{1s}{1s} \\
  &\frac{1s}{1s} \quad \frac{1s}{1s} \quad \frac{1s}{1s}
\end{align*}
\]

\[\Delta J = \frac{1s^2}{1s} \quad \frac{1s^2}{1s} \quad \frac{1s^2}{1s}
\]

\[\sqrt{\text{total}}\]

\[\text{para- Helium, anti-symmetric spin, symmetric space}
\]

\[\text{ortho helium, symmetric Spin, antisymmetric Space}
\]

\text{note: no } 1s^2 \quad 3s
\text{state exists due to Pauli exclusion!}

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

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

\[
H_0 = \sum_i \frac{p_i^2}{2m} - \frac{e^2}{4\pi\epsilon_0} \left( \frac{2}{r_i} + \frac{1}{r_i} \right)
\]

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

"residual electrostatic interaction"

move 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 it's a better description for larger \( l \) (due to the centrifugal 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

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

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

\[
E_0 = \frac{\epsilon^2}{4\pi \epsilon_0} \frac{1}{Zq_o} = \left( \frac{\epsilon^2}{4\pi \epsilon_0} \right)^2 \frac{m}{2\hbar^2}
\]

\[
\delta_l = 1.35 \quad \delta_p = 0.96 \quad \delta_d = 0.01 \quad \delta_s = 0.
\]

eg. for \( N_0 \)

\( n \geq 5 \)

Now go back to the general problem...
Extend this to multi-electron atoms:

\[
H = \sum_i \frac{p_i^2}{2m} - \frac{Ze^2}{\epsilon_0 r_i} + S(r_i) = \sum_{ij} \left( \frac{e^2}{\epsilon_0 r_{ij}} - S(r_i) \right)
\]

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 \( H_0 \) contributions.

One can also parameterize \( S(r) \) as

\[
S(r) = -\frac{Z(r)e^2}{\epsilon_0 r}, \quad \text{where} \quad Z(r) = \begin{cases} \frac{Z}{r} & r << a_0 \\ 1 & r >> a_0 \end{cases}
\]

In practice, the solution for \( S(r) \) and \( \Psi_i(r) \) are done self-consistently: pick a good guess for \( S(r) \), solve for \( \Psi_i(r) \), calculate the average potential created by \( \Psi_i(r) \) \( \Psi_j(r) \) \( \cdots \) \( \Psi_k(r) \), \( S'(r) \), solve for \( \Psi_i(r) \) etc. Called the Hartree-technique.

Very similar to Hydrogen -> radially symmetric potential!
for example:

$$S(r_i) = -\frac{Ze^2}{4\pi\epsilon_0 r_i} + \langle \sum_i \int \frac{e^2}{4\pi\epsilon_0 r_{ij}} \psi_i^* \psi_j \, d^3r_j \rangle$$

average over angles.

What about symmetry?

The Hartree method gives solutions of the form

$$\Psi = \prod_i \psi_i(r_i) \rightarrow \text{not symmetric.}$$

A way to symmetrize $N$ electron wavefunctions is given by the Slater determinant:

$$\Psi = \frac{1}{\sqrt{N!}} \left| \begin{array}{cccc} \psi_a(1) & \psi_a(2) & \cdots & \psi_a(N) \\ \psi_b(1) & \psi_b(2) & \cdots & \psi_b(N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_x(1) & \psi_x(2) & \cdots & \psi_x(N) \end{array} \right|$$

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

$$\Psi = \frac{1}{\sqrt{N!}} \sum_p (-1)^p \prod_{i=1}^N \psi_i(P_i)$$

where $p$ are permutations of $N$ objects.

Using $\Psi$ in the self-consistent solution is called the Hartree-Fock method. Parity operator

Can be very good! Since $[H_{\text{He}}, \hat{P}] = 0$,

we can find simultaneous eigenvalues of $H + \text{parity}$. 
What about the other, ignored terms in the Hamiltonian? A rough list of Contributions to $H_A$, in roughly decreasing orders of magnitude:

<table>
<thead>
<tr>
<th>H contribution</th>
<th>Degeneracy</th>
<th>Good quantum #'s</th>
<th>state labels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherically symmetric electrostatic (single-particle)</td>
<td>accounts for most of the &quot;direct&quot; integral, or screening. Lifts the degeneracy of states within a configuration that have different $l$.</td>
<td>$[H_{cf}, \vec{A}^2] = 0$</td>
<td>&quot;Configuration&quot; examples:</td>
</tr>
<tr>
<td>$H_{cf} = \sum_i \left( \frac{p_i^2}{2m} - \frac{Ze^2}{4\pi\epsilon_0 r_i} + S(r_i) \right)$</td>
<td>so $A_l, S_l, L, S$</td>
<td>$A = l, \ell, \ell, L, S$</td>
<td>B: $1s^22s^22p$</td>
</tr>
<tr>
<td>Residual electrostatic</td>
<td>lifts the degeneracy due to symmetry: lifts the $S$ degeneracy</td>
<td>$[H_{re}, \vec{L}_i^2] \neq 0$</td>
<td>Mg: $1s^22s^22p^63s^2$</td>
</tr>
<tr>
<td>$H_{re} = \sum_i \left( \sum_j \frac{e^2}{4\pi\epsilon_0 r_{ij}} - S(r_i) \right)$</td>
<td>$L, S, M_L, M_S \rightarrow$ good</td>
<td>$L, S, M_L, M_S \rightarrow$ good</td>
<td>1st of H-like single particle functions</td>
</tr>
<tr>
<td>Spin-orbit</td>
<td>lifts degeneracy between states with different $J$ when $L \neq 0$ and $S \neq 0$</td>
<td>$[H_{so}, \vec{L}^2] \neq 0$</td>
<td>&quot;Term&quot; examples:</td>
</tr>
<tr>
<td>$H_{so} = \sum_i \beta_i \vec{S}_i \cdot \vec{L}_i$</td>
<td>$\vec{J} = \vec{L} + \vec{S}$</td>
<td>$[H_{so}, \vec{S}^2] \neq 0$ good</td>
<td>B: $1s^22s^22p^2^2P$</td>
</tr>
<tr>
<td>$= \beta_{so} \vec{S} \cdot \vec{L}$</td>
<td>$[H_{so}, \vec{J}^2] = 0$ J, $M_J$</td>
<td>$[H_{so}, \vec{J}^2] = 0$</td>
<td>Mg: $1s^22s^22p^63s^21s$</td>
</tr>
<tr>
<td>Hyperfine</td>
<td>splits the degeneracy of $J$ states with different $I$</td>
<td>$[H_{HFS}, \vec{S}^2] \neq 0$</td>
<td>&quot;Level&quot; examples:</td>
</tr>
<tr>
<td>$H_{HFS} = A \vec{I} \cdot \vec{J}$</td>
<td>$F, M_F \rightarrow$ good</td>
<td>$[H_{HFS}, \vec{J}^2] \neq 0$</td>
<td>B: $1s^22s^22p^2^2P_{1/2}, ^2P_{3/2}$</td>
</tr>
<tr>
<td>$\vec{I} =$ nuclear moment</td>
<td>$F = \vec{J} + \vec{I}$</td>
<td>$\beta =$ $1s^22s^22p^2^2P_{1/2}$ etc.</td>
<td></td>
</tr>
</tbody>
</table>

\[ H_{HFS} = A \vec{I} \cdot \vec{J} \]
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 \beta = \frac{e^2}{2m_e^2c^2} \frac{1}{4\pi\varepsilon_0} \left\langle \frac{1}{r^3} \right\rangle

\[ [H_{SO}, \hat{L}^2] \neq 0 \quad [H_{SO}, \hat{S}^2] \neq 0 \quad [H_{SO}, \hat{J}^2] = 0 \rightarrow J \pm M_J \text{ are good quantum numbers} \]

\[ \hat{J} = \hat{l} + \hat{s} \]

\[ \hat{J}^2 = \hat{l}^2 + \hat{s}^2 + 2 \hat{l} \cdot \hat{s} \]

\[ \hat{s} \cdot \hat{l} = \frac{1}{2}(\hat{j}^2 - \hat{l}^2 - \hat{s}^2) \]

So

\[ H_{SO} = \beta \left( \frac{\hat{j}^2}{2} - \hat{l}^2 - \hat{s}^2 \right) \]

If \( H_{SO} \) is very small, then \( l \) and \( s \) are almost good quantum numbers, use perturbation theory to calculate the energy shift.

\[ \text{Example:} \quad \text{1s, 2s} \rightarrow \text{states for 2p levels} \]

\[ |J = \frac{3}{2}; \ell = 1, s = \frac{1}{2} \rangle, \quad |J = \frac{1}{2}; \ell = 1, s = \frac{1}{2} \rangle \]

\[ \langle \frac{3}{2}; \frac{1}{2} | H_{SO} | \frac{3}{2}; \frac{1}{2} \rangle = \frac{\beta k^2}{2} \left( J(J+1) - \ell(\ell+1) - S(S+1) \right) = \frac{\beta k^2}{2} \Delta E_{SO} = \frac{3}{2} \beta k^2 \]

\[ \langle \frac{1}{2}; \frac{1}{2} | H_{SO} | \frac{1}{2}; \frac{1}{2} \rangle = \frac{\beta k^2}{2} \]

\[ \Delta E_{SO} = \frac{3}{2} \beta k^2 \]

\[ = - \beta k^2 \]

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\[ \Delta E_{SO} = \frac{3}{2} \beta k^2 \]

\[ \Delta E_{SO} = \frac{3}{2} \beta k^2 \]
\[ \beta = \frac{e^2}{2m^2c^2} \frac{1}{\hbar^2} \langle \frac{1}{r^2} \rangle \]

for \( n \) \( l \) states \( \Rightarrow \beta = \frac{e^2}{2m^2c^2} \frac{1}{\hbar^2} \left[ \frac{1}{(n^3a_0)^3} \frac{1}{l(l+\frac{1}{2})}(l+\frac{1}{2}) \right] \)

for \( S = \frac{1}{2} \)
\[ j = l+\frac{1}{2} \quad \Delta E_{50} = E_{50}(l+\frac{1}{2}) - E_{50}(l-\frac{1}{2}) = \beta \hbar^2 j = \beta \hbar^2 \left( l + \frac{1}{2} \right) \]

\[ \Delta E_{50} = E_0 \frac{\alpha^2}{n^3 l(l+1)} \]
\[ E_0 = 13.6 \text{eV} = \frac{e^2}{4\pi \varepsilon_0} \frac{1}{2a_0} \]
\[ E_n = -\frac{13.6 \text{eV}}{n^2} \text{hydrogen} \]

\[ = \frac{\alpha^2}{n^3 l(l+1)} |E_n(n)| \quad (l \neq 0) \]

Spin orbit or fine structure is smaller than the gross hydrogen structure by \( \alpha^2 \), and the \( 2p \) states have the largest splitting.

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What about systems with more than 1 electron?

\( \Rightarrow \) the calculation depends on whether

Most common \( \Rightarrow H_{re} \gg H_{so} \quad \Rightarrow L, S \text{ are pretty good quantum } #s. \)

Less common \( \Rightarrow H_{re} \ll H_{so} \quad \Rightarrow \hat{J}_1, \hat{J}_2 \ldots \hat{J}_n \text{ are pretty good quantum } #s. \)