Lessons from He $(z=2)$ atom:

if we ignore $e-e$ repulsion [equivalent in solar system context to ignoring Jupiter-Earth attraction] the resulting Hamiltonian in this non-interacting system breaks into sum of two Hamiltonians $\rightarrow E = E_1 + E_2 = \frac{-1}{2}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right) Z^2$

However its clear that for large orbits $(n_2 \gg 1)$ — and particularly the large ℓ orbits which avoid "coming" close to nucleus — the electrostatic force will be reduced because the positive charge on nucleus will be partially cancelled by surrounding cloud of negatively charged e^-. Thus an outer electron sees an effective central charge $Z_{eff} = Z-1$. Thus in our case $n_1=1$; $n_2 \gg 1$ an energy $= \frac{-1}{2}\left(Z^2 + \frac{(Z-1)^2}{n_2^2}\right)$

Hartree attempted to take account of the surrounding electron cloud by a "self-consistent" method. As a starting guess assume e^- in H-atom orbits; from $|\psi|^2$ calculate charge density. Recalculate V using central nucleus & surrounding negative cloud — re solve TISE for this potential; recalculate charge density etc. Continue until process produces consistent (steady) results. This process is put on firm mathematical foundation in "Hartree-Fock" method.

H.06.html & H.07.html [also text p 212] proceeds without the complex calculations of Hartree — Simply calculate $\langle H \rangle$ as an estimate of how the more complex calculations will come out. We do use properly "anti symmetric" Fermion states for the 2 electrons.

Consider ground state: $\psi_{1s}(r_1)\,\psi_{1s}(r_2)\,(\uparrow\downarrow - \downarrow\uparrow)\frac{1}{\sqrt{2}}$

Spacial states: $[\psi_{1s}(r_1)\,\psi_{2s}(r_2) \pm \psi_{1s}(r_2)\,\psi_{2s}(r_1)]$

$[\psi_{1s}(r_1)\,\psi_{2p}(r_2) \pm \psi_{1s}(r_2)\,\psi_{2p}(r_1)]$

matched with appropriate $\overset{antisymmetric}{\underset{symmetric}{}}$ spin states

Results

Triplet

$[\psi_{1s}(r_1)\psi_{2s}(r_2) - \psi_{1s}(r_2)\psi_{2s}(r_1)]\uparrow\uparrow$ ^3S "orthohelium"

$[\psi_{1s}(r_1)\psi_{2p}(r_2) - \psi_{1s}(r_2)\psi_{2p}(r_1)]\uparrow\uparrow$ ^3P

Singlet

$[\psi_{1s}(r_1)\psi_{2s}(r_2) + \psi_{1s}(r_2)\psi_{2s}(r_2)](\uparrow\downarrow - \downarrow\uparrow)\frac{1}{\sqrt{2}}$ ^1S "parahelium"

$[\psi_{1s}(r_1)\psi_{2p}(r_2) + \psi_{1s}(r_2)\psi_{2p}(r_2)](\uparrow\downarrow - \downarrow\uparrow)\frac{1}{\sqrt{2}}$ ^1P

$-.495$ ^1P —

$-.509$ ^1S —   — ^3P $-.512$

                             — ^3S $-.531$

These results are not particulaly accurate [splittings off by factor of 2; in fact ^1S below ^3P] but we nevertheless generalize:

① High spin states – because they are symmetric – force the spacial state to be antisymmetric which produces larger separation between e^- & hence less repulsive energy → high spin ⟹ lower energy

② orbits with same n (same semimajor axis) but different l ($l\uparrow$ ⟹ more circular, less eccentric)

Small l large l

The larger l state will experience more electron cloud shielding hence smaller Z_{eff}, hence large E

$n=3$ — s   — p   — d   "l-tilt"

→ In comparing electron "configurations" with same n but different l; smaller l ⟹ lower energy

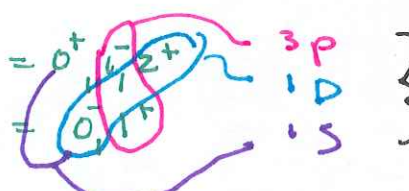→ the n^2 degeneracy of H-atom ($3s, 3p, 3d$ degenerate) is "broken" in multi-electron atoms

Hunds rules for Russell-Saunders (RS) aka LS coupling
→ determine total orbital angular momentum & total Spin
angular momentum first, then couple these to get
total total angular momentum

[contrast $j\delta$ coupling: first add each electron's
orbital angular momentum to its spin then add
up these to get total total angular momentum]

① Max S
② Max L
③ if ≤ half full   minimize J (otherwise max J)

Examples:

Boron — one valence electron : $2p \to$ $^2P_{1/2}$ ($^2P_{3/2}$ above)

Carbon — $2p^2$: $\overrightarrow{1+1} = 0^+, 1, 2^+$ ^3P } reverse for low
  $\overrightarrow{\frac{1}{2}+\frac{1}{2}} = 0, 1$ ^1D order
  ^1S
  $gs = {}^3P_0$

Nitrogen — $2p^3$ — look at table for allowed terms
  → slater det of 3 distinct p orbitals
  $2p$ $^2D, {}^4S$ with $\uparrow\uparrow\uparrow$
  $gs = {}^4S_{3/2}$

Oxygen — $2p^4$ — deal with holes! like C except $^3P_2$

Fluorine — $2p^5$ — like B except flip J: $^2P_{3/2}$

Neon — $2p^6$ — closed shell $^1S_0$

Sodium — $3s$ — $^2S_{1/2}$

Magnesium — $3s^2$ — closed shell $^1S_0$

Ti — $3d^2$ $\overrightarrow{2+2} = 0^+, 1^-, 2^+, 3^-, 4^+$ $^3F, {}^3P$
  $\overrightarrow{\frac{1}{2}+\frac{1}{2}} = 0^-, 1^+$ $\Rightarrow {}^1S, {}^1D, {}^1G$
  gs $^3F_2$

Periodic table with labels: *n* (blue, left column for rows 1–7), *ns* (green bracket over H–He columns), *np* (green bracket over B–Ne columns), (n−1)d (green bracket over transition metals), (n−2)f (green bracket over lanthanides/actinides).

n																		
1	H	He																
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt									

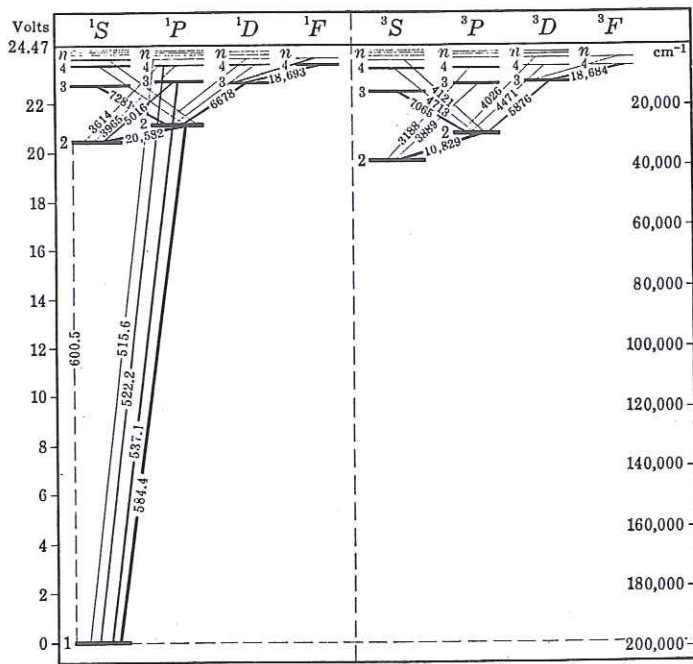| La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No

Fig. 27. **Energy Level Diagram for Helium.** The running numbers and true principal quantum numbers of the emission electron are here identical. The series in the visible and near ultraviolet regions correspond to the indicated transitions between terms with $n \geqq 2$.
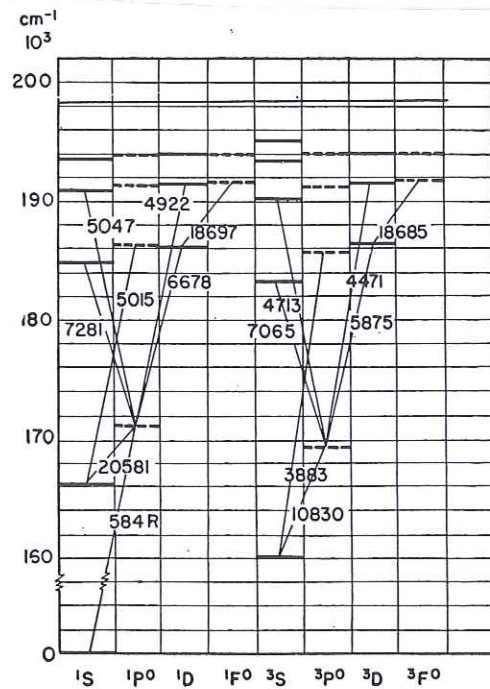

FIG. 7c-1. Energy-level diagram of He I—simplest atom with two valence electrons. The wavelengths of the principal lines are indicated.