Sec. 5.1.3. Now all together: the space dependence **and** the spin (still in 1D for simplicity)

$$\psi_S(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) + \psi_b(x_1)\psi_a(x_2)]$$

$$\psi_{AS}(\mathbf{r}_1,\mathbf{r}_2) = \frac{1}{\sqrt{2}}[\psi_a(x_1)\psi_b(x_2) - \psi_b(x_1)\psi_a(x_2)]$$

$$\chi_S(\mathbf{S}_1,\mathbf{S}_2) = \frac{1}{\sqrt{2}}(\uparrow_1\downarrow_2 + \downarrow_1\uparrow_2) \qquad \chi_{AS}(\mathbf{S}_1,\mathbf{S}_2) = \frac{1}{\sqrt{2}}(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2)$$

For 2 electrons (i.e. fermions) in two different states:

$\Psi = \psi_S(\mathbf{r}_1,\mathbf{r}_2)\,\chi_{AS}(\mathbf{S}_1,\mathbf{S}_2)$ OK!

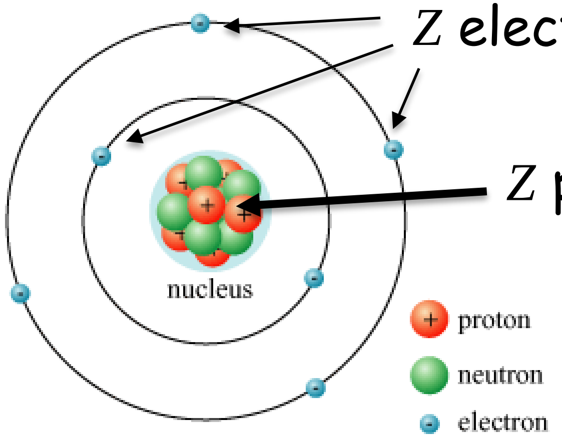
$\Psi = \psi_{AS}(\mathbf{r}_1,\mathbf{r}_2)\,\chi_S(\mathbf{S}_1,\mathbf{S}_2)$ OK!

$\Psi = \psi_S(\mathbf{r}_1,\mathbf{r}_2)\,\chi_S(\mathbf{S}_1,\mathbf{S}_2)$ NO

$\Psi = \psi_{AS}(\mathbf{r}_1,\mathbf{r}_2)\,\chi_{AS}(\mathbf{S}_1,\mathbf{S}_2)$ NO

If $a=b$, then **only** $\Psi = \psi_S(\mathbf{r}_1,\mathbf{r}_2)\,\chi_{AS}(\mathbf{S}_1,\mathbf{S}_2)$ is possible (Pauli).

5.2 Atoms



The Hamiltonian is:

$$H = \sum_{j=1}^{Z}\left\{-\frac{\hbar^2}{2m}\nabla_j^2 - \left(\frac{1}{4\pi\epsilon_0}\right)\frac{Ze^2}{r_j}\right\} + \frac{1}{2}\left(\frac{1}{4\pi\epsilon_0}\right)\sum_{j\neq k}^{Z}\frac{e^2}{|\mathbf{r}_j - \mathbf{r}_k|}$$

one-body e-p attraction
"the easy part"

e-e repulsion
"the difficult part"

Solving exactly is impossible ☹

$$H\ \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z)\chi(\mathbf{s}_1, \mathbf{s}_2, \ldots, \mathbf{s}_Z) =$$

$$= E\ \psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z)\chi(\mathbf{s}_1, \mathbf{s}_2, \ldots, \mathbf{s}_Z)$$

No **r** dependence here

In writing the Sch Eq we assumed that the spins may be coupled among themselves and/or with a **uniform** magnetic field, but the spin orientation does not depend on position.

Because electrons are fermions, the entire wave function must be **antisymmetric.**

5.2.1 Helium (Z=2)

$$H = \left\{ -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1} \right\} + \left\{ -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_2} \right\} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}$$

First, neglect the e-e repulsion
(on page 322, Ch 8, we will improve on this)

The space-like portion of the wave function in general will be (before symmetrization):

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2)$$

$$E = 4(E_n + E_{n'})$$

For **ground state**, we place both electrons at n=1, l=0, m=0.

$$E_n = -\left[\frac{m}{2\hbar^2}\left(\frac{2e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}$$

$$\psi_0(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) = \frac{8}{\pi a^3}e^{-2(r_1+r_2)/a}$$

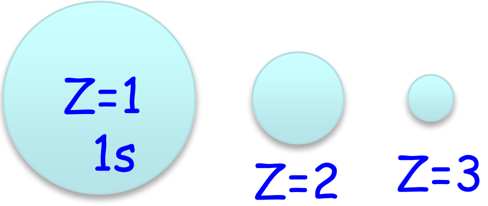
$$E_0 = 8(-13.6 \text{ eV}) = -109 \text{ eV}$$

$4+4 = 2^2+2^2$

Rapidly with increasing Z, big energies are induced!

-109 eV with Z=2 vs -13.6 eV with Z=1

Bohr radius reduced by factor 2;
in general by a factor Z.



Some consequences of AS vs S:

Because the full wave function has a "space portion" and a "spin portion", the first excited states of He have two possibilities

$$\Psi_{2e} = \psi_S(\mathbf{r}_1,\mathbf{r}_2)\ \chi_{AS}(\mathbf{S}_1,\mathbf{S}_2)$$

$$\Psi_{2e} = \psi_{AS}(\mathbf{r}_1,\mathbf{r}_2)\ \chi_S(\mathbf{S}_1,\mathbf{S}_2) \longleftarrow$$

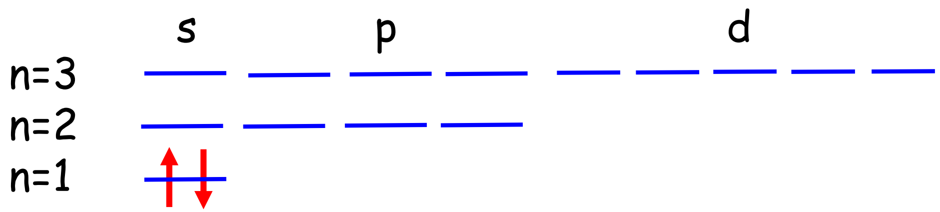
First excited state is triplet S=1

then, with all other things equal, the thus-far ignored e-e repulsion, that has nothing to do with spin, prefers the AS space portion because electrons are further apart than in the S space portion (see page 211). Confirmed experimentally that the first excited state has spin 1.

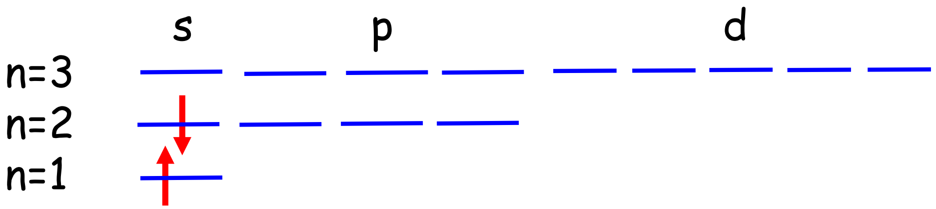
Now repeating using the Chemistry class cartoons: The space portion is symmetric, thus the spin portion must be antisymmetric.

$$\psi = \psi(\mathbf{r}_1, \mathbf{r}_2)\,\chi(\mathbf{s}_1, \mathbf{s}_2) = \frac{8}{\pi a^3} e^{-2(r_1+r_2)/a}\ \frac{1}{\sqrt{2}}(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2)$$

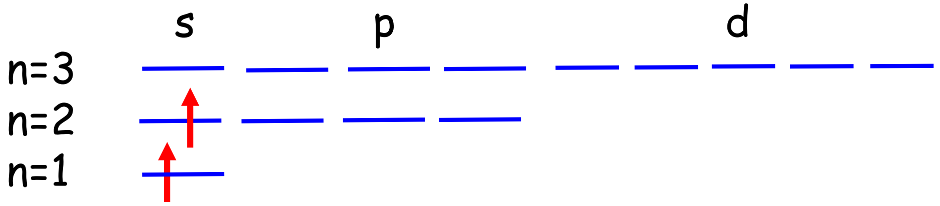
The ground state cartoon version is:



Excited states?



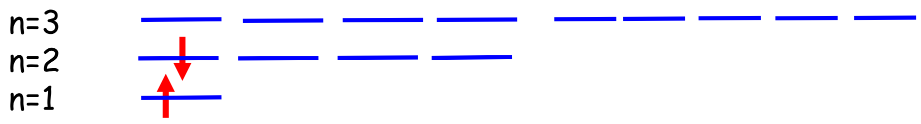
Singlet



Triplet

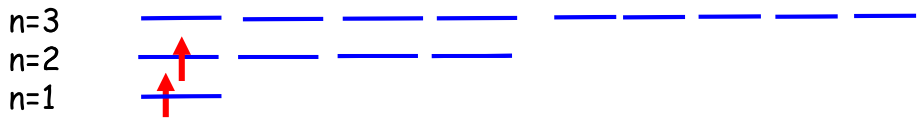
This portion is repeated: Excited states? Two options

…



$$\Psi_{singlet} = \psi_S(\mathbf{r}_1,\mathbf{r}_2)\,\chi_{AS}(\mathbf{S}_1,\mathbf{S}_2) =$$

$$= \frac{1}{\sqrt{2}}[\psi_{100}(\mathbf{r}_1)\psi_{200}(\mathbf{r}_2)+\psi_{200}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)] \quad \frac{1}{\sqrt{2}}(\uparrow_1\downarrow_2 - \downarrow_1\uparrow_2)$$



$$\Psi_{triplet} = \psi_{AS}(\mathbf{r}_1,\mathbf{r}_2)\,\chi_{S}(\mathbf{S}_1,\mathbf{S}_2) =$$

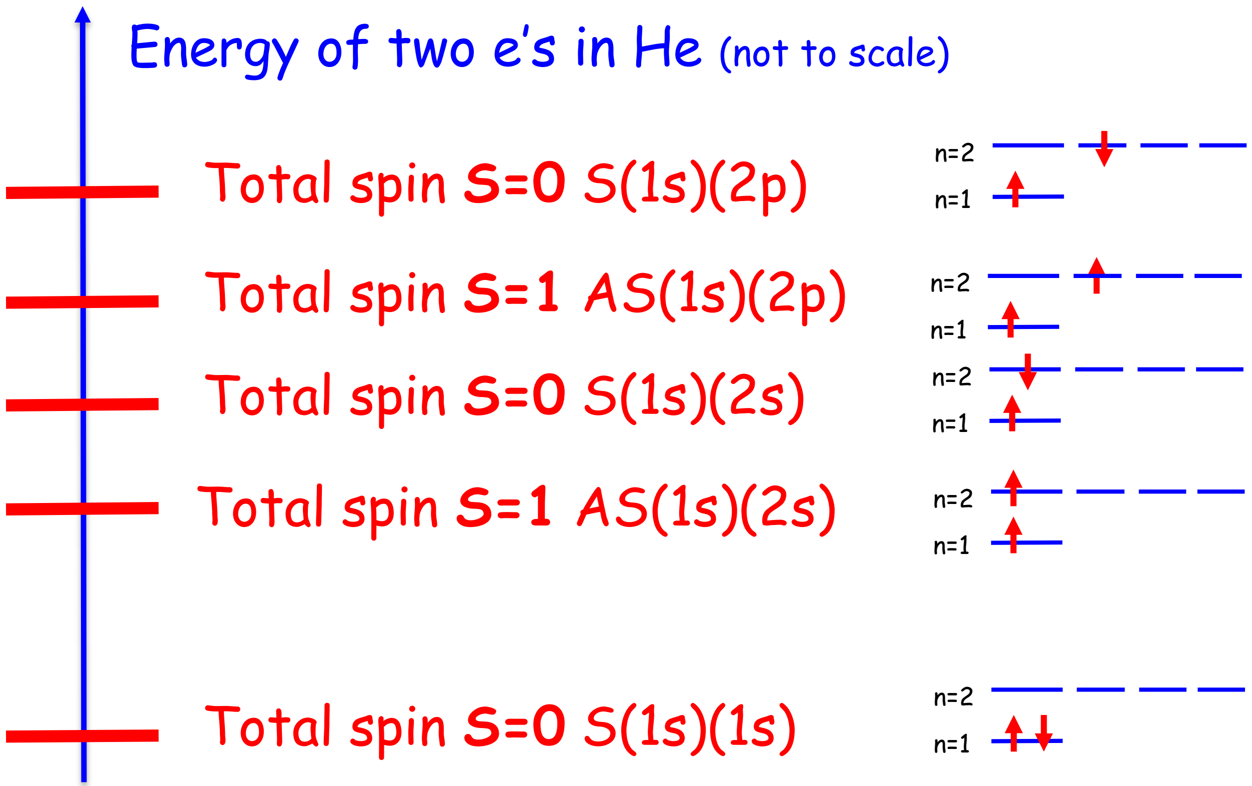
$$= \frac{1}{\sqrt{2}}[\psi_{100}(\mathbf{r}_1)\psi_{200}(\mathbf{r}_2)-\psi_{200}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)] \quad \frac{1}{\sqrt{2}}(\uparrow_1\downarrow_2 + \downarrow_1\uparrow_2)$$

If e-e neglected, then singlet
and triplet are degenerate

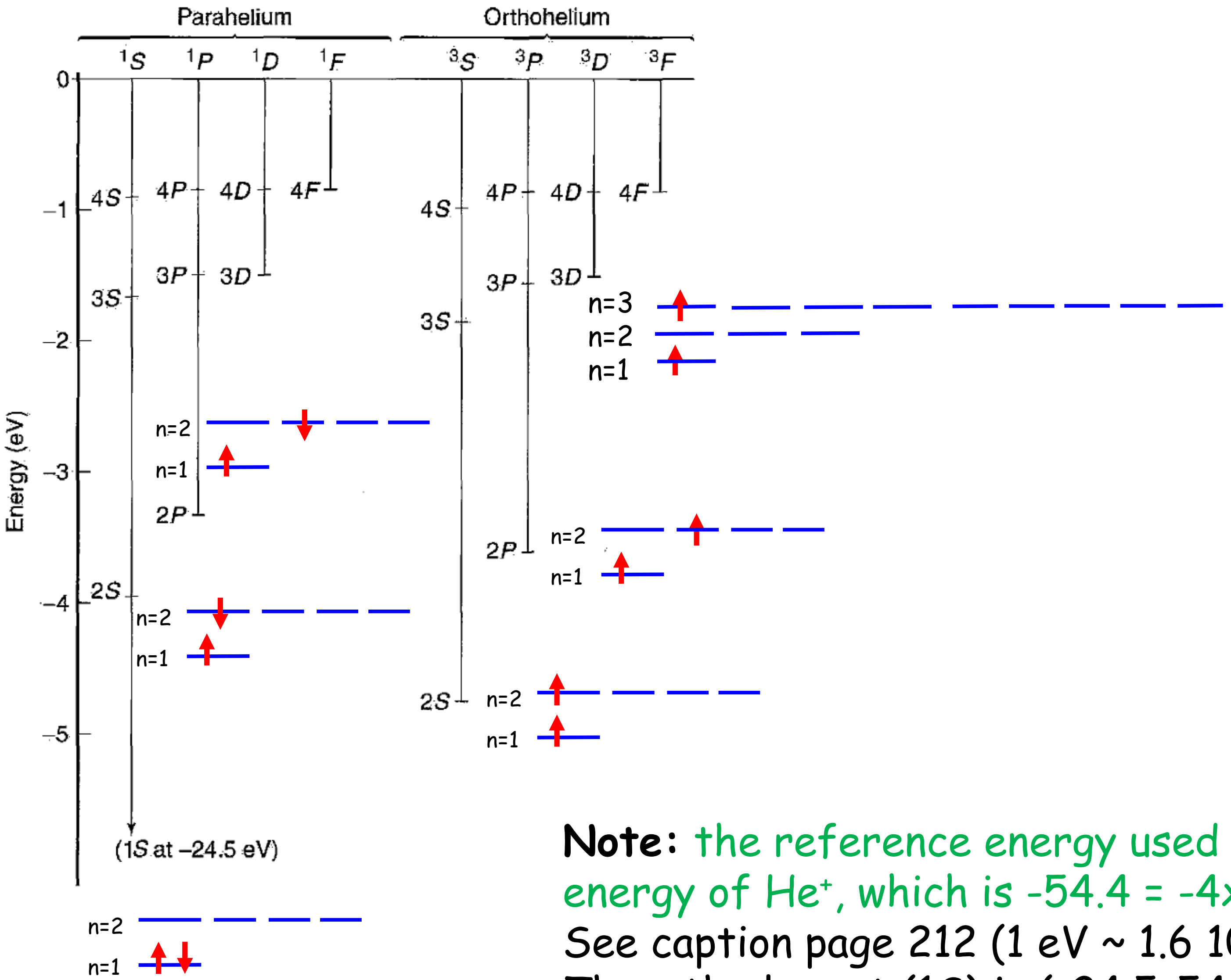
If e-e is brought back, at least qualitatively, then the degeneracy must be broken

Due to the effective "exchange forces", the AS space-like combination keeps the two electrons a bit further apart … (for AS sector the exchange force is "repulsive"; for S sector is "attractive")

Then, the energy levels for two electrons is:

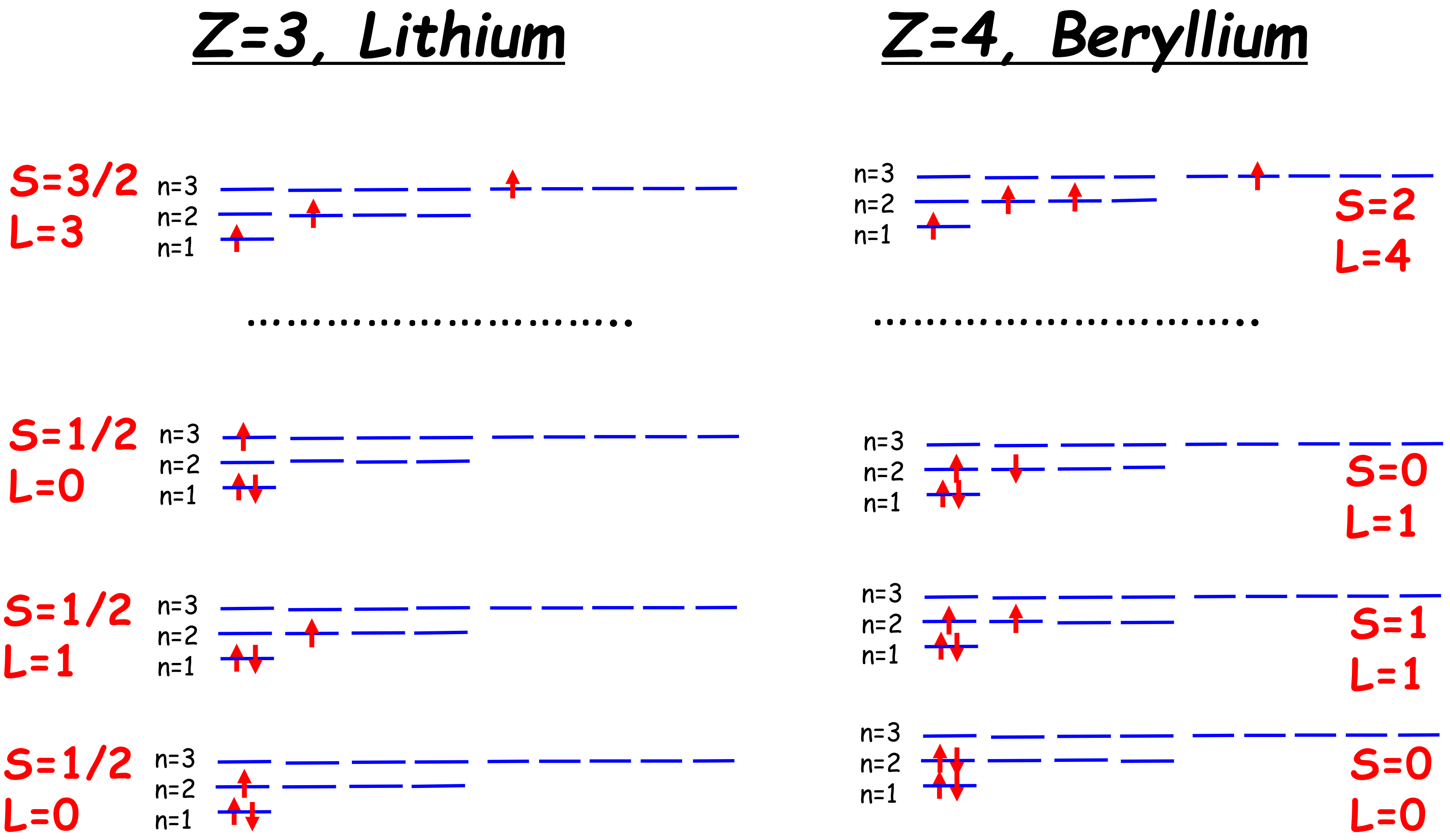


Real numbers from book



Note: the reference energy used is the energy of He^+, which is -54.4 = -4x(13.6) eV. See caption page 212 (1 eV ~ 1.6 10^{-19} J). Thus, the lowest (1S) is (-24.5-54.4) eV, etc. compared with -109 eV dropping e-e repul.

Not in book, excited states



The excited states become complicated very fast!