

Helium and exchange symmetry

- Atoms with 2 valence electrons: He and the group II element (second column in the periodic table) – Beryllium Magnesium, Calcium, etc.
- These atoms have exchange energy.
- We shall use He as an example.

Exchange symmetry:

- Consider a multi electron atom with N electrons:
- The wave function – depends on the coordinates of the electrons:

$$\Psi \equiv \Psi(r_1, r_2, \dots, r_K, r_L, \dots, r_N)$$

- Electrons are indistinguishable. The many electrons wave function must have exchange symmetry:

$$\begin{aligned} & |\Psi(r_1, r_2, \dots, r_K, r_L, \dots, r_N)|^2 \\ &= |\Psi(r_1, r_2, \dots, r_L, r_K, \dots, r_N)|^2 \end{aligned}$$

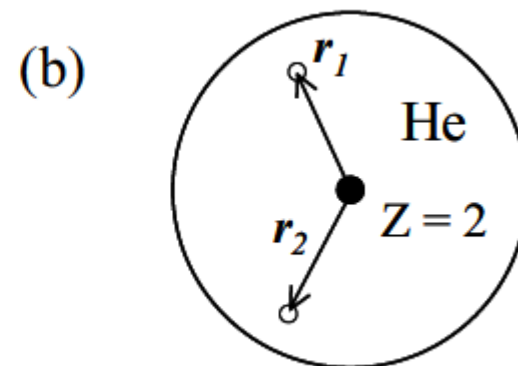
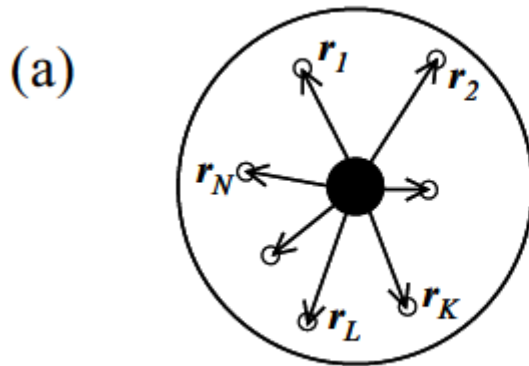
Thus the wavefunction will be either symmetric or antisymmetric:

$$\Psi(r_1, r_2, \dots, r_K, r_L, \dots, r_N) = \pm \Psi(r_1, r_2, \dots, r_L, r_K, \dots, r_N)$$

- + sign bosons; - sign Fermions
- Electrons with spin $\frac{1}{2}$ are Fermions. The anti symmetric wavefunction is the basis for the Pauli exclusion principle,

Helium wavefunctions:

- The He wavefunction is a multielectron atom with $n=2$.



- The wavefunction is a multiplication of the spatial and the spin wavefunctions:

$$\Psi = \psi_{\text{spatial}}(r_1, r_2) \psi_{\text{spin}}$$

The total wavefunction must be antisymmetric.

- There are 2 possible combinations:
Recall: Both the spatial and the spin wavefunction, are multiplications of 2 single electron wavefunctions.

ψ_{spatial}	ψ_{spin}
symmetric	anti-symmetric ($S = 0$)
anti-symmetric	symmetric ($S = 1$)

The spin wavefunctions are dependent on S :

- The triplet wavefunctions are symmetric
- The singlet wavefunction is antisymmetric:

Spin wave function	symmetry	M_S
$\uparrow_1 \uparrow_2$	+	+1
$\frac{1}{\sqrt{2}}(\uparrow_1 \downarrow_2 + \downarrow_1 \uparrow_2)$	+	0
$\frac{1}{\sqrt{2}}(\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2)$	-	0
$\downarrow_1 \downarrow_2$	+	-1

- The second WF belongs to a triplet. The third is a singlet.

The orbital wavefunction:

- The ground state is $1s^2$ – necessarily symmetric.
- In the excited states one or 2 electrons are in a higher state – characterized by n, l :
- The spatial part of He wavefunctions has the form: $u_A(\mathbf{r}_1) u_B(\mathbf{r}_2)$
- In which A, B marks a pair of n, l values.
- Thus the spatial wave function (with exchange) is:

$$\psi_{AB}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left(u_A(\mathbf{r}_1) u_B(\mathbf{r}_2) \pm u_B(\mathbf{r}_1) u_A(\mathbf{r}_2) \right)$$

Cont.

- $1/\sqrt{2}$ is a normalization factor, +, - refer to symmetric and antisymmetric wavefunction, respectively.
- Thus, the total wavefunction must be the multiplication of the spatial and the spin parts:

S	M_S	ψ_{spin}	ψ_{spatial}
0	0	$\frac{1}{\sqrt{2}}(\uparrow_1 \downarrow_2 - \downarrow_1 \uparrow_2)$	$\frac{1}{\sqrt{2}}(u_A(r_1)u_B(r_2) + u_B(r_1)u_A(r_2))$
1	+1	$\uparrow_1 \uparrow_2$	$\frac{1}{\sqrt{2}}(u_A(r_1)u_B(r_2) - u_B(r_1)u_A(r_2))$
	0	$\frac{1}{\sqrt{2}}(\uparrow_1 \downarrow_2 + \downarrow_1 \uparrow_2)$	
	-1	$\downarrow_1 \downarrow_2$	

The spin and the spatial parts of the wavefunction – are **not** independent!!!

- The Pauli exclusion principle: In the ground state two electrons in $1s^2$
- In the spatial wavefunction, when A and B are identical – The asymmetric wave function is zero.
- This is a demonstration of the Pauli exclusion principle, and the rule (connected to Hund's law) that $L+S$ must be even. (when $L=0$, $S=1$ – is not allowed)
- Namely S must be 0 – singlet state.

Slater determinants

- The antisymmetric wave function can be written as a determinant:

$$\psi_{\text{spatial}} = \frac{1}{\sqrt{2}} \begin{vmatrix} u_A(\mathbf{r}_1) & u_A(\mathbf{r}_2) \\ u_B(\mathbf{r}_1) & u_B(\mathbf{r}_2) \end{vmatrix}$$

- This can be generalized in atoms with many electrons to:

$$\Psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_\alpha(1) & u_\alpha(2) & \cdots & u_\alpha(N) \\ u_\beta(1) & u_\beta(2) & \cdots & u_\beta(N) \\ \vdots & \vdots & \ddots & \vdots \\ u_\nu(1) & u_\nu(2) & \cdots & u_\nu(N) \end{vmatrix}$$

- The determinant is 0 if 2 rows are equal.

The exchange energy:

- For He atom, the Hamiltonian is: (not including fine structure).

$$\hat{H} = \left(-\frac{\hbar^2}{2m} \nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} \right) + \left(-\frac{\hbar^2}{2m} \nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} \right) + \frac{e^2}{4\pi\epsilon_0 r_{12}};$$

- The Coulomb repulsion terms were treated before by the central field approximation.
- In He there is one such term. this enables a more systematic solution: Generally speaking the energy is given by the expectation value:

$$\langle E \rangle = \int \int \psi_{\text{spatial}}^* \hat{H} \psi_{\text{spatial}} d^3 r_1 d^3 r_2$$

For He, the Hamiltonian Is split

- As:
$$\hat{H} = \hat{H}_1 + \hat{H}_2 + \hat{H}_{12} ;$$

- Where:
$$\hat{H}_i = -\frac{\hbar^2}{2m} \nabla_i^2 - \frac{2e^2}{4\pi\epsilon_0 r_i}$$

and
$$\hat{H}_{12} = \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_1 - \mathbf{r}_2|}$$

The energy is split to 3:

$$E = E_1 + E_2 + E_{12}$$

$$E_i = \int \int \psi_{\text{spatial}}^* \hat{H}_i \psi_{\text{spatial}} d^3 r_1 d^3 r_2$$

and
$$E_{12} = \int \int \psi_{\text{spatial}}^* \hat{H}_{12} \psi_{\text{spatial}} d^3 r_1 d^3 r_2$$

The first 2 terms are the hydrogenic energy terms:

- Namely: $E_1 + E_2 = -\frac{4R_H}{n_1^2} - \frac{4R_H}{n_2^2}$
- The third term is the coulomb repulsion energy:

$$E_{12} = \int \int \psi_{\text{spatial}}^* \frac{e^2}{4\pi\epsilon_0 r_{12}} \psi_{\text{spatial}} d^3 r_1 d^3 r_2$$

- Detailed evaluation of the exchange integral:
We restrict ourselves to terms: $(1s, nl)$
that include the excited states. Since we are interested in spectroscopy.

The spatial part of the wavefunction:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left(u_{1s}(\mathbf{r}_1) u_{nl}(\mathbf{r}_2) \pm u_{nl}(\mathbf{r}_1) u_{1s}(\mathbf{r}_2) \right)$$

- The + sign related to singlet (S=0) and the – sign to triplet (S=1).
- First we evaluate H_1 :

$$\begin{aligned} E_1 &= \int \int \Psi^* \hat{H}_1 \Psi d^3 r_1 d^3 r_2 \\ &= \frac{1}{2} \int \int \left(u_{1s}^*(\mathbf{r}_1) u_{nl}^*(\mathbf{r}_2) \pm u_{nl}^*(\mathbf{r}_1) u_{1s}^*(\mathbf{r}_2) \right) \\ &\quad \hat{H}_1 \left(u_{1s}^*(\mathbf{r}_1) u_{nl}^*(\mathbf{r}_2) \pm u_{nl}^*(\mathbf{r}_1) u_{1s}^*(\mathbf{r}_2) \right) d^3 r_1 d^3 r_2 \end{aligned}$$

The integral splits to 4 separate integrals:

- Opening the parentheses

$$\begin{aligned} E_1 &= \frac{1}{2} \int \int u_{1s}^*(\mathbf{r}_1) u_{nl}^*(\mathbf{r}_2) \hat{H}_1 u_{1s}(\mathbf{r}_1) u_{nl}(\mathbf{r}_2) d^3 r_1 d^3 r_2 \\ &+ \frac{1}{2} \int \int u_{nl}^*(\mathbf{r}_1) u_{1s}^*(\mathbf{r}_2) \hat{H}_1 u_{nl}(\mathbf{r}_1) u_{1s}(\mathbf{r}_2) d^3 r_1 d^3 r_2 \\ &\pm \frac{1}{2} \int \int u_{1s}^*(\mathbf{r}_1) u_{nl}^*(\mathbf{r}_2) \hat{H}_1 u_{nl}(\mathbf{r}_1) u_{1s}(\mathbf{r}_2) d^3 r_1 d^3 r_2 \\ &\pm \frac{1}{2} \int \int u_{nl}^*(\mathbf{r}_1) u_{1s}^*(\mathbf{r}_2) \hat{H}_1 u_{1s}(\mathbf{r}_1) u_{nl}(\mathbf{r}_2) d^3 r_1 d^3 r_2 \end{aligned}$$

Recall:

$u_{nl}(\mathbf{r}_1)$ is an eigenstate of \hat{H}_1

$$\hat{H}_1 u_{nl}(\mathbf{r}_1) = E_{nl} u_{nl}(\mathbf{r}_1)$$

and

\hat{H}_1 has no effect on \mathbf{r}_2 ,

$$\begin{aligned} E_1 &= \frac{1}{2} E_{1s} \int u_{1s}^*(\mathbf{r}_1) u_{1s}(\mathbf{r}_1) d^3 r_1 \int u_{nl}^*(\mathbf{r}_2) u_{nl}(\mathbf{r}_2) d^3 r_2 \\ &+ \frac{1}{2} E_{nl} \int u_{nl}^*(\mathbf{r}_1) u_{nl}(\mathbf{r}_1) d^3 r_1 \int u_{1s}^*(\mathbf{r}_2) u_{1s}(\mathbf{r}_2) d^3 r_2 \\ &\pm \frac{1}{2} E_{nl} \int u_{1s}^*(\mathbf{r}_1) u_{nl}(\mathbf{r}_1) d^3 r_1 \int u_{nl}^*(\mathbf{r}_2) u_{1s}(\mathbf{r}_2) d^3 r_2 \\ &\pm \frac{1}{2} E_{1s} \int u_{nl}^*(\mathbf{r}_1) u_{1s}(\mathbf{r}_1) d^3 r_1 \int u_{1s}^*(\mathbf{r}_2) u_{nl}(\mathbf{r}_2) d^3 r_2 \\ &= \frac{1}{2} E_{1s} + \frac{1}{2} E_{nl} + 0 + 0. \end{aligned}$$

Similarly for E_2 :

- We get:

$$\begin{aligned} E_2 &= \int \int \Psi^* \hat{H}_2 \Psi d^3 r_1 d^3 r_2, \\ &= +\frac{1}{2} \int \int u_{1s}^*(\mathbf{r}_1) u_{nl}^*(\mathbf{r}_2) \hat{H}_2 u_{1s}(\mathbf{r}_1) u_{nl}(\mathbf{r}_2) d^3 r_1 d^3 r_2 \\ &\quad +\frac{1}{2} \int \int u_{nl}^*(\mathbf{r}_1) u_{1s}^*(\mathbf{r}_2) \hat{H}_2 u_{nl}(\mathbf{r}_1) u_{1s}(\mathbf{r}_2) d^3 r_1 d^3 r_2 \\ &\quad \pm \frac{1}{2} \int \int u_{1s}^*(\mathbf{r}_1) u_{nl}^*(\mathbf{r}_2) \hat{H}_2 u_{nl}(\mathbf{r}_1) u_{1s}(\mathbf{r}_2) d^3 r_1 d^3 r_2 \\ &\quad \pm \frac{1}{2} \int \int u_{nl}^*(\mathbf{r}_1) u_{1s}^*(\mathbf{r}_2) \hat{H}_2 u_{nl}(\mathbf{r}_1) u_{1s}(\mathbf{r}_2) d^3 r_1 d^3 r_2 \\ &= +\frac{1}{2} E_{nl} + \frac{1}{2} E_{1s} + 0 + 0. \end{aligned}$$

Evaluation of the Column repulsion term:

- $$E_{12} = \int \int \Psi^* \frac{e^2}{4\pi\epsilon_0 r_{12}} \Psi d^3 r_1 d^3 r_2$$
$$= \frac{1}{2} \int \int \left(u_{1s}^*(\mathbf{r}_1) u_{nl}^*(\mathbf{r}_2) \pm u_{nl}^*(\mathbf{r}_1) u_{1s}^*(\mathbf{r}_2) \right) \frac{e^2}{4\pi\epsilon_0 r_{12}}$$
$$\left(u_{1s}^*(\mathbf{r}_1) u_{nl}^*(\mathbf{r}_2) \pm u_{nl}^*(\mathbf{r}_1) u_{1s}^*(\mathbf{r}_2) \right) d^3 r_1 d^3 r_2,$$

Again we get 4 integrals:

$$\begin{aligned}
 E_{12} &= +\frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \int u_{1s}^*(\mathbf{r}_1) u_{nl}^*(\mathbf{r}_2) \frac{1}{r_{12}} u_{1s}(\mathbf{r}_1) u_{nl}(\mathbf{r}_2) d^3r_1 d^3r_2 \\
 &+ \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \int u_{nl}^*(\mathbf{r}_1) u_{1s}^*(\mathbf{r}_2) \frac{1}{r_{12}} u_{nl}(\mathbf{r}_1) u_{1s}(\mathbf{r}_2) d^3r_1 d^3r_2 \\
 &\pm \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \int u_{1s}^*(\mathbf{r}_1) u_{nl}^*(\mathbf{r}_2) \frac{1}{r_{12}} u_{nl}(\mathbf{r}_1) u_{1s}(\mathbf{r}_2) d^3r_1 d^3r_2 \\
 &\pm \frac{1}{2} \frac{e^2}{4\pi\epsilon_0} \int \int u_{nl}^*(\mathbf{r}_1) u_{1s}^*(\mathbf{r}_2) \frac{1}{r_{12}} u_{1s}(\mathbf{r}_1) u_{nl}(\mathbf{r}_2) d^3r_1 d^3r_2 \\
 &= +\frac{D}{2} + \frac{D}{2} \pm \frac{J}{2} \pm \frac{J}{2},
 \end{aligned}$$

Where $D_{AB} = \frac{e^2}{4\pi\epsilon_0} \int \int u_A^*(\mathbf{r}_1) u_B^*(\mathbf{r}_2) \frac{1}{r_{12}} u_A(\mathbf{r}_1) u_B(\mathbf{r}_2) d^3r_1 d^3r_2$.

and: $J_{AB} = \frac{e^2}{4\pi\epsilon_0} \int \int u_A^*(\mathbf{r}_1) u_B^*(\mathbf{r}_2) \frac{1}{r_{12}} u_B(\mathbf{r}_1) u_A(\mathbf{r}_2) d^3r_1 d^3r_2$.

The total energy

- of the configuration (n_1l_1, n_2l_2)

$$E(n_1l_1, n_2l_2) = -\frac{4R_H}{n_1^2} - \frac{4R_H}{n_2^2} + D_{AB} \pm J_{AB}$$

- The exchange splitting is not small (in contrast to other spin related interactions).
- As an example J_{AB} for the first He excited state (1s2s configuration) is 0.8eV.

- **Recall:**

$$\psi_{AB}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} \left(u_A(\mathbf{r}_1) u_B(\mathbf{r}_2) \pm u_B(\mathbf{r}_1) u_A(\mathbf{r}_2) \right)$$

Looking at this formula:

- If we put $r_1=r_2$ we get $\psi_{\text{spatial}} = 0$ for the anti-symmetric wave function.

The two electrons have a low probability of coming close together in the triplet state – This reduce the Coulomb repulsion. In the singlet state the probability is larger – larger Coulomb repulsion.

The exchange energy is commonly written as:

- $\Delta E_{\text{exchange}} = -JS_1 \bullet S_2$
- Namely, when the spins are aligned (anti aligned) – the energy goes down (up).
- This explains ferromagnetism – The spins prefer to be parallel.
- The dipole - dipole interactions are negligible compared to the exchange interactions.

The He term diagram:

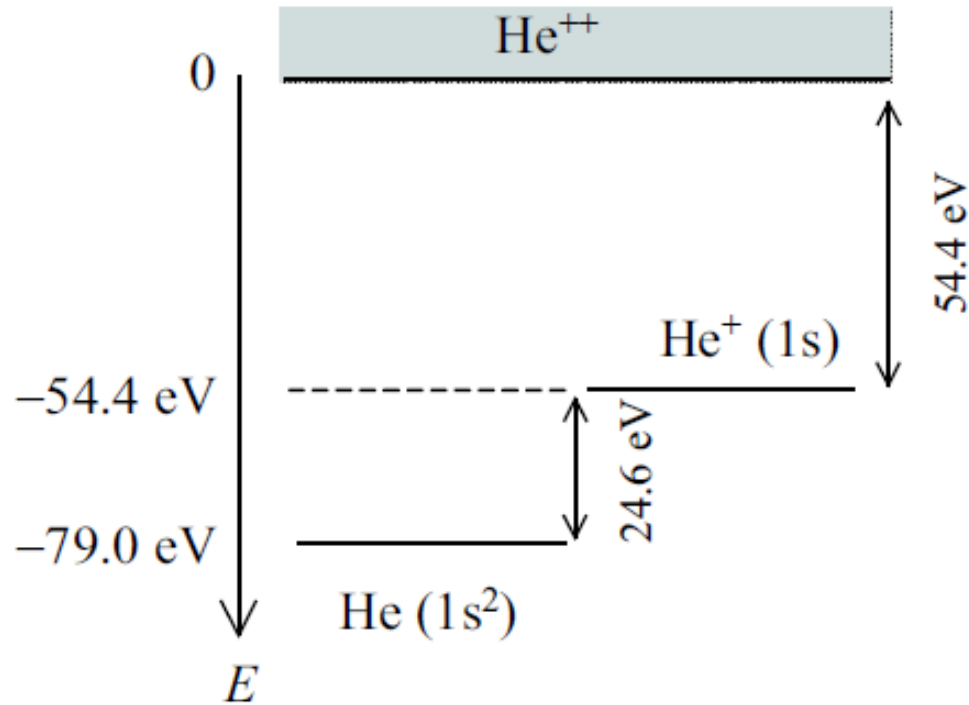
- Term can be evaluated if we know the direct and exchange Coulomb energies:
- The Ground state is the $1s^2$ term. It can be only in the $S=0$ configuration. Thus:

$$\begin{aligned} E(1s^2) &= -\frac{4R_H}{1^2} - \frac{4R_H}{1^2} + \left(D_{1s^2} + J_{1s^2} \right) \\ &= -54.4 \text{ eV} - 54.4 \text{ eV} + 29.8 \text{ eV} \\ &= -79.0 \text{ eV} . \end{aligned}$$

- The direct and exchange energies are determine from the first ionization potential.

ionization potentials:

- The excited states of He:



- After the first ionization, we are left with the hydrogenic atom $1S^1$ with energy $-Z^2 R_H = -54.4 \text{ eV}$ which is the second ionization potential.

Cont.

- This means that the ground state is -79 eV. Thus using

$$\begin{aligned} E(1s^2) &= -\frac{4R_H}{1^2} - \frac{4R_H}{1^2} + (D_{1s^2} + J_{1s^2}) \\ &= -54.4 \text{ eV} - 54.4 \text{ eV} + 29.8 \text{ eV} \\ &= -79.0 \text{ eV} . \end{aligned}$$

- We get $(D_{1s^2} + J_{1s^2}) = 29.8 \text{ eV}$.

Optical spectra of He:

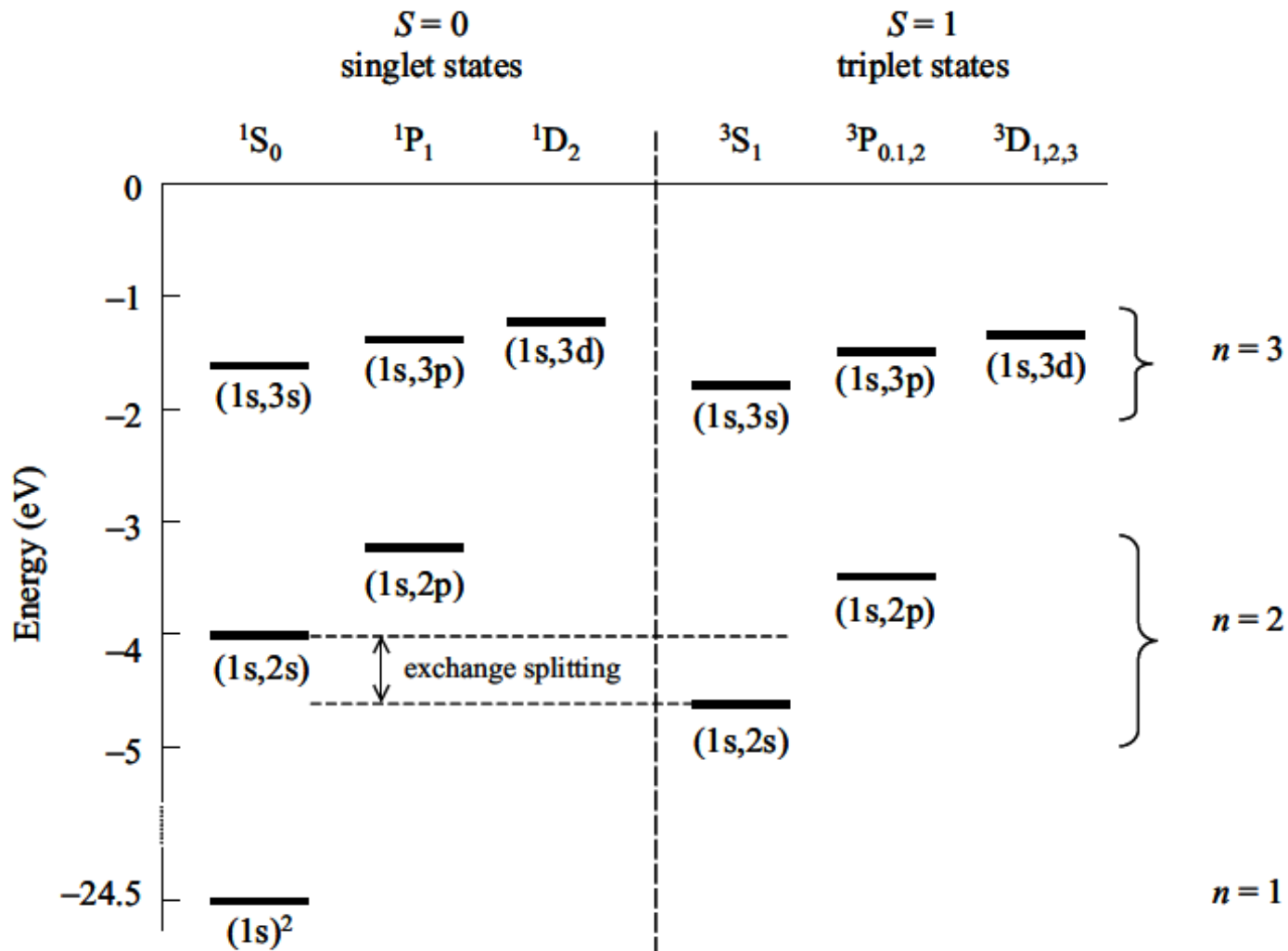
- We do not consider two electrons jump – into a $2s2s$ state. Such a jump will be into an energy $2 \times \frac{3}{4}R_H$ (-20.4eV) - larger than the first ionization energy) -54.4eV.

The excited states are given below:

Ground state	$1s\ 1s (\equiv 1s^2)$
First excited state	$1s\ 2s$
Second excited state	$1s\ 2p$
Third excited state	$1s\ 3s$
Fourth excited state	$1s\ 3p$
\vdots	
Ionization limit	$1s\ \infty l$

Each excited state has a singlet and triplet states ($S=0$; $S=1$)

- $S=0$ states – show the normal Zeeman effect



The energy terms approach $-R_h/n^2$

- Selection rules $\Delta S=0$ forbid transitions between singlet and triplet states.
- Relaxation from 2S to 1S is forbidden by the selection rule: $\Delta l=\pm 1$.
- Relaxation from the triplet 1S2S configuration is forbidden by the selection rule $\Delta S=0$.
- These states are metastable – very long relaxation times.
- These behavior is characteristic also to other atoms of group II element (Be, Mg. Ca)