

## Chapter 4: Multi-electron Atoms

4.1 Identical particles: bosons and fermions

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In this chapter, we delve into the foundational quantum physics of many-body systems, focusing specifically on helium and other multi-electron atoms. Key topics include the symmetry properties of many-body wave functions, the Pauli exclusion principle, singlet and triplet states in two spin-1/2 systems, exchange energy, electronic configurations, spectroscopic term symbols, and Hund's rules.

## 4.1 Identical particles: bosons and fermions

Fundamental particles, like the electron, are all identical, or indistinguishable. Therefore, a wave function  $\psi(\mathbf{r}_1, \mathbf{r}_2)$  of a quantum system of two identical spinless particles should have this property:

$$|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2 = |\psi(\mathbf{r}_2, \mathbf{r}_1)|^2, \quad (1)$$

i.e. the probability for the “first” to be at  $\mathbf{r}_1$  and the “second” to be at  $\mathbf{r}_2$  must be equal to the probability for the “first” to be at  $\mathbf{r}_2$  and the “second” to be at  $\mathbf{r}_1$ . In other words, if we can't tell “first” from “second”, the two probabilities must be equal. Eq. (1) indicates the following symmetry

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \pm \psi(\mathbf{r}_2, \mathbf{r}_1). \quad (2)$$

This symmetry of quantum many-body wave functions is another distinctive feature of quantum particles, absent in classical physics. It has significant implications, which we will explore later in this chapter and you will learn in quantum statistics in PHYS20352.

To incorporate spin (and/or other degrees of freedom), we use the notation  $x_1 = (\mathbf{r}_1, s_1)$  where  $s_1$  denotes the spin degree of freedom for particle 1, similarly  $x_2 = (\mathbf{r}_2, s_2)$  for particle 2. The particles with the property of the symmetric wave function,

$$\psi(x_1, x_2) = +\psi(x_2, x_1),$$

are called **bosons**, e.g. photons or helium-4 atoms. They have integer spin,  $s$ , e.g.  $s = 1$  for a photon. Particles with the antisymmetric wave function,

$$\psi(x_1, x_2) = -\psi(x_2, x_1),$$

are called **fermions**, e.g. electrons or hydrogen atoms. They have half-integer spin, as we have already seen for the electron with  $s = 1/2$ .

To extend the discussion to an  $N$ -particle system with a wave function

$$\psi = \psi(x_1, x_2, \dots, x_N),$$

exchange any pair of two coordinates  $x_i$  and  $x_j$  will produce + sign for a  $N$ -boson system and – sign for a  $N$ -fermion system.

We can also introduce the exchange operator  $\hat{P}$  (similar to that of parity) with the definition

$$\hat{P}\psi(x_1, x_2) = \psi(x_2, x_1), \quad (3)$$

and prove that  $\hat{P}$  has two eigenvalues  $\pm 1$ , see Examples 4 Q1.

## 4.2 Pauli exclusion principle

The starting point for studying a quantum many-body system is the **independent-particle approximation**, which assumes each particle's wave function is independent. Under this approach, the many-body wave function of the system is approximated as a product of single-body wave functions. For instance, the wave functions of a multi-electron atom are approximated as a product of hydrogen-like wave functions.

We first consider a system of two spinless particles with single-body wave functions  $\psi_\alpha(\mathbf{r})$  and  $\psi_\beta(\mathbf{r})$ , where  $\alpha$  and  $\beta$  are sets of quantum numbers fully describing the single-body state (e.g.  $(n, l, m_l)$  of a hydrogen wave function  $\psi_{n,l,m_l}$ ). One approximate state of the 2-body system is then given by the product

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2),$$

meaning that particle 1 is in (or occupies) the  $\alpha$ -state and particle 2 is in (or occupies) the  $\beta$  state. Since these two particles are identical, the state can also be represented in the reverse configuration. Now consider the symmetry requirement discussed in last section, we can use the symmetric combination

$$\psi^S(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2) + \psi_\alpha(\mathbf{r}_2)\psi_\beta(\mathbf{r}_1)], \quad \text{with } \psi^S(\mathbf{r}_1, \mathbf{r}_2) = \psi^S(\mathbf{r}_2, \mathbf{r}_1) \quad (4)$$

as an approximation for a two-boson system, and use the antisymmetric combination

$$\psi^A(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_\alpha(\mathbf{r}_1)\psi_\beta(\mathbf{r}_2) - \psi_\alpha(\mathbf{r}_2)\psi_\beta(\mathbf{r}_1)], \quad \text{with } \psi^A(\mathbf{r}_1, \mathbf{r}_2) = -\psi^A(\mathbf{r}_2, \mathbf{r}_1) \quad (5)$$

as an approximation for a two-fermion system. The factor  $1/\sqrt{2}$  is for the normalization purpose. Furthermore, we observe that for bosons, it is possible to choose the same one-body wave function; for instance,

$$\psi^S(\mathbf{r}_1, \mathbf{r}_2) = \psi_\alpha(\mathbf{r}_1)\psi_\alpha(\mathbf{r}_2).$$

This indicates that two or more bosons can occupy the same single-body state. For fermions, however, it is not possible to construct an antisymmetric wave function using a single one-body wave function. For example, if we set  $\alpha = \beta$ , we find:

$$\psi^A(\mathbf{r}_1, \mathbf{r}_2) = 0.$$

In other words, two fermions cannot occupy the same state simultaneously. This leads to the **Pauli exclusion principle**: a single state can be occupied by no more than one fermion.

Example of bosons: photon gas (black-body radiations), Helium-4 quantum liquid, dilute ultra-cold atomic gases (Lithium-6), etc. Bosons always have integer spin quantum, including zero, such as  $s = 0, 1, 2, 3$  etc.

Example of fermions: electrons in metals, Helium-3 quantum liquid, neutron stars, dilute ultra-cold atomic gases (Lithium-7), etc. Fermions always have half-odd-integer spin quantum, such as  $s = 1/2, 3/2, 5/2$  etc.

In general, systems of bosons and fermions exhibit fundamentally different behaviours. A bosonic system can undergo Bose-Einstein condensation at low temperatures, where many particles occupy the same lowest-energy state, leading to phenomena such as superfluidity. In contrast, a fermionic system cannot experience Bose-Einstein condensation directly. However, if fermions form pairs, these pairs behave like bosons and can exhibit superfluidity, as seen in phenomena such as superconductivity.

In this Year-2 course, however, we focus exclusively on multi-electron atoms, beginning with helium.

### 4.3 Helium atom

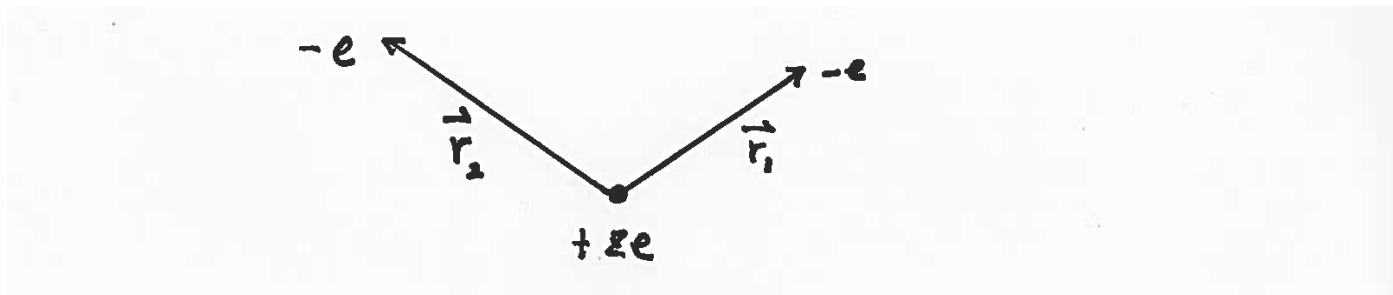


Figure 1: Helium atom.

We consider a nucleus of charge  $Ze$  and two electrons. Thus, for different  $Z$  values, this could correspond to a helium atom ( $Z = 2$ ) but also a  $\text{Li}^+$  or  $\text{Be}^{2+}$  ion. The Hamiltonian is given by, ignoring the spin-orbit interaction,

$$\hat{H} = \hat{H}_0 + \hat{V}(r_{12}), \quad (6)$$

where  $\hat{H}_0$  contains two separate hydrogen-like terms,

$$\hat{H}_0 = \hat{H}_1 + \hat{H}_2, \quad \hat{H}_i = \frac{\hat{p}_i^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r_i}, \quad i = 1, 2 \quad (7)$$

and  $\hat{V}$  is the Coulomb repulsion potential between the two electrons

$$\hat{V}(r_{12}) = \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_{12}}, \quad r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|, \quad (8)$$

where  $r_{12}$  is the separation between the two electrons.

**Exercise:** Show that the symmetric and antisymmetric wave functions given by Eqs. (4-5) with one-electron Hydrogen states (e.g.  $\psi_\alpha \rightarrow \psi_{n,l,m_l}$ ) are eigenfunctions of  $\hat{H}_0$ .

Before going further, we need to consider the effect of antisymmetrization of the wave function as electrons are fermions. We write our approximate wave function of  $\hat{H}$  of Eq. (6) in a separable form,

$$\Psi(\mathbf{r}_1, s_1; \mathbf{r}_2, s_2) = \psi(\mathbf{r}_1, \mathbf{r}_2) \chi(s_1, s_2), \quad (9)$$

i.e., a product of the orbital and spin wave functions since  $\hat{H}$  is spin-independent.  $\Psi$  has to be antisymmetric, but it could be  $\psi$  symmetric and  $\chi$  antisymmetric or  $\psi$  antisymmetric and  $\chi$  symmetric.

Let's consider the  $\chi$  part of the wave function. For a system of two electrons, the total spin quantum number  $S = 0, 1$  by the angular momentum addition theorem,  $S$  is the quantum number of the total spin  $\hat{\mathbf{S}} = \hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2$ . There are four eigenstates of total spin  $S$ :

(i) A single antisymmetric state (singlet), with  $S = 0$ ,

$$\chi^A(s_1, s_2) = \frac{1}{\sqrt{2}} [\chi_+(1)\chi_-(2) - \chi_-(1)\chi_+(2)]; \quad M_S = 0 \quad (10)$$

or, in Dirac notation

$$|\chi^A\rangle = \frac{1}{\sqrt{2}} (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle).$$

(ii) Three symmetric states (triplet) with  $S = 1$ ,

$$\begin{aligned} \chi_1^S(s_1, s_2) &= \chi_+(1)\chi_+(2), & M_S &= 1; \\ \chi_0^S(s_1, s_2) &= \frac{1}{\sqrt{2}} [\chi_+(1)\chi_-(2) + \chi_-(1)\chi_+(2)], & M_S &= 0; \\ \chi_{-1}^S(s_1, s_2) &= \chi_-(1)\chi_-(2), & M_S &= -1. \end{aligned}$$

The total electron spin can be measured and we call the singlet state with  $S = 0$  **parahelium** and the triplet states with  $S = 1$  **orthohelium**.

The orbital wave function  $\psi(\mathbf{r}_1, \mathbf{r}_2)$  will be constructed from single-electron states, i.e.

$$\begin{aligned}\psi_{1s}(\mathbf{r}) &= \psi_{1,0,0}(\mathbf{r}) = Ae^{-Zr/a_0}, \\ \psi_{2s}(\mathbf{r}) &= \psi_{2,0,0}(\mathbf{r}) = B \left(1 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}, \\ \psi_{2p,m=-1}(\mathbf{r}) &= \psi_{2,1,-1}(\mathbf{r}) = R_{2,1}(r)Y_{1,-1}(\theta, \phi), \\ &\dots\end{aligned}$$

### Parahellium

Since  $\chi$  is antisymmetric,  $\psi$  must be symmetric so that  $\Psi$  is antisymmetric. Thus, the ground state is

$$\psi_{1s1s}^S(\mathbf{r}_1, \mathbf{r}_2) = \psi_{1s}(\mathbf{r}_1)\psi_{1s}(\mathbf{r}_2). \quad (11)$$

Its energy is calculated as

$$\begin{aligned}E &= \int d^3r_1 d^3r_2 \left( \psi_{1s}^*(r_1)\psi_{1s}^*(r_2) \right) \left( \hat{H}_1 + \hat{H}_2 + \hat{V} \right) \left( \psi_{1s}(r_1)\psi_{1s}(r_2) \right) \\ &= 2E_{1s} + \frac{e^2}{4\pi\epsilon_0} \int d^3r_1 d^3r_2 \frac{1}{r_{12}} \left| \psi_{1s}(r_1) \right|^2 \left| \psi_{1s}(r_2) \right|^2 \\ &= -2Z^2 E_R + \frac{5}{4} Z E_R = -74.8 \text{ eV}.\end{aligned}$$

The last integral is the energy shift due to the classical Coulomb repulsion between two electrons, both with probability distribution  $|\psi_{1s}|^2$  (you are not expected to do this integral - we can just look it up). Compared to the double-ionization energy of helium, 79.0 eV, this is pretty accurate! Second-order (or higher) perturbation theory makes this almost perfect.

We can apply the similar analysis to the parahellium ground state of the helium-like ions, such as  $\text{Li}^+$ ,  $\text{B}^{+2}$ , etc. See Example 4 Q3(b) where you will need the result of the special integral following Eq. (11).

### Orthohellium

This time  $\chi$  is symmetric, so  $\psi$  must be antisymmetric. So the two electrons cannot both be in a  $1s$  state. Thus the ground state is  $1s2s$  (detailed consideration, which we will discuss next week, shows that the  $1s2s$  state has a lower energy than the  $1s2p$  state). Thus, the ground state is

$$\psi_{1s2s}^A(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_{1s}(r_1)\psi_{2s}(r_2) - \psi_{2s}(r_1)\psi_{1s}(r_2)]. \quad (12)$$

Its energy is

$$\begin{aligned} E &= \frac{1}{2} \int d^3r_1 d^3r_2 \left( \psi_{1s}^*(r_1) \psi_{2s}^*(r_2) - \psi_{2s}^*(r_1) \psi_{1s}^*(r_2) \right) \left( \hat{H}_1 + \hat{H}_2 + \hat{V} \right) \left( \psi_{1s}(r_1) \psi_{2s}(r_2) - \psi_{2s}(r_1) \psi_{1s}(r_2) \right) \\ &= E_{1s} + E_{2s} + E_C - E_{ex}, \end{aligned}$$

where  $E_C$  is again a classical Coulomb repulsion

$$E_C = \frac{e^2}{4\pi\epsilon_0} \int d^3r_1 d^3r_2 \frac{1}{r_{12}} \left| \psi_{1s}(r_1) \right|^2 \left| \psi_{2s}(r_2) \right|^2,$$

and  $E_{ex}$

$$E_{ex} = \frac{e^2}{4\pi\epsilon_0} \int d^3r_1 d^3r_2 \frac{1}{r_{12}} \psi_{1s}^*(r_1) \psi_{2s}^*(r_2) \psi_{2s}(r_1) \psi_{1s}(r_2)$$

is new and called the **exchange energy**. It has no classical counterpart - it is of completely quantum origin, related to the identical-particle nature of electrons. We observe that  $E_{ex}$  lowers the energy of the ground state, because of the exclusion principle:  $\psi^A(\mathbf{r}_1, \mathbf{r}_2) \rightarrow 0$  as  $\mathbf{r}_2 \rightarrow \mathbf{r}_1$ , so the electrons are further apart on average than would be expected from independent particles. This is one source of the Hund's rules to be discussed later: the state of multi-electron atoms with maximum total spin quantum number has lower energy due to the mutual Coulomb repulsion between the electrons.

### Excited Parahelium

Parahelium also has a  $1s 2s$  state – its first excited state,

$$\psi_{1s 2s}^S(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}} [\psi_{1s}(r_1) \psi_{2s}(r_2) + \psi_{2s}(r_1) \psi_{1s}(r_2)] . \quad (13)$$

Its energy is

$$E = E_{1s} + E_{2s} + E_C + E_{ex},$$

where  $E_C$  and  $E_{ex}$  are identical to the previous results. Parahelium's first excited state is higher than orthohelium's ground state, because electrons spend more time near each other in the symmetric state and thus the Coulomb repulsion is stronger, giving a more positive correction. This discussion of energy will be useful for solution of Examples 4 Q2(b).

## 4.4 Electronic configuration and the periodic table

In this section, we extend our discussion from helium to all the elements of the periodic table. By building on our understanding of hydrogen orbitals and applying

some intuitive reasoning, we can explain many of the patterns observed in the periodic table. Our focus will be on determining the ground state of each atom, without delving into excited states, transitions, or related phenomena. To achieve this, we will primarily rely on two key principles: (a) the independent-particle approximation and (b) the Pauli exclusion principle.

First, we review the hydrogen wave functions. Neglecting spin-orbit coupling, the hydrogen wave functions  $\psi_{n,l,m_l,m_s}$  are characterized by the four quantum numbers  $(n, l, m_l, m_s)$ :

$$\begin{aligned} n &= 1, 2, 3, \dots \\ l &= 0, 1, 2, \dots \\ m_l &= 0, \pm 1, \pm 2, \dots, \pm l \\ m_s &= \pm \frac{1}{2}. \end{aligned}$$

For single-electron atoms (hydrogen-like atoms, discussed in Chapter 2), the energy levels are given by

$$E_n = -\frac{Z^2 E_R}{n^2},$$

each with degeneracy of  $2n^2$ .

For multi-electron atoms, however, the energy levels generally depend on  $l$  as well, denoted as  $E_{nl}$ , due to the interactions between the electrons, as demonstrated earlier in the case of helium. For instance, the  $(2p)$  orbitals have slightly higher energy than that of the  $(2s)$  orbital because the  $(2p)$  wave functions are pushed further away from the origin thus “see” less of the nuclear charge. The degeneracy of an energy level  $E_{nl}$  is determined by the allowed values of  $m_s$  and  $m_l$ , and is therefore equal to  $2(2l + 1)$ . This degeneracy corresponds to the maximum number of electrons that can occupy the orbitals according to the Pauli exclusion principle:

$$\begin{aligned} s &\quad \text{orbital : 2 electrons} \\ p &\quad \text{orbital : 6 electrons} \\ d &\quad \text{orbital : 10 electrons} \\ f &\quad \text{orbital : 14 electrons} \\ g &\quad \text{orbital : 18 electrons} \\ \dots & \end{aligned}$$

The above discussion results in the following order of the energy levels  $E_{nl}$  arranged in increasing energy:

$$E_{nl} : 1s, 2s, 2p, 3s, 3p, [4s, 3d], 4p, [5s, 4d], 5p, [6s, 4f, 5d], 6p, [7s, 5f, 6d], \dots \quad (14)$$



Note that increasing  $n$  raises the energy, while decreasing  $l$  lower it. As a result, the levels in squared brackets (eg  $[4s, 3d]$ ) have very similar energies, though the precise details lie beyond the scope of our qualitative discussion. To determine the **electronic configuration** of an atom's ground state, we simply fill the electrons into the lowest available energy levels from Eq. (14), following the Pauli exclusion principle.

Table 1: The ground-state electronic configuration of elements

Atomic number ( $Z$ )	Elements	Configuration
1	H	$(1s)$
2	He	$(1s)^2$
3	Li	$(\text{He})(2s)$
4	Be	$(\text{He})(2s)^2$
5	B	$(\text{He})(2s)^2(2p)$
6	C	$(\text{He})(2s)^2(2p)^2$
7	N	$(\text{He})(2s)^2(2p)^3$
8	O	$(\text{He})(2s)^2(2p)^4$
9	F	$(\text{He})(2s)^2(2p)^5$
10	Ne	$(\text{He})(2s)^2(2p)^6$
11	Na	$(\text{Ne})(3s)$
12	Mg	$(\text{Ne})(3s)^2$
13	Al	$(\text{Ne})(3s)^2(3p)$
14	Si	$(\text{Ne})(3s)^2(3p)^2$
15	P	$(\text{Ne})(3s)^2(3p)^3$
16	S	$(\text{Ne})(3s)^2(3p)^4$
17	Cl	$(\text{Ne})(3s)^2(3p)^5$
18	Ar	$(\text{Ne})(3s)^2(3p)^6$
19	K	$(\text{Ar})(4s)$
20	Ca	$(\text{Ar})(4s)^2$
21	Sc	$(\text{Ar})(4s)^2(3d)$
22	Ti	$(\text{Ar})(4s)^2(3d)^2$
23	V	$(\text{Ar})(4s)^2(3d)^3$
24	Cr	$(\text{Ar})(4s)(3d)^5$
25	Mn	$(\text{Ar})(4s)^2(3d)^5$
...	...	...

We start with hydrogen, the single electron is in the  $(1s)$  orbital; for helium, its ground-state configuration is  $(1s)^2$  as mentioned before. Note that  $(1s)^2$  is a closed shell as we cannot fill more electron. The 3rd electron of lithium has to take the next

(2s) orbital:

$$\text{Li} = (1s)^2(2s) = (\text{He})(2s) .$$

The electronic configuration of beryllium is

$$\text{Be} = (\text{He})(2s)^2 ,$$

and

$$\begin{aligned} \text{B} &= (\text{He})(2s)^2(2p) , \\ \text{C} &= (\text{He})(2s)^2(2p)^2 , \end{aligned}$$

etc., until

$$\text{Ne} = (\text{He})(2s)^2(2p)^6 ,$$

a closed shell configuration again as no more electron can be put in.

Next elements are

$$\begin{aligned} \text{Na} &= (\text{Ne})(3s) , \\ \text{Mg} &= (\text{Ne})(3s)^2 , \end{aligned}$$

etc. until Ag:

$$\text{Ag} = (\text{Ne})(3s)^2(3p)^6 ,$$

a closed shell configuration. See Table 1 for more ground state configurations of atoms. Note: for chromium, the ground state electronic configuration is  $(\text{Ar})(4s)(3d)^5$ , instead of  $(\text{Ar})(4s)^2(3d)^4$ .

Many properties of atoms can largely explained by their ground-state electronic configurations. For example, noble gas atoms (He, Ne, Ar, etc.) are particularly stable and chemically inert due to their closed-shell configurations, which require significantly higher energy to excite the atoms to the next energy level. Atoms with similar ground-state electronic configurations of the partially filled shells share similar properties, including comparable optical spectra and chemical behaviour. For instance, alkali metals such as Li, Na, K all have the last electron in the  $(ns)$  sub-shell; halogens like F, Cl have five electrons in the  $(np)^5$  sub-shell; and alkali earth elements Mg, Ca have  $(ns)^2$  in their outermost unfilled sub-shell.

## 4.5 Hund's Rules and Spectroscopic Notation

The electronic configurations as discussed above do not uniquely determine the ground state of atoms due to the many possible values of the angular momenta. Additionally, when spin-orbit coupling is considered, the total angular momentum

quantum number  $J$  must be included. To fully specify the electronic state, atomic physicists use **spectroscopic notations** (some text book called **term** or **term symbols**) to represent a specific state or energy level of an atom or ion with fixed total spin and orbital angular momentum quantum numbers.

A general spectroscopic term symbol is written as

$$^{2S+1}L_J \quad (15)$$

where

- i.  $S$  is the total spin quantum number given in number;
- ii.  $L$  is the total orbital quantum number given in notations:  $S, P, D, F, G, H, \dots$  for  $L = 0, 1, 2, 3, 4, 5, \dots$ ;
- iii.  $J$  is the total angular momentum given in number.;
- iv. And the number  $(2S + 1)$  is called **multiplicity** in literature.

For example, helium in the ground-state configuration  $(1s)^2$  has total spin  $S = 0$ , total orbital angular momentum  $L = 0$  hence in letter notation  $S$ , and total angular momentum  $J = 0$ , the spectroscopic term is  $^1S_0$ .

Lithium with the ground-state configuration  $(1s)^2(2s)$  has the ground-state spectroscopic term  $^2S_{1/2}$ .

We next consider carbon with the ground-state electronic configuration

$$\text{C} = (1s)^2(2s)^2(2p)^2.$$

We observe:

- a. This configuration includes multiple states, each characterized by distinct angular momentum quantum numbers.
- b. Our primary focus is to determine the values of the quantum numbers - specifically the total  $S$ ,  $L$  and total  $J$  - for the lowest energy state (i.e. the ground state). To achieve this, we only need to consider the partially filled subshell  $(2p)^2$  with two electrons, since the closed shells such as  $(1s)^2(2s)^2$  always has  $S = L = 0$  in the ground-state.
- c. The sub-shell  $(2p)^2$  allows for possible values of  $S = 0, 1$ ,  $L = 0, 1, 2$  and  $J = 0, 1, 2, 3$  as determined by the angular momentum addition theorem. However, which combination corresponds to the ground state?

- d. The ground-state energy level is represented by the term  ${}^3P_0$ , corresponding to  $S = 1$ ,  $L = 1$ , and  $J = 0$ . These values of  $(S, L, J)$  are determined by accounting for the effects of the inter-electron Coulomb interactions and spin-orbit coupling, summarized by Hund's rules.

## Hund's Rules

1. **Hund's first rule:** consistent with the Pauli principle, state with the highest total spin  $S$  will have the lowest energy;
2. **Hund's second rule:** for a give total spin, the state with the highest total orbital angular momentum  $L$  will have the lowest energy;
3. **Hund's third rule:** if a sub-shell  $(n, l)$  is no more than half-filled, then the lowest energy level has  $J = |L - S|$ ; if it is more than half-filled, the  $J = L + S$  has the lowest energy.

The first two of Hund's rules arise from considerations of Coulomb repulsion between electrons, while the third rule is primarily a consequence of spin-orbit coupling. More explanation is given in a Footnote.

For carbon, the partially filled shell  $(2p)^2$  contains two electrons. Since  $l = 1$ ,  $m_l = 1, 0, -1$ . To satisfy the Pauli exclusion principle, the two electron are placed in the states  $m_l = 1$  and  $0$ , both with spin up, resulting in the maximum spin  $S = 1$  (Rule 1) and maximum orbital  $L = 1 + 0 = 1$  (Rule 2), as shown in the following simple diagram

$$\uparrow \quad \uparrow \quad -$$

As the shell is less than half-filled,  $J = |L - S| = 0$  (Rule 3). Consequently, the ground-state spectroscopic term for carbon is  ${}^3P_0$ .

We next consider sulfur S with  $Z = 16$ :

$$\text{S} = (\text{Ne})(3s)^2(3p)^4,$$

where the part-filled shell  $(3p)^4$  has four electrons. First, we fill first 3 spin-up electrons on each of the  $m_l = 1, 0, -1$  states (Rule 1). The 4th electron then has to be down spin (Pauli exclusion principle) occupying the  $m_l = 1$  state (Rule 2):

$$\uparrow\downarrow \quad \uparrow \quad \uparrow$$

So the total  $S = 3 \times 1/2 - 1 \times 1/2 = 1$  and total  $L = (1 + 0 - 1) + 1 = 1$ . Since it is over half-filled,  $J = L + S = 2$  (Rule 3). The ground state spectroscopic term is therefore  ${}^3P_2$ .

Vanadium V ( $Z = 23$ ) has the ground state configuration:

$$V = (\text{Ar})(4s)^2(3d)^3,$$

where the part-filled shell  $(3d)^3$  has three electrons. As  $l = 2$ ,  $m_l$  has 5 possible values,  $m_l = 2, 1, 0, -1, -2$ . We fill the three electrons all with spin up on  $m_l = 2, 1, 0$  (Rules 1 and 2).

$$\uparrow \quad \uparrow \quad \uparrow \quad - \quad -$$

So  $S = 3 \times 1/2 = 3/2$  and  $L = 2+1+0 = 3$ . It is under half-filled, so  $J = |L-S| = 3/2$ . The ground state spectroscopic term is  ${}^4F_{3/2}$ .

Selenium Se ( $Z = 34$ ) has the ground state configuration:

$$\text{Se} = (\text{Ar})(4s)^2(3d)^{10}(4p)^4.$$

The part-filled shell is  $(4p)^4$  with four electrons. It is similar to sulfur with the ground-state term  ${}^3P_2$ .

## Summary of Chapter 4

- Two types of quantum particles: bosons with symmetric wave functions and fermions with antisymmetric wave functions.
- Independent-electron approximation: multi-electron wave functions of atoms are approximated as products of the single-electron hydrogen wave functions.
- Pauli exclusion principle: A single-electron state, such as one of the hydrogen orbitals, can accommodate at most an electron (or 2 electrons after inclusion the spin degree of freedom).
- Parahelium: The spin wave function is an antisymmetric singlet state with  $S = 0$ , while the orbital wave functions are symmetric.
- Orthohelium: The spin wave functions are symmetric triplet states with  $S = 1$ , while the orbital wave functions are antisymmetric symmetric.
- Exchange energy: Appeared in the energy expectation value as an integral involving different orbitals, which has no classical counterpart.
- Electronic configuration of atoms: filling up the atomic energy levels  $E_{nl}$  according to the Pauli exclusion principle.
- Hund's Rules: determining the value of the total  $S, L$  and  $J$ , which specify the ground state of atoms.

- The ground-state spectroscopic term of atoms:  $(2S+1)L_J$ .

**Footnote: Physical explanation of Hund's rules**

An antisymmetric spatial wave function will reduce the Coulomb repulsion between the electrons. This in turn means that the spin wavefunction must be symmetric. And therefore that all the spins are aligned with maximum  $S$ . Also trying to spread out the electrons to minimize their Coulomb repulsion leading to the maximum  $L$ .

For the 3rd rule, recall that the spin-orbit interaction for a single electron was proportional to

$$j(j+1) - l(l+1) - s(s+1)$$

with a positive coefficient. Thus, the energy is minimized by taking the smallest possible value of  $J$ , i.e.  $|L - S|$ . As we add more electrons, the same argument can be used for their total spin and total orbital angular momentum and, up to the point where the orbital is half full. For the cases of the over-half-filled configurations, we can use the same argument but for “holes”. A full orbital has zero spin and zero orbital angular momentum. Thus we can think of a full-but-one orbital as being a full orbital plus a hole. The hole can be thought of as a particle with the same properties as an electron but with the opposite charge. Therefore it has opposite spin-orbit coupling. Therefore we have to maximize  $J$  to minimize the energy, hence  $J = L + S$ .