

4 Multi-electron systems

4.1 Revision: The bound states of atomic hydrogen

In this section: A recap of essential facts about the bound states of one-electron atomic systems, important for the following.

In order to make sense of this part of the course, it is important that you are familiar with the quantum mechanical description of the bound states of atomic hydrogen as summarized in Section 5 of the QM Primer. Just to mention some of the key facts:

- The non-relativistic Hamiltonian of atomic hydrogen is

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\epsilon_0}\frac{e^2}{r}, \quad (4.1)$$

in the approximation where the reduced mass of the electron-nucleus system is taken to be the mass of the electron, m (which amounts to taking the mass of the nucleus to be infinite). Recall that the term in $1/r$ in the Hamiltonian is the potential energy of the electron due to its Coulomb interaction with the nucleus. The term in ∇^2 can be understood as corresponding to the kinetic energy of the electron.

- We denote the eigenfunctions of this Hamiltonian by $\psi_{nlm}(\mathbf{r})$, where n , l and m are the principal quantum number, the orbital angular momentum quantum number and the magnetic quantum number. The corresponding bound state eigenenergies depend on n but not on l or m .
- Hydrogenic ions can be treated in the same way as atomic hydrogen. (Hydrogenic ions are atoms which have lost all their electrons but one and are thus composed of a multiply charged nucleus and a single electron, for instance He^+ , Li^{2+} , etc.) The only difference is that the potential energy of the electron is a factor Z stronger, where Z is the atomic number (the number of protons in the nucleus). The corresponding Hamiltonian is

$$H = -\frac{\hbar^2}{2m}\nabla^2 - \frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}. \quad (4.2)$$

Exactly as in the case of atomic hydrogen, the eigenfunctions of this Hamiltonian can be labelled by the three quantum numbers n , l and m and the eigenenergies depend only on n .

- Due to spin-orbit coupling, the energy eigenstates of the atom are actually linear combinations of products of the form $\psi_{nlm}(\mathbf{r})\chi_{1/2,m_s}$, where the spatial wave function $\psi_{nlm}(\mathbf{r})$ is one of the eigenfunctions of the Hamiltonian

(4.1) or (4.2) and $\chi_{1/2, m_s}$ is a spin state. If spin-orbit coupling is taken into account, the energy eigenstates of the atom are no longer eigenstates of L_z , although they are still eigenstates of \mathbf{L}^2 . They are also eigenstates of \mathbf{S}^2 , of \mathbf{J}^2 and of J_z , where \mathbf{S} is the spin operator and \mathbf{J} is the total angular momentum operator, i.e.,

$$\mathbf{J} = \mathbf{L} + \mathbf{S}. \quad (4.3)$$

(The operator J_z is the z -component of \mathbf{J} .)

This short list of key facts is not exhaustive. Please read through Sections 5.1 and 5.2 of the QM Primer to make sure that you are familiar with all the results you need to know to study this part of the course.

4.2 Revision: Coupling angular momenta

In this section: Summing angular momentum operators; the eigenvalues of the resulting operators.

The total angular momentum operator \mathbf{J} defined by Eq. (4.3) is a particular instance of an operator constructed by summing two other angular momentum operators. In Eq. (4.3), one sums the orbital angular momentum operator for an electron (\mathbf{L}) with the spin operator for the same electron (\mathbf{S}). As we will see when studying helium, it is sometimes necessary to sum orbital angular momentum operators or spin operators pertaining to different electrons.

Suppose that \mathbf{J}_1 and \mathbf{J}_2 are two angular momentum operators (it does not matter whether they are orbital angular momentum operators or spin operators or sums of some of those). This implies that the eigenvalues of \mathbf{J}_1^2 and of \mathbf{J}_2^2 are of the form $j_1(j_1 + 1)\hbar^2$ and $j_2(j_2 + 1)\hbar^2$, respectively. Suppose further that one sum \mathbf{J}_1 and \mathbf{J}_2 to form a new operator \mathbf{J} :

$$\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2. \quad (4.4)$$

Then, the following results always hold:

- The operator \mathbf{J} is an angular momentum operator.
- \mathbf{J}^2 , \mathbf{J}_1^2 , \mathbf{J}_2^2 and J_z have common eigenstates. (J_z is the z -component of \mathbf{J} . Since $\mathbf{J} = \mathbf{J}_1 + \mathbf{J}_2$, $J_z = J_{1z} + J_{2z}$.)
- In these eigenstates the eigenvalues of \mathbf{J}^2 are $j(j + 1)\hbar^2$ where the number j is an integer or a half integer whose possible values range from $|j_1 - j_2|$ to $j_1 + j_2$ by integer step:

$$|j_1 - j_2| \leq j \leq j_1 + j_2. \quad (4.5)$$

- The eigenvalues of J_z are $m_j\hbar$ where the number m_j can take any value between $-j$ and j by integer step.

We stress that although we use the same notation for the total operator as in Section 4.1, the angular momentum operators J_1 and J_2 do not need be the \mathbf{L} and \mathbf{S} operators for a hydrogen atom or hydrogenic ion. The results quoted above are completely general.

4.3 The Hamiltonian of helium

In this section: Writing the Hamiltonian of the helium atom; two-electron wave functions.

Passing to helium, we now have two electrons, electron 1 and electron 2 say, moving in the Coulomb field of the nucleus. Taking the latter to be a static point charge, the total energy is thus the sum of the kinetic energy of electron 1, of the kinetic energy of electron 2 and of the total potential energy of the two electrons. Correspondingly, the Hamiltonian of helium can be written

$$H = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1} - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_2} + \frac{1}{4\pi\epsilon_0}\frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (4.6)$$

in the approximation where spin-orbit and other relativistic effects are neglected and the mass of the nucleus is taken to be effectively infinite (i.e., we neglect reduced-mass corrections). Here \mathbf{r}_1 and \mathbf{r}_2 are the position vectors of the two electrons with respect to the nucleus, $r_1 = |\mathbf{r}_1|$ and $r_2 = |\mathbf{r}_2|$. If we denote by x_1, y_1, z_1 the Cartesian coordinates of electron 1 and by x_2, y_2, z_2 those of electron 2,

$$\nabla_1^2 \equiv \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial y_1^2} + \frac{\partial^2}{\partial z_1^2}, \quad \nabla_2^2 \equiv \frac{\partial^2}{\partial x_2^2} + \frac{\partial^2}{\partial y_2^2} + \frac{\partial^2}{\partial z_2^2}, \quad (4.7)$$

and

$$|\mathbf{r}_1 - \mathbf{r}_2| = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}. \quad (4.8)$$

($|\mathbf{r}_1 - \mathbf{r}_2|$ is the distance between the two electrons.)

The terms in $1/r_1$ and $1/r_2$ in the Hamiltonian represent the potential energy arising from the interaction of each of the electrons with the nucleus (which has a charge of $2e$ here, hence the factor of 2 compared to atomic hydrogen), while the term in $1/|\mathbf{r}_1 - \mathbf{r}_2|$ arises from the Coulomb interaction of the two electrons (the sign is opposite to that of the other potential energy terms since the electrons repel each other whereas the nucleus attracts them).

This Hamiltonian depends on the coordinates of each of the electrons. Hence, the wave functions of the atom are, in general, functions of six spatial coordinates. The time-dependent wave functions can be denoted by $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$. Thus

$$|\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3r_1 d^3r_2$$

is the probability that at time t electron 1 is located within an infinitesimal volume d^3r_1 centered about the point of position vector \mathbf{r}_1 and that at the same time electron 2 is located within an infinitesimal volume d^3r_2 centered about the point of position vector \mathbf{r}_2 . (Here as in the rest of these notes, we use the symbol d^3r to denote a volume element. In terms of Cartesian coordinates, $d^3r_1 = dx_1 dy_1 dz_1$ and $d^3r_2 = dx_2 dy_2 dz_2$.) For this interpretation to make sense, the wave function must be normalized in such a way that

$$\int |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 d^3r_1 d^3r_2 = 1. \quad (4.9)$$

Note 1: Another way of stating the same is to write the wave function as a function of the Cartesian coordinates of the two electrons and to say that

$$|\Psi(x_1, y_1, z_1, x_2, y_2, z_2, t)|^2 dx_1 dy_1 dz_1 dx_2 dy_2 dz_2$$

is the probability that at time t electron 1 is located between x_1 and $x_1 + dx_1$ in the x -direction, between y_1 and $y_1 + dy_1$ in the y -direction and between z_1 and $z_1 + dz_1$ in the z -direction and that electron 2 is located between x_2 and $x_2 + dx_2$ in the x -direction, between y_2 and $y_2 + dy_2$ in the y -direction and between z_2 and $z_2 + dz_2$ in the z -direction.

In this part of the course we are specifically interested by the energy eigenstates of the atom. Recall that the time-dependent wave functions representing such states factorize into a product of a time-independent wave function and a time-dependent oscillating exponential: for any energy eigenstate,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, t) = \exp(-iEt/\hbar) \psi(\mathbf{r}_1, \mathbf{r}_2), \quad (4.10)$$

where the eigenenergy E and the eigenfunction $\psi(\mathbf{r}_1, \mathbf{r}_2)$ are solutions of the time-independent Schrödinger equation,

$$H\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2). \quad (4.11)$$

We will only consider bound state solutions of this equation in the following.

4.4 Product states

In this section: Treating the two electrons as if they did not interact with each other; exchange degeneracy.

It is useful to write the Hamiltonian (4.6) in the following form:

$$H = H_1 + H_2 + V_{ee}(\mathbf{r}_1, \mathbf{r}_2), \quad (4.12)$$

where H_1 and H_2 are the Hamiltonians of electron 1 and of electron 2, and $V_{ee}(\mathbf{r}_1, \mathbf{r}_2)$ is the electron-electron interaction term. Namely,

$$H_1 = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_1}, \quad H_2 = -\frac{\hbar^2}{2m}\nabla_2^2 - \frac{1}{4\pi\epsilon_0}\frac{2e^2}{r_2}, \quad (4.13)$$

and

$$V_{ee}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{4\pi\epsilon_0} \frac{e^2}{|\mathbf{r}_1 - \mathbf{r}_2|}. \quad (4.14)$$

Although this two-electron Hamiltonian is relatively simple, finding its eigenenergies and eigenfunctions is not possible analytically. The difficulty comes from the $V_{ee}(\mathbf{r}_1, \mathbf{r}_2)$ potential, which couples the two electrons to each other. The calculation would be straightforward if this term could be ignored, as we will now see.

The Hamiltonian would indeed reduce to $H_1 + H_2$ in this approximation. Since both H_1 and H_2 are the Hamiltonian of a single electron moving in the Coulomb field of a helium nucleus (namely, the Hamiltonian (4.2) with $Z = 2$) their eigenfunctions and eigenenergies can be calculated easily. These eigenfunctions and eigenenergies are defined by the equations

$$H_1\psi_{nlm}(\mathbf{r}_1) = E_n\psi_{nlm}(\mathbf{r}_1) \quad (4.15)$$

and

$$H_2\psi_{nlm}(\mathbf{r}_2) = E_n\psi_{nlm}(\mathbf{r}_2). \quad (4.16)$$

(Since H_1 and H_2 are identical, apart from the electron label, they have the same spectrum of eigenenergies, and therefore we can use the same symbol for the eigenenergies of H_2 as for those of H_1 .) Then, knowing these eigenfunctions and eigenenergies, we also know the eigenfunctions and eigenenergies of $H_1 + H_2$. To see this, note that

$$\begin{aligned} (H_1 + H_2)\psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2) &= [H_1\psi_{nlm}(\mathbf{r}_1)]\psi_{n'l'm'}(\mathbf{r}_2) + \psi_{nlm}(\mathbf{r}_1)[H_2\psi_{n'l'm'}(\mathbf{r}_2)] \\ &= E_n\psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2) + E_{n'}\psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2) \\ &= (E_n + E_{n'})\psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2). \end{aligned} \quad (4.17)$$

The product wave functions $\psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2)$ are thus eigenfunctions of $H_1 + H_2$ and the corresponding eigenenergies are $E_n + E_{n'}$. It then follows from general mathematical theorems that any eigenfunction of $H_1 + H_2$ is either of the form $\psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2)$ or is a linear combination of such product wave functions.

Note 1: The above is an application of the method of separating variables for linear partial differential equations.

Note 2: Note that the wave function $\psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2)$ corresponds to the same energy, $E_n + E_{n'}$, as the wave function $\psi_{n'l'm'}(\mathbf{r}_1)\psi_{nlm}(\mathbf{r}_2)$. The eigenenergies of $H_1 + H_2$ are therefore degenerate with respect to which electron is in the state (nlm) and which electron is in the state $(n'l'm')$. In other words, they are degenerate with respect to the exchange of the electron labels. Such a degeneracy is referred to as “exchange degeneracy”.

There is exchange degeneracy because the two electrons are identical. For example, if these two electrons had different masses, the eigenenergies of H_1 and those of H_2 would not be the same for a same principal quantum number. Hence the wave functions $\psi_{nlm}(\mathbf{r}_1)\psi_{n'l'm'}(\mathbf{r}_2)$ and $\psi_{n'l'm'}(\mathbf{r}_1)\psi_{nlm}(\mathbf{r}_2)$ would correspond to different energy levels, and there would be no exchange degeneracy.

It is important to understand that while both H_1 and H_2 are Hamiltonians of single particle systems, $H_1 + H_2$ is the Hamiltonian of a two-particle system (namely the system formed by the two electrons considered as a whole, in the approximation where these electrons are not considered to interact with each other). The wave functions of this two-particle systems depend on the variables of each of the two particles. However, when $H_1 + H_2$ acts on these wave functions, H_1 acts only on the variables of electron 1 and H_2 acts only on the variables of electron 2.

The ground state energy of $H_1 + H_2$ is obtained by taking both E_n and $E_{n'}$ as small as possible, i.e., by taking $n = n' = 1$. The corresponding eigenfunction is $\psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)$. In this state, both electron 1 and electron 2 are in the 1s state of their respective one-electron Hamiltonian.

The first excited energy level of $H_1 + H_2$ is obtained by taking $n = 1$ and $n' = 2$ or $n = 2$ and $n' = 1$. The corresponding wave functions could be any of the following products,

$$\begin{aligned} &\psi_{100}(\mathbf{r}_1)\psi_{200}(\mathbf{r}_2), \quad \psi_{100}(\mathbf{r}_1)\psi_{21-1}(\mathbf{r}_2), \quad \psi_{100}(\mathbf{r}_1)\psi_{210}(\mathbf{r}_2), \quad \psi_{100}(\mathbf{r}_1)\psi_{211}(\mathbf{r}_2), \\ &\psi_{200}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2), \quad \psi_{21-1}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2), \quad \psi_{210}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2), \quad \psi_{211}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2), \end{aligned}$$

or indeed any linear combination of these products.

4.5 Interacting electrons: Para states and ortho states

In this section: Space-symmetric states and space-antisymmetric states.

We have seen in Section 4.4 that in the approximation where the interaction between the two electrons is neglected, then the Hamiltonian reduces to $H_1 + H_2$, and that $H_1 + H_2$ has eigenfunctions, e.g., $\psi_{100}(\mathbf{r}_1)\psi_{210}(\mathbf{r}_2)$, which depend in a different way on the coordinates of electron 1 than on those of electron 2: exchanging the labels of the two electrons would change $\psi_{100}(\mathbf{r}_1)\psi_{210}(\mathbf{r}_2)$ into

$\psi_{210}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)$, which is a different wave function (although both correspond to the same energy, $E_1 + E_2$). The Hamiltonian $H_1 + H_2$ also has eigenfunctions such as

$$[\psi_{100}(\mathbf{r}_1)\psi_{210}(\mathbf{r}_2) + \psi_{210}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)]/\sqrt{2},$$

which are symmetric in the spatial coordinates of the two electrons, and

$$[\psi_{100}(\mathbf{r}_1)\psi_{210}(\mathbf{r}_2) - \psi_{210}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)]/\sqrt{2}$$

which are antisymmetric. Symmetric means that the wave function does not change at all when \mathbf{r}_1 and \mathbf{r}_2 are swapped, and antisymmetric that swapping \mathbf{r}_1 and \mathbf{r}_2 is equivalent to multiplying the wave function by -1 . The eigenfunction $\psi_{100}(\mathbf{r}_1)\psi_{210}(\mathbf{r}_2)$ is neither symmetric nor antisymmetric [i.e., it is not the case that $\psi_{100}(\mathbf{r}_1)\psi_{210}(\mathbf{r}_2) \equiv \psi_{210}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)$, and it is not the case either that $\psi_{100}(\mathbf{r}_1)\psi_{210}(\mathbf{r}_2) \equiv -\psi_{210}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)$].

It turns out the *full* Hamiltonian, with the electron-electron interaction included, does not have bound states eigenfunctions that are neither symmetric nor antisymmetric. Instead, one finds the following:

- The bound state eigenfunctions of the full Hamiltonian are either symmetric or antisymmetric for the interchange of \mathbf{r}_1 and \mathbf{r}_2 . That is, if $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is a solution of Eq. (4.11) with H given by Eq. (4.6), then either $\psi(\mathbf{r}_2, \mathbf{r}_1) = \psi(\mathbf{r}_1, \mathbf{r}_2)$ or $\psi(\mathbf{r}_2, \mathbf{r}_1) = -\psi(\mathbf{r}_1, \mathbf{r}_2)$. In the first case, one says that the wave function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ describes a *space-symmetric state*. In the other case (with the minus sign), one says that it describes a *space-antisymmetric state*. (The terms “symmetric” and “antisymmetric” only refer to whether the wave function changes sign or not when the coordinates of the two electrons are swapped.) Space-symmetric states and space-antisymmetric states are often referred to as “para states” and “ortho states”, respectively.
- Para states have different energies than ortho states. The energy levels of helium thus divide into levels corresponding to space-symmetric states and levels corresponding to space-antisymmetric states.

We will see in Section 4.11 that para and ortho states also correspond to different spin states.

Note 1: To see why the energy levels of the full Hamiltonian correspond either to space-symmetric states or to space-antisymmetric states, consider the following.

Suppose that $\psi_a(\mathbf{r}_1, \mathbf{r}_2)$ is an eigenfunction of H , and take $\psi_b(\mathbf{r}_1, \mathbf{r}_2)$ to be the function obtained by swapping the position of the two electrons in $\psi_a(\mathbf{r}_1, \mathbf{r}_2)$:

$$\psi_b(\mathbf{r}_1, \mathbf{r}_2) \equiv \psi_a(\mathbf{r}_2, \mathbf{r}_1).$$

Thus $\psi_b(\mathbf{r}_1, \mathbf{r}_2)$ describes a state in which the wave function varies with respect to the coordinates of electron 2 in the same way as the wave function $\psi_a(\mathbf{r}_1, \mathbf{r}_2)$ varies with respect to the coordinates of electron 1, and vice versa. Since $\psi_a(\mathbf{r}_1, \mathbf{r}_2)$ is an eigenfunction of H , we have that

$$[H_1 + H_2 + V_{ee}(\mathbf{r}_1, \mathbf{r}_2)]\psi_a(\mathbf{r}_1, \mathbf{r}_2) = E_a\psi_a(\mathbf{r}_1, \mathbf{r}_2),$$

where E_a is one of the eigenenergies of H . Now, exchange the electron labels, so that \mathbf{r}_1 becomes \mathbf{r}_2 and \mathbf{r}_2 becomes \mathbf{r}_1 . This gives

$$[H_2 + H_1 + V_{ee}(\mathbf{r}_2, \mathbf{r}_1)]\psi_a(\mathbf{r}_2, \mathbf{r}_1) = E_a\psi_a(\mathbf{r}_2, \mathbf{r}_1).$$

But $H_2 + H_1 + V_{ee}(\mathbf{r}_2, \mathbf{r}_1) \equiv H_1 + H_2 + V_{ee}(\mathbf{r}_1, \mathbf{r}_2)$. Hence we find that

$$[H_1 + H_2 + V_{ee}(\mathbf{r}_1, \mathbf{r}_2)]\psi_b(\mathbf{r}_1, \mathbf{r}_2) = E_a\psi_b(\mathbf{r}_1, \mathbf{r}_2).$$

This equation shows that the state described by the wave function $\psi_b(\mathbf{r}_1, \mathbf{r}_2)$ is also an eigenstate of the Hamiltonian and has the same eigenenergy as the state described by the wave function $\psi_a(\mathbf{r}_1, \mathbf{r}_2)$.

Then, there are two possibilities: either $\psi_a(\mathbf{r}_1, \mathbf{r}_2)$ and $\psi_b(\mathbf{r}_1, \mathbf{r}_2)$ represent the same state, or they don't. We now see that the latter is impossible, and that the former leads to the conclusion that the wave function is either symmetric or antisymmetric in \mathbf{r}_1 and \mathbf{r}_2 .

1. If $\psi_b(\mathbf{r}_1, \mathbf{r}_2)$ represents the same state as $\psi_a(\mathbf{r}_1, \mathbf{r}_2)$, then one must have that

$$\psi_b(\mathbf{r}_1, \mathbf{r}_2) = \lambda\psi_a(\mathbf{r}_1, \mathbf{r}_2),$$

with λ a constant. Exchanging the electron labels in this last equation gives

$$\psi_b(\mathbf{r}_2, \mathbf{r}_1) = \lambda\psi_a(\mathbf{r}_2, \mathbf{r}_1).$$

Since $\psi_b(\mathbf{r}_2, \mathbf{r}_1) \equiv \psi_a(\mathbf{r}_1, \mathbf{r}_2)$ and $\psi_a(\mathbf{r}_2, \mathbf{r}_1) \equiv \psi_b(\mathbf{r}_1, \mathbf{r}_2)$, we obtain

$$\psi_a(\mathbf{r}_1, \mathbf{r}_2) = \lambda^2\psi_a(\mathbf{r}_1, \mathbf{r}_2).$$

The upshot is that λ^2 is necessarily equals to 1. Therefore either $\lambda = 1$ and $\psi_a(\mathbf{r}_2, \mathbf{r}_1) = \psi_a(\mathbf{r}_1, \mathbf{r}_2)$, or $\lambda = -1$ and $\psi_a(\mathbf{r}_2, \mathbf{r}_1) = -\psi_a(\mathbf{r}_1, \mathbf{r}_2)$. The energy level thus corresponds either to a space-symmetric state or to a space-antisymmetric state.

2. If instead $\psi_a(\mathbf{r}_1, \mathbf{r}_2)$ and $\psi_b(\mathbf{r}_1, \mathbf{r}_2)$ would represent different states, then these two wave functions would be linearly independent. We could then construct two new (unnormalized) wave functions, $\phi^+(\mathbf{r}_1, \mathbf{r}_2)$ and $\phi^-(\mathbf{r}_1, \mathbf{r}_2)$, by addition and subtraction:

$$\begin{aligned}\phi^+(\mathbf{r}_1, \mathbf{r}_2) &= \psi_a(\mathbf{r}_1, \mathbf{r}_2) + \psi_b(\mathbf{r}_2, \mathbf{r}_1), \\ \phi^-(\mathbf{r}_1, \mathbf{r}_2) &= \psi_a(\mathbf{r}_1, \mathbf{r}_2) - \psi_b(\mathbf{r}_2, \mathbf{r}_1).\end{aligned}$$

Like and $\psi_a(\mathbf{r}_1, \mathbf{r}_2)$ and $\psi_b(\mathbf{r}_1, \mathbf{r}_2)$, $\phi^+(\mathbf{r}_1, \mathbf{r}_2)$ and $\phi^-(\mathbf{r}_1, \mathbf{r}_2)$ would then both be eigenfunctions of H belonging to the same energy level. However, since $\phi^-(\mathbf{r}_1, \mathbf{r}_2) = -\phi^-(\mathbf{r}_2, \mathbf{r}_1)$, this wave function must vanish at $\mathbf{r}_1 = \mathbf{r}_2$, i.e., when the two electrons are located at a same position. By contrast, there is no reason why $\phi^+(\mathbf{r}_1, \mathbf{r}_2)$ would always vanish at $\mathbf{r}_1 = \mathbf{r}_2$. Therefore, the probability that the two electrons are close to each other must be smaller in the state $\phi^-(\mathbf{r}_1, \mathbf{r}_2)$ than in the state $\phi^+(\mathbf{r}_1, \mathbf{r}_2)$, leading to a higher potential energy in the latter state. Hence, it would be an extraordinary coincidence if the two states $\phi^+(\mathbf{r}_1, \mathbf{r}_2)$ and $\phi^-(\mathbf{r}_1, \mathbf{r}_2)$ had the same energy. If they don't have the same energy, then necessarily $\psi_a(\mathbf{r}_1, \mathbf{r}_2)$ and $\psi_b(\mathbf{r}_1, \mathbf{r}_2)$ cannot be linearly independent, and instead $\psi_b(\mathbf{r}_1, \mathbf{r}_2) = \pm\psi_a(\mathbf{r}_1, \mathbf{r}_2)$.

4.6 Exchange splitting

In this section: The exchange degeneracy is lifted by the electron-electron interaction; the exchange integral; para states and ortho states have different energies.

This section assumes some knowledge of degenerate perturbation theory. If your recollection of the corresponding part of the level 2 course is somewhat unclear, it would probably be useful for you to consult your notes from last year, or a Quantum Mechanics textbook, or Chapter 6 of the QM Primer, before attacking this section.

Let us illustrate the result stated in Section 4.5 by an approximate calculation of an energy level for the full Hamiltonian. To this end, we start from the eigenfunctions of $H_1 + H_2$ (Section 4.4) and use perturbation theory to take the electron-electron interaction into account. Thus we split the full Hamiltonian into an unperturbed Hamiltonian H_0 and a perturbation Hamiltonian H' , with

$$H_0 = H_1 + H_2, \quad H' = V_{ee}(\mathbf{r}_1, \mathbf{r}_2). \quad (4.18)$$

We will look specifically at the perturbation of the first excited energy level of H_0 , as an example. To keep things simple, we ignore the possibility that in the unperturbed state either one of the two electrons could be in a 2p state. The unperturbed (zero-order) wave functions could then be $\psi_{100}(\mathbf{r}_1)\psi_{200}(\mathbf{r}_2)$, $\psi_{200}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)$, or any linear combination of these two product wave functions (recall the discussion at the end of Section 4.4). As these different wave functions

represent distinct eigenstates of H_0 corresponding to a same eigenenergy, we use degenerate perturbation theory.

Following the standard procedure, we first write down the zero-order wave functions we start from. Here, the obvious choice is

$$\psi_a^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{200}(\mathbf{r}_2) \quad (4.19)$$

and

$$\psi_b^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = \psi_{200}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2). \quad (4.20)$$

Both $\psi_a^{(0)}(\mathbf{r}_1, \mathbf{r}_2)$ and $\psi_b^{(0)}(\mathbf{r}_1, \mathbf{r}_2)$ correspond to the same zero-order energy:

$$H_0\psi_a^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = E^{(0)}\psi_a^{(0)}(\mathbf{r}_1, \mathbf{r}_2), \quad (4.21)$$

$$H_0\psi_b^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = E^{(0)}\psi_b^{(0)}(\mathbf{r}_1, \mathbf{r}_2), \quad (4.22)$$

with $E^{(0)} = E_1 + E_2$. The perturbative calculation then shows that to first order in H' the unperturbed energy level shifts and splits into two sub-levels, one of energy $E^{(0)} + J + K$ and one of energy $E^{(0)} + J - K$, where J and K are defined by the following integrals:

$$J = \int \psi_{100}^*(\mathbf{r}_1)\psi_{200}^*(\mathbf{r}_2)V_{ee}(\mathbf{r}_1, \mathbf{r}_2)\psi_{100}(\mathbf{r}_1)\psi_{200}(\mathbf{r}_2) d^3r_1 d^3r_2 \quad (4.23)$$

and

$$K = \int \psi_{100}^*(\mathbf{r}_1)\psi_{200}^*(\mathbf{r}_2)V_{ee}(\mathbf{r}_1, \mathbf{r}_2)\psi_{200}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2) d^3r_1 d^3r_2. \quad (4.24)$$

Note that in this last integral the electron labels are exchanged between the state appearing on the left of V_{ee} and that appearing on the right; for this reason, K is often referred to as the “exchange integral” (J is the “Coulomb” or the “direct” integral). We see that in this approximation, there is an energy gap of $2K$ between the two sub-levels the unperturbed level splits into.

Note 1: The calculation runs as follows. To first order in H' , the unperturbed energy $E^{(0)}$ becomes $E^{(0)} + E^{(1)}$, with $E^{(1)}$ either one of the two solutions of the determinant equation

$$\begin{vmatrix} H'_{aa} - E^{(1)} & H'_{ba} \\ H'_{ab} & H'_{bb} - E^{(1)} \end{vmatrix} = 0. \quad (4.25)$$

In the present case, the matrix elements H'_{aa} , H'_{ba} , H'_{ab} and H'_{bb} are given by the following integrals:

$$\begin{aligned} H'_{aa} &= \int \psi_a^{(0)*}(\mathbf{r}_1, \mathbf{r}_2)H'\psi_a^{(0)}(\mathbf{r}_1, \mathbf{r}_2) d^3r_1 d^3r_2 \\ &= \int \psi_{100}^*(\mathbf{r}_1)\psi_{200}^*(\mathbf{r}_2)V_{ee}(\mathbf{r}_1, \mathbf{r}_2)\psi_{100}(\mathbf{r}_1)\psi_{200}(\mathbf{r}_2) d^3r_1 d^3r_2, \end{aligned}$$

$$\begin{aligned}
H'_{ba} &= \int \psi_b^{(0)*}(\mathbf{r}_1, \mathbf{r}_2) H' \psi_a^{(0)}(\mathbf{r}_1, \mathbf{r}_2) d^3r_1 d^3r_2 \\
&= \int \psi_{200}^*(\mathbf{r}_1) \psi_{100}^*(\mathbf{r}_2) V_{ee}(\mathbf{r}_1, \mathbf{r}_2) \psi_{100}(\mathbf{r}_1) \psi_{200}(\mathbf{r}_2) d^3r_1 d^3r_2, \\
H'_{ab} &= \int \psi_a^{(0)*}(\mathbf{r}_1, \mathbf{r}_2) H' \psi_b^{(0)}(\mathbf{r}_1, \mathbf{r}_2) d^3r_1 d^3r_2 \\
&= \int \psi_{100}^*(\mathbf{r}_1) \psi_{200}^*(\mathbf{r}_2) V_{ee}(\mathbf{r}_1, \mathbf{r}_2) \psi_{200}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) d^3r_1 d^3r_2, \\
H'_{bb} &= \int \psi_b^{(0)*}(\mathbf{r}_1, \mathbf{r}_2) H' \psi_b^{(0)}(\mathbf{r}_1, \mathbf{r}_2) d^3r_1 d^3r_2 \\
&= \int \psi_{200}^*(\mathbf{r}_1) \psi_{100}^*(\mathbf{r}_2) V_{ee}(\mathbf{r}_1, \mathbf{r}_2) \psi_{200}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) d^3r_1 d^3r_2.
\end{aligned}$$

One can show that all these matrix elements are real, not complex, and also that $H'_{aa} = H'_{bb}$ and $H'_{ba} = H'_{ab}$. (The proof use the fact that $V_{ee}(\mathbf{r}_1, \mathbf{r}_2) = V_{ee}(\mathbf{r}_2, \mathbf{r}_1)$; it is left as an exercise.) It is customary to denote H'_{aa} and H'_{bb} by the letter J and H'_{ba} and H'_{ab} by the letter K . Eq. (4.25) can then be written as

$$\begin{vmatrix} J - E^{(1)} & K \\ K & J - E^{(1)} \end{vmatrix} = 0. \quad (4.26)$$

That is $[J - E^{(1)}]^2 - K^2 = 0$, which gives the two possible values of $E^{(1)}$:

$$E^{(1)} = J + K \quad \text{and} \quad E^{(1)} = J - K. \quad (4.27)$$

Note 2: Calculating the integrals J and K is not particularly difficult but is outside the scope of the course. See Appendix I for an example of such calculations.

The two wave functions corresponding to these two energy sub-levels reduce to different linear combinations of zero-order eigenfunctions of H_0 in the limit where the perturbation H' is turned off, namely

$$\phi_S^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = [\psi_{100}(\mathbf{r}_1) \psi_{200}(\mathbf{r}_2) + \psi_{200}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2)] / \sqrt{2} \quad (4.28)$$

for $J + K$ and

$$\phi_A^{(0)}(\mathbf{r}_1, \mathbf{r}_2) = [\psi_{100}(\mathbf{r}_1) \psi_{200}(\mathbf{r}_2) - \psi_{200}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2)] / \sqrt{2} \quad (4.29)$$

for $J - K$. As could be expected from the results of Section 4.5, the “correct” zero-order wave functions are thus either space-symmetric or space-antisymmetric, and these two possibilities correspond to two different eigenenergies of the total Hamiltonian.

Note 3: Explanation: According to degenerate perturbation theory, the perturbed wave functions reduce to specific linear combinations of the zero-order wave functions in the limit where the perturbation is turned off. If the possible values of $E^{(1)}$ are given by the solutions of Eq. (4.25), then the “correct” linear combinations are given by $c_a\psi_a^{(0)} + c_b\psi_b^{(0)}$ with c_a and c_b such that

$$\begin{pmatrix} H'_{aa} - E^{(1)} & H'_{ba} \\ H'_{ab} & H'_{bb} - E^{(1)} \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0. \quad (4.30)$$

In the present case, Eq. (4.30) becomes

$$\begin{pmatrix} -K & K \\ K & -K \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0 \quad (4.31)$$

for $E^{(1)} = J + K$ and

$$\begin{pmatrix} K & K \\ K & K \end{pmatrix} \begin{pmatrix} c_a \\ c_b \end{pmatrix} = 0 \quad (4.32)$$

for $E^{(1)} = J - K$. These two equations show that $c_b = c_a$ when $E^{(1)} = J + K$ and that $c_b = -c_a$ when $E^{(1)} = J - K$. Taking $c_a = 1/\sqrt{2}$ for normalization leads to the functions $\phi^{(0)+}(\mathbf{r}_1, \mathbf{r}_2)$ and $\phi^{(0)-}(\mathbf{r}_1, \mathbf{r}_2)$ quoted above.

The splitting found in this example is an instance of “exchange splitting”. The resulting difference in energy between the two configurations is far from small for low lying excited states in helium, (here $2K \approx 1.2$ eV for the 1s2s configuration), which is not surprising since it originates from the electrostatic interaction between the two electrons. Exchange splitting of energy levels is in fact a general feature of the bound states of interacting electrons. It is found in many complex atoms as well as in a variety of other systems.

Note 4: Both J and K are positive (that J is positive is readily apparent from the definition of this quantity, since $|\psi_{100}(\mathbf{r}_1)\psi_{200}(\mathbf{r}_2)|^2 V_{ee}(\mathbf{r}_1, \mathbf{r}_2)$ is never negative; however, that K is also positive is difficult to see without calculating this integral). Since J and K are both positive, the perturbative calculation predicts that the ortho state (space-antisymmetric, $E^{(1)} = J - K$) is lower in energy than the para state (space-symmetric, $E^{(1)} = J + K$). In fact, ortho states are lower in energy than their para counterparts for all the bound states of helium. This difference can be traced to the fact, already mentioned in Section 4.4, that in a space-symmetric state the two electrons tend to have a higher probability to be close together than in a space-antisymmetric state, which increases their potential energy (increases, not decreases, since the electrons repel each other).

Note 5: As seen in Section 4.4, the ground state eigenenergy of H_0 is $E_1 + E_1$ and corresponds to the configuration in which both electron 1 and electron 2 are in the 1s state of their respective one-electron Hamiltonian. Since this eigenenergy is not degenerate, one can use ordinary perturbation theory to estimate the effect of the electron-electron interaction in that configuration. To first order in $V_{ee}(\mathbf{r}_1, \mathbf{r}_2)$, one finds the corresponding energy shift to be

$$E^{(1)} = \int \psi_{100}^*(\mathbf{r}_1) \psi_{100}^*(\mathbf{r}_2) V_{ee}(\mathbf{r}_1, \mathbf{r}_2) \psi_{100}(\mathbf{r}_1) \psi_{100}(\mathbf{r}_2) d^3r_1 d^3r_2.$$

This integral can be calculated using the results derived in Appendix I.

Note 6: How good is perturbation theory here? In so far as calculating accurate bound state energies and wave functions is concerned, this approach is pretty poor. For example, the exact ground state energy of helium is about -79 eV. (This energy is known both experimentally and theoretically to many places.) To zero order in V_{ee} , perturbation theory gives -109 eV. As shown in one of the exercises of Worksheet 6, the first order correction brings this energy to -75 eV, much closer to the exact value but still quite far off. To take another example, the first order treatment of $V_{ee}(\mathbf{r}_1, \mathbf{r}_2)$ predicts 1.2 eV for the exchange splitting of the 1s2s energy levels of helium (that's $2K$), whereas the actual splitting is about 0.8 eV.

Treating $V_{ee}(\mathbf{r}_1, \mathbf{r}_2)$ perturbatively is therefore a rather rough approach. In fact, it is much better to use the variational method for calculating the energy levels of helium, and extremely accurate results can be obtained in this way.

Note 7: The fact that the 1s2p states of H_0 have the same zero-order energy as the 1s2s states does not invalidate our analysis. The 1s2p states can be readily included in the perturbative treatment of $V_{ee}(\mathbf{r}_1, \mathbf{r}_2)$. However, one finds that this interaction does not mix the 1s2s states with the 1s2p states, which means that the latter do not affect how the 1s2s energy level shifts and splits from its zero-order position.

4.7 Total orbital angular momentum

The total orbital angular momentum for helium; the corresponding quantum numbers L and M .

The wave functions $\psi_{nlm}(\mathbf{r})$ we have used a number of times in the course are eigenfunctions not only of the Hamiltonian (4.1) or (4.2) but also of the operators \mathbf{L}^2 and L_z , where \mathbf{L} is the orbital angular momentum operator and L_z is the z -component of \mathbf{L} . Specifically,

$$\mathbf{L}^2 \psi_{nlm}(\mathbf{r}) = l(l+1)\hbar^2 \psi_{nlm}(\mathbf{r}), \quad L_z \psi_{nlm}(\mathbf{r}) = m\hbar \psi_{nlm}(\mathbf{r}). \quad (4.33)$$

In the case of helium, each of the two electrons has its own angular momentum operator, \mathbf{L}_1 for electron 1 and \mathbf{L}_2 for electron 2. \mathbf{L}_1 acts only on the coordinates of electron 1 and \mathbf{L}_2 acts only on the coordinates of electron 2. For example, in terms of the spherical polar coordinates of the two electrons, (r_1, θ_1, ϕ_1) and (r_2, θ_2, ϕ_2) ,

$$L_{1z} = -i\hbar \frac{\partial}{\partial \phi_1} \quad \text{and} \quad L_{2z} = -i\hbar \frac{\partial}{\partial \phi_2}, \quad (4.34)$$

and it is clear that L_{1z} acts only on the coordinate ϕ_1 and L_{2z} acts only on the coordinate ϕ_2 .

Because the two electrons interact with each other, it is generally not the case that the bound state eigenfunctions $\psi(\mathbf{r}_1, \mathbf{r}_2)$ of the helium Hamiltonian are also eigenfunctions of \mathbf{L}_1^2 , L_{1z} , \mathbf{L}_2^2 or L_{2z} . However, one can show that they are necessarily eigenfunctions of \mathbf{L}^2 , where here \mathbf{L} is the total orbital angular momentum operator:

$$\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2. \quad (4.35)$$

These eigenfunctions can be taken also to be eigenfunctions of the z -component of \mathbf{L} , $L_z = L_{1z} + L_{2z}$. (Don't be confused by the notation: at the beginning of this section \mathbf{L} denoted the angular momentum operator for the *single* electron of a hydrogenic atom or ion, whereas here and in the following, \mathbf{L} is the *total* orbital angular momentum operator of the *whole* two-electron system.)

Note 1: It is understood that here we refer to the eigenfunctions of the Hamiltonian (4.6), which does not include spin-orbit coupling. The energy eigenstates are no longer eigenfunctions of L_z when spin-orbit coupling is taken into account.

Referring to the general results summarized in Section 4.2, we know that the eigenvalues of \mathbf{L}^2 are of the form $L(L+1)\hbar^2$, with $L = 0, 1, 2, \dots$, and that the eigenvalues of L_z are $M\hbar$ with $-L \leq M \leq L$. As is customary for multi-electron systems, we use capital letters for the quantum numbers L and M ; lower case symbols (l, m) are normally used only for one-electron systems, such as atomic hydrogen.

Note 2: Why the eigenfunctions of helium aren't also eigenfunctions of \mathbf{L}_1^2 and \mathbf{L}_2^2 , besides \mathbf{L}^2 , can be understood from the following consideration. If they were classical particles, neither the angular momentum of electron 1 nor that of electron 2 would be constants of motion, since the two electrons interact with each other; however, the *total* angular momentum of the two electrons would be constant (unless there would be an external force acting on the system, that is, such as an external electric field — recall that the total angular momentum of a system of mass points is always a constant of motion if the system is isolated but may vary in time in the presence of external forces).

Note 3: Formally, the non-relativistic helium Hamiltonian has a complete set of eigenstates which are also eigenstates of \mathbf{L}^2 and of L_z because the total angular momentum operator \mathbf{L} commutes with the Hamiltonian (4.6). The fact that these operators commute can be established by direct calculation. However, the reader who would know enough angular momentum theory will recognize that \mathbf{L} cannot not commute with the Hamiltonian of Eq. (4.6) since this Hamiltonian is invariant under rotation. \mathbf{L}_1 and \mathbf{L}_2 commute with H_1 and H_2 but not with $V_{ee}(\mathbf{r}_1, \mathbf{r}_2)$

4.8 Complete set of coordinates

In this section: The spin “coordinate”.

Let us start with the case of a one-electron system, an atom of hydrogen for example. In 3D one needs three independent variables to define the position of the electron, e.g., its x -, y - and z -coordinates. In other words, in 3D an electron has three spatial degrees of freedom. Imagine that one would measure where the electron is at a particular time, t_0 say (the experiment might be difficult to carry out but is not impossible in principle). If before this measurement the electron is in a state of wave function $\Psi(\mathbf{r}, t)$, then the probability that it is found within an infinitesimal volume d^3r about a point of position vector \mathbf{r}_0 is $|\Psi(\mathbf{r}_0, t_0)|^2 d^3r$.

A precise measurement of the position of this electron would be incompatible with a precise measurement, at the same time, of its linear momentum or its orbital angular momentum. Indeed, both the linear momentum and the orbital angular momentum are represented by operators which do not commute with the position operator, and the result of a joint measurement of two observables which do not commute is necessarily uncertain (recall previous Quantum Mechanics courses). The x , y and z position operators do commute with each other, and therefore there is no uncertainty relation limiting the precision at which the corresponding spatial coordinates can be measured. It may well be that the *probability* of finding a particular value x_0 for the x -coordinate will depend on the result obtained for the y - and z -coordinates, but the corresponding physical *observables* are independent from each other.

Now, the electron also has a spin degree of freedom. Since the electron’s spin operator commutes with its position operator, it is in principle possible also to measure the spin of the electron in the z -direction, together with the electron’s position. The probability that one gets spin up or spin down may vary with position. However, the spin observable (the spin operator) does not depend on the electron’s spatial coordinates. The spin in the z -direction is thus a fourth degree of freedom, distinct from the electron’s three spatial degrees of freedom. In the same way as the position with respect to the x -, y - and z -axes correspond

to three spatial coordinates, one can associate a spin coordinate, σ , to the spin in the z -direction. However, contrary to x , y and z , this spin coordinate does not vary continuously: a measurement of the spin in the z -direction can only have two different outcomes (spin up or spin down), and therefore σ can only take two different values (e.g., $\hbar/2$ for spin up and $-\hbar/2$ for spin down, which are the corresponding eigenvalues of S_z).

Taking spin into account, each electron in a multi-electron system can thus be assigned a complete set of coordinates, usually denoted by the letter q , which includes its spin coordinate, σ . Namely, for the i -th electron, $q_i \equiv (x_i, y_i, z_i, \sigma_i)$ in terms of the Cartesian coordinates of this electron, or $q_i \equiv (\mathbf{r}_i, \sigma_i)$ in terms of its position vector.

Note 1: Why only one spin coordinate, corresponding to the spin in the z -direction, not also spin coordinates corresponding to the spin in the x - or y -directions? If the atom is not perturbed, e.g., by an external electric or magnetic field, there is nothing special with the z -direction from a Physics point of view. The choice of this direction to define the spin coordinate is a mere convention. However, there is good reason why there is only one spin coordinate: one cannot assign precise values ($\pm\hbar/2$) simultaneously to the electron's spin in the z -direction *and* to its spin in the x - y - or any other direction. Mathematically, this impossibility stems from the fact that the respective operators (S_z , S_x , S_y , etc.) do not commute (recall that different components of a same spin operator never commute). It would not make sense, therefore, to have several independent spin coordinates, each one corresponding to the spin in a different direction.

4.9 Singlet and triplet spin states

In this section: Spin states of a system of two spin-1/2 particles; singlet and triplet states.

Extending the discussion of the previous sections to include spin, we now describe the energy eigenstates of the helium atom by spin-dependent wave functions $\psi(q_1, q_2)$. As the Hamiltonian does not depend on the spin operator, including spin can be done by simply multiplying the eigenfunctions of the Hamiltonian by the relevant spin states.

Since we have two electrons, we have two spin operators — an operator \mathbf{S}_1 , which acts only on the spin state of electron 1, and an operator \mathbf{S}_2 , which acts only on the spin state of electron 2. As they act on different spin states, the three components of \mathbf{S}_1 commute with the three components of \mathbf{S}_2 . We denote the joint eigenstates of \mathbf{S}_1^2 and of S_{1z} by $\chi_{s,m_s}(1)$, and the joint eigenstates of \mathbf{S}_2^2 and of S_{2z} by $\chi_{s,m_s}(2)$. Recall that the quantum numbers s and m_s are such that

$$\mathbf{S}_1^2 \chi_{s,m_s}(1) = s(s+1)\hbar^2 \chi_{s,m_s}(1) \quad \text{and} \quad S_{1z} \chi_{s,m_s}(1) = m_s \hbar \chi_{s,m_s}(1), \quad (4.36)$$

and similarly for \mathbf{S}_2^2 , S_{2z} and $\chi_{s,m_s}(2)$. Because an electron is a spin-1/2 particle, the only relevant spin states here are those for which $s = 1/2$. Hence the only possible values of m_s are $1/2$ and $-1/2$, which correspond respectively to a state of spin up and a state of spin down. To simplify the notation, in the following we will denote the state of spin up ($\chi_{1/2,1/2}$) by α and the state of spin down ($\chi_{1/2,-1/2}$) by β .

Given a solution $\psi(\mathbf{r}_1, \mathbf{r}_2)$ of the time-independent Schrödinger equation, we have the following possibilities for the corresponding spin-dependent energy eigenstates:

$$\psi(\mathbf{r}_1, \mathbf{r}_2)\alpha(1)\alpha(2), \quad \psi(\mathbf{r}_1, \mathbf{r}_2)\alpha(1)\beta(2), \quad \psi(\mathbf{r}_1, \mathbf{r}_2)\beta(1)\alpha(2), \quad \psi(\mathbf{r}_1, \mathbf{r}_2)\beta(1)\beta(2),$$

as well as any linear combination of these four states. All these states have the same energy since the Hamiltonian does not depend on spin. However, we will see in Section 4.11 that some do not represent physically realizable states.

Each of the four spin states listed above is an eigenstate of \mathbf{S}_1^2 , \mathbf{S}_2^2 , S_{1z} and S_{2z} . For example,

$$\begin{aligned} S_{2z}\psi(\mathbf{r}_1, \mathbf{r}_2)\alpha(1)\beta(2) &= \psi(\mathbf{r}_1, \mathbf{r}_2)\alpha(1)[S_{2z}\beta(2)] \\ &= (-\hbar/2)\psi(\mathbf{r}_1, \mathbf{r}_2)\alpha(1)\beta(2). \end{aligned} \quad (4.37)$$

However, it is useful to work instead with the joint eigenstates of \mathbf{S}^2 , \mathbf{S}_1^2 , \mathbf{S}_2^2 and S_z , where \mathbf{S} is the total spin operator:

$$\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2. \quad (4.38)$$

We will denote these joint eigenstates by the symbol $\chi_{S,M_S}(1,2)$. From the general results summarized in Section 4.2, we have

$$\mathbf{S}^2 \chi_{S,M_S}(1,2) = S(S+1)\hbar^2 \chi_{S,M_S}(1,2), \quad (4.39)$$

with $|1/2 - 1/2| \leq S \leq 1/2 + 1/2$, and

$$S_z \chi_{S,M_S}(1,2) = M_S \hbar \chi_{S,M_S}(1,2), \quad (4.40)$$

with $-S \leq M_S \leq S$. The first inequality constraints the total spin quantum number S to be either 0 or 1. Therefore M_S can only be 0 if $S = 0$, whereas if $S = 1$, M_S can be equal to -1 , 0 or 1. The corresponding spin states are given in Table 4.1. $S = 1$ states are called triplet states, since there are three possibilities for M_S . There is only one possibility when $S = 0$, and therefore states with $S = 0$ are called singlet states.

Table 4.1: Singlet ($S = 0$) and triplet ($S = 1$) spin states of two electrons

S	M_S	$\chi_{S,M_S}(1, 2)$
0	0	$[\alpha(1)\beta(2) - \beta(1)\alpha(2)]/\sqrt{2}$
1	1	$\alpha(1)\alpha(2)$
1	0	$[\alpha(1)\beta(2) + \beta(1)\alpha(2)]/\sqrt{2}$
1	-1	$\beta(1)\beta(2)$

Note 1: The general method by which such joint eigenstates can be found is outside the scope of the course; checking that the states listed in the table are indeed eigenstates of \mathbf{S}^2 and S_z is left as an exercise.

Note 2: Another notation for the spin states α and β is $|\uparrow\rangle$ and $|\downarrow\rangle$. For example, the singlet state is often written $(|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2)/\sqrt{2}$, or in an even more compact notation, $(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$.

Note 3: Recall that \mathbf{S}_1 acts only on the spin state of electron 1 and \mathbf{S}_2 only on the spin state of electron 2. Therefore, the matrices representing the components of \mathbf{S}_1 act only on the column vectors representing the spin state of electron 1, and those representing the components of \mathbf{S}_2 act only on the column vectors representing the spin state of electron 2.

Note 4: It is often said that in triplet states the spins of the two electrons are aligned whereas in singlet states they are antialigned. Table 4.1 shows that in the z -direction, the spins are antialigned when $S = 0$, as one of the electrons is in a state of spin up and the other in a state of spin down. It also shows that they are aligned in the $M_S = 1$ and $M_S = -1$ triplet states (being both up or both down). Confusingly, in the $M_S = 0$ triplet state the two spins are antialigned in the z -direction, not aligned. However, one can show that in that state they are aligned in the x -direction, not in the z -direction. (The calculation is left as a problem for the reader.) By contrast, one can also show that in the $M_S = 0$ singlet state a measurement of the two spins would always find them antialigned, for any direction they would be measured in. (The proof of this assertion is also left as a problem for the reader.)

The spin-dependent wave functions of the energy eigenstates of helium can therefore be written in the following form,

$$\psi_{S,M_S}(q_1, q_2) = \psi(\mathbf{r}_1, \mathbf{r}_2) \chi_{S,M_S}(1, 2), \quad (4.41)$$

where as above $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is a solution of the time-independent Schrödinger equation. We will come back to this point in Section 4.11, where we will see that the space-symmetric states are necessarily singlet spin states and that the space-antisymmetric states are necessarily triplet spin states. This correspondence between spin states and the symmetry of the wave function stems from the fact that the two electrons are identical in every respect.

4.10 Identical particles in Quantum Mechanics

In this section: Completely symmetric states and completely antisymmetric states; bosons and fermions; relation between spin and symmetry.

Two macroscopic objects are never totally identical to each other. However similar they might be, a sufficiently close inspection will always reveal differences. This is not the case for objects such as electrons or atoms: two atoms of the same species have exactly the same energy levels, exactly the same energy eigenfunctions and exactly the same physical and chemical properties. Likewise, there is no difference whatsoever between an electron and another electron. Identical quantum particles are thus indistinguishable from each other. This simple fact has deep and far ranging consequences, and is of key importance.

To understand why, you need to be aware that the wave function (including spin) of a system of N identical particles is a function of the N coordinates of these particles, q_1, q_2, \dots, q_N . For example, the wave function of a system of four identical particles could be a certain function $\Psi_a(q_1, q_2, q_3, q_4, t)$. Swapping the coordinates of particles 1 and 2 in the wave function would lead to the wave function $\Psi_b(q_1, q_2, q_3, q_4, t) \equiv \Psi_a(q_2, q_1, q_3, q_4, t)$ (thus Ψ_b varies in the same way with respect to q_1 than the Ψ_a varies with respect to q_2 , and vice versa). Formally, one can introduce the operator P_{ij} which permutes the coordinates q_i and q_j , so that, in this example, $\Psi_b(q_1, q_2, q_3, q_4, t) \equiv P_{12}\Psi_a(q_1, q_2, q_3, q_4, t)$.

Key Point 1: The physical properties of a quantum systems including several identical particles cannot depend on which of these particles has coordinates q_1 , which has coordinates q_2 , etc. (We include spin in the coordinates, as explained in Section 4.8. However, here we do not assume that the particles are electrons or have a spin of $1/2$; the present discussion is completely general.)

- For example, take a system of two identical particles, and imagine swapping them: the system after the swap is undistinguishable from the system before the swap and has exactly the same observable properties.

- We have already encountered this symmetry and looked at some of its consequences, in Section 4.5. The helium Hamiltonian depends exactly in the same way on the coordinates of electron 1 as on the coordinates of electron 2. This could not be otherwise since the two electrons are identical. Therefore the energy levels of this atom do not depend on which of the two electrons is electron 1 and which is electron 2.
- The word “particle” here does not refer exclusively to particles that are not known to be composed of more elementary entities, such as electrons and quarks. Instead, by “particles”, we mean any quantum object treated as a whole, e.g., an atomic nucleus or even a whole molecule.

Key Point 2: Swapping two identical particles either leaves the wave function unchanged or changes its sign. That is, either $P_{ij}\Psi(q_1, \dots, q_N, t) \equiv \Psi(q_1, \dots, q_N, t)$ or $P_{ij}\Psi(q_1, \dots, q_N, t) \equiv -\Psi(q_1, \dots, q_N, t)$, for any pair i, j of identical particles. (We stress that this rule applies only to the interchange of *identical* particles. There are no such rules for the interchange of particles of a different nature.)

Note 1: Why swapping the coordinates of two identical particles can only amount to multiplying the wave function by 1 or by -1 can be seen from the following argument. Since the two particles are undistinguishable from each other, the states $\Psi(q_1, \dots, q_N, t)$ and $P_{ij}\Psi(q_1, \dots, q_N, t)$ must have exactly the same physical properties. Thus all the predictions on the outcome of possible experiments one could derive from $\Psi(q_1, \dots, q_N, t)$ must be the same as those one could derive from $P_{ij}\Psi(q_1, \dots, q_N, t)$. For this to be possible, one must have

$$P_{ij}\Psi(q_1, \dots, q_N, t) = \exp(i\chi)\Psi(q_1, \dots, q_N, t),$$

where χ is a constant which does not depend on q_i and q_j . [This condition is sufficient, as multiplying a wave function by a constant phase factor does not change the probabilities that can be inferred from that wave function. A proof that this condition is also necessary can be found in E. E. Witmer and J. P. Vinti, Phys. Rev. **47**, 538 (1935), and is outside the scope of this course.] Permuting q_i and q_j again, one gets

$$\begin{aligned} P_{ij}P_{ij}\Psi(q_1, \dots, q_N, t) &= P_{ij}[P_{ij}\Psi(q_1, \dots, q_N, t)] \\ &= P_{ij}\exp(i\chi)\Psi(q_1, \dots, q_N, t) \\ &= \exp(i\chi)P_{ij}\Psi(q_1, \dots, q_N, t) \\ &= [\exp(i\chi)]^2\Psi(q_1, \dots, q_N, t). \end{aligned}$$

Since swapping the coordinates q_i and q_j twice in the wave function amounts to not swapping them at all, $P_{ij}P_{ij}\Psi(q_1, \dots, q_N, t) = \Psi(q_1, \dots, q_N, t)$. Hence $[\exp(i\chi)]^2 = 1$, which means that either $\exp(i\chi) = 1$ or $\exp(i\chi) = -1$.

Note 2: In the case where there are more than two identical particles, whether the wave function changes sign or remains constant cannot depend on which coordinates are swapped. Why this needs to be so can be understood by looking at the case of a system containing three identical particles, described by a wave function $\psi(q_1, q_2, q_3)$. Let us suppose that this wave function would remain the same when q_1 is permuted with q_2 but would change sign when q_1 is permuted with q_3 . Therefore

$$\psi(q_1, q_2, q_3) = -\psi(q_3, q_2, q_1) = -\psi(q_3, q_1, q_2) = \psi(q_1, q_3, q_2).$$

However, one can also obtain the opposite result using a different sequence of permutations:

$$\psi(q_1, q_2, q_3) = \psi(q_2, q_1, q_3) = -\psi(q_2, q_3, q_1) = -\psi(q_1, q_3, q_2).$$

The contradiction between these two results shows that it is not possible for the wave function to be symmetric in one pair of particles and antisymmetric in another pair of the same particles: the wave function is either completely symmetric or completely antisymmetric.

Note 3: We have seen that the energy levels of the helium Hamiltonian split into levels corresponding to space-symmetric eigenstates and levels corresponding to space-antisymmetric eigenstates. Is this related to what we are talking about here? The answer is yes in some respects: The eigenfunctions of the Hamiltonian given by Eq. (4.6) would not be space-symmetric or space-antisymmetric if this operator was not symmetric in the coordinates of the two electrons. Moreover there can be exchange degeneracy only if the particles involved are identical (see Section 4.4). For example, the zero-order wave functions $\psi_a^{(0)}(\mathbf{r}_1, \mathbf{r}_2)$ and $\psi_b^{(0)}(\mathbf{r}_1, \mathbf{r}_2)$ defined by Eqs. (4.19) and (4.20) would correspond to two *distinct* energy levels of the unperturbed Hamiltonian H_0 if the two electrons had unequal masses. However, to first order in the electron-electron interaction, the energy gap between these two levels would still be larger than to zero order, similarly to what is found when the two electrons are (correctly) considered to have the same mass.

Key Point 3: One finds that there is complete symmetry for, e.g., photons,¹ and complete antisymmetry for, e.g., electrons, protons, neutrons, etc. Quantum objects for which there is symmetry are called bosons, those for which there

¹Photons cannot be described by way of a wave function. However, the property of the wave functions to be either completely symmetric or completely antisymmetric for the interchange of two identical particles carries over to Quantum Field Theory, which is the appropriate theoretical framework for a quantum description of light.

is antisymmetry are called fermions. In Quantum Statistical Mechanics, bosons follow the Bose-Einstein statistics and fermions the Fermi-Dirac statistics.

Key Point 4: Composite systems such as nuclei and atoms are themselves fermions if they include an odd number of fermions; otherwise they are bosons.

- Example 1: An atom of hydrogen-1 (a proton and an electron) is a boson. To see this, first imagine that one has two such atoms, sufficiently apart from each other that each one can be treated as a bound state of an electron and a proton. Atom 1 has an electron of coordinates q_1 and a proton of coordinates Q_1 , and atom 2 has an electron of coordinates q_2 and a proton of coordinates Q_2 . Let $\Psi(q_1, Q_1, q_2, Q_2, t)$ be a wave function describing a quantum state of the joint system system formed by these two atoms. Swapping atom 1 and atom 2 amounts to swapping electron 1 and electron 2 as well as to swapping proton 1 and proton 2. This transforms the wave function into $\Psi(q_2, Q_2, q_1, Q_1, t)$. Now, both electrons and protons are fermions. Thus each of these two swaps amounts to multiplying the wave function by a factor (-1) , so that $\Psi(q_2, Q_2, q_1, Q_1, t) = (-1)^2 \Psi(q_1, Q_1, q_2, Q_2, t) = \Psi(q_1, Q_1, q_2, Q_2, t)$. Hence, swapping the two atoms does not change their joint wave function at all, which means that an atom of hydrogen-1, considered as a whole, is a boson.
- Example 2: An atom of deuterium (hydrogen-2) is a fermion. The nucleus of deuterium (a deuteron) is composed of a proton and a neutron. An atom of this species is thus a bound state of three fermions, i.e., an electron of coordinates q , a proton of coordinates Q and a neutron of coordinates Q' . Hence, swapping two such atoms transforms any of their joint wave functions $\Psi(q_1, Q_1, Q'_1, q_2, Q_2, Q'_2, t)$ into the wave function $\Psi(q_2, Q_2, Q'_2, q_1, Q_1, Q'_1, t)$. Since

$$\begin{aligned} \Psi(q_2, Q_2, Q'_2, q_1, Q_1, Q'_1, t) &= (-1)^3 \Psi(q_1, Q_1, Q'_1, q_2, Q_2, Q'_2, t) \\ &= -\Psi(q_1, Q_1, Q'_1, q_2, Q_2, Q'_2, t), \end{aligned}$$

the swap of the two atoms changes the sign of the wave function, which means that an atom of deuterium, considered as a whole, is indeed a fermion.

- Example 3: By the same token, an atom of helium-4 (two electrons, two protons and two neutrons) is a boson whereas an atom of helium-3 (two electrons, two protons and only one neutron) is a fermion.
- Example 4: Since electrons are fermions, the wave functions of helium (including spin) must be antisymmetric in the two electrons, irrespective on whether the atom as a whole is a fermion or a boson.

Key Point 5: There is a remarkable correspondence between the spin of a particle (or a composite system) and whether it is a boson or a fermion: quantum objects with an integer spin (0, 1, etc.) are always bosons, and those with a half-integer spin (1/2, 3/2, etc.) are always fermions. (This correspondence between spin quantum number and whether the system is a boson or a fermion is an extremely well established experimental fact. It can also be mathematically proved — that’s the famous spin-statistics theorem — but the proof is complicated and involves advanced concepts of Quantum Field Theory and Special Relativity.)

4.11 The spectrum of helium

In this section: Singlet and triplet states of helium; spin-orbit coupling; term symbols; intercombination lines.

We now come back to our survey of the bound states of helium. We had left it, at the end of Section 4.9, with the observation that the bound state wave functions can be written in the form of a product of a spatial wave function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ and a spin state $\chi_{S,M_S}(1, 2)$. The total spin quantum number, S , can be either 0 (singlet states) or 1 (triplet states). We saw that depending on the energy level, $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is either symmetric or antisymmetric in \mathbf{r}_1 and \mathbf{r}_2 . The spin states $\chi_{S,M_S}(1, 2)$ are also either symmetric or antisymmetric in the two electrons. As shown by Table 4.1, the singlet spin state is antisymmetric (it changes sign when electron 1 is swapped with electron 2) and the triplet spin states are symmetric (they do not change sign).

Since the Hamiltonian does not depend on spin, there is no mathematical reason why the value of S should depend on whether the spatial wave function is symmetric or antisymmetric. However, there is a physical reason: because the electrons are fermions, a wave function $\psi_{S,M_S}(q_1, q_2)$ may represent a possible state of helium only if it changes sign when the two electrons are swapped. Given that $\psi_{S,M_S}(q_1, q_2) = \psi(\mathbf{r}_1, \mathbf{r}_2)\chi_{S,M_S}(1, 2)$, the spatial wave function $\psi(\mathbf{r}_1, \mathbf{r}_2)$ must change sign if the spin state $\chi_{S,M_S}(1, 2)$ does not, and conversely $\chi_{S,M_S}(1, 2)$ must change sign if $\psi(\mathbf{r}_1, \mathbf{r}_2)$ does not. Hence space-symmetric states are always singlet states and space-antisymmetric states are always triplet states.

Note 1: As is explained in Section 4.6, each of the energy levels of the zero-order Hamiltonian $H_1 + H_2$ shifts and splits under the effect of the electron-electron interaction. To first order in that interaction, the bound states energies are given in terms of the sum or the difference of the J and K integrals: $E^{(1)} = J + K$ for the space-symmetric states and $E^{(1)} = J - K$ for the space-antisymmetric states. Hence $E^{(1)} = J + K$ for the singlet states and $E^{(1)} = J - K$ for the triplet states. One can show that singlet and triplet states are eigenstates of the operator

$$J - \frac{K}{2} \left[1 + \frac{4}{\hbar^2} \mathbf{S}_1 \cdot \mathbf{S}_2 \right],$$

where \mathbf{S}_1 and \mathbf{S}_2 are the spin operators for electrons 1 and 2 (see Worksheet 6). The corresponding eigenvalues are $J + K$ for singlet states and $J - K$ for triplet states. Hence, everything happens as if the energy splitting between singlet and triplet states was due to a spin-dependent interaction between the two electrons, the Hamiltonian of the interaction depending on \mathbf{S}_1 and \mathbf{S}_2 through the dot product $\mathbf{S}_1 \cdot \mathbf{S}_2$. This effective interaction is called the exchange interaction. It plays an important role in the theory of magnetism in solids.

It should be understood, however, that the primary physical origin of the splitting between singlet and triplet energy levels is the electrostatic interaction between the two electrons, not an actual spin-spin interaction. Because each electron has a magnetic moment proportional to its spin operator, there is a magnetic coupling between the two electron spins; however, this effect is not taken into account in the Hamiltonian (4.6) and is very small compared to the exchange effects considered here.

Besides its singlet or triplet character, each of the energy levels of the helium Hamiltonian (4.6) can also be characterized by a principal quantum number, n , and a total orbital angular momentum quantum number, L . [Recall, from Section 4.7, that the eigenfunctions of this Hamiltonian are also eigenfunctions of \mathbf{L}^2 , where \mathbf{L} is the total orbital angular momentum operator defined by Eq. (4.35), and that the eigenvalues of \mathbf{L}^2 are $L(L + 1)\hbar^2$ with $L = 0, 1, 2, \dots$] The principal quantum number is 1 for the ground state. Like the ground state of the Hamiltonian $H_1 + H_2$ of Section 4.4, this state is space-symmetric (hence is a singlet state) and its orbital angular momentum quantum number L is zero. The principal quantum number is larger than 1 for the excited states ($n = 2, 3, \dots$).

The value of L is often referred to by a symbol letter: $L = 0$ states are called S-states, $L = 1$ states are called P-states, $L = 2$ states, D-states, etc. These symbols are the same as for atomic hydrogen, but with the difference that for complex atoms one normally uses upper case letters. Whether the states are singlet or triplet is indicated by a superscript specifying the spin multiplicity. A state with principal quantum number n , orbital angular momentum quantum number L and total spin quantum number S is thus referred to by the symbol $n^{2S+1}L$, with L replaced by the corresponding symbol letter. For example, a state of helium with principal quantum number $n = 2$ can be a 2^1S state (“two singlet S” state, corresponding to $S = 0$ and $L = 0$), a 2^3S state (“two triplet S state”, with $S = 1$ and $L = 0$), a 2^1P state ($S = 0$, $L = 1$) or a 2^3P state ($S = 1$, $L = 1$). The ground state of helium is the 1^1S state.

In the case of atomic hydrogen, all states of a same principal quantum number have the same energy (in the non-relativistic approximation). For helium,

however, states of different values of L always have different energies, even if they have the same principal quantum number.

Note 2: The dependence on L of the eigenenergies of helium is readily apparent in the perturbative approach of Section 4.6. The states $\psi_{100}(\mathbf{r}_1)\psi_{200}(\mathbf{r}_2)$ and $\psi_{200}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)$ which we took as the zero-order basis states are eigenstates of \mathbf{L}^2 with $L = 0$, and so are their symmetric or antisymmetric linear combinations. Instead of $\psi_{100}(\mathbf{r}_1)\psi_{200}(\mathbf{r}_2)$ and $\psi_{200}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)$, we could have taken, e.g., $\psi_{100}(\mathbf{r}_1)\psi_{210}(\mathbf{r}_2)$ and $\psi_{210}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2)$ as zero-order basis states. As can be easily verified, these two states and any of their linear combinations are eigenstates of \mathbf{L}^2 with $L = 1$. The zero-order energy would have been the same, but this other choice would have led to different J and K integrals, hence to different first order energies.

There is also a spin-orbit interaction in helium, as in hydrogen (see Section 4.1 above, or Section 5.2 of the QM Primer for a more complete account). This interaction, which is not included in Eq. (4.6), couples the spin of each electron to its orbital angular momentum. The resulting states are eigenstates of the operator \mathbf{J}^2 , where \mathbf{J} is the sum of the total orbital angular momentum operator \mathbf{L} and the total spin operator \mathbf{S} . The eigenvalues of \mathbf{J}^2 are $J(J+1)\hbar^2$. The possible values of the total angular momentum quantum number J in a state with orbital angular momentum quantum number L and spin quantum number S are restricted by the inequality

$$|L - S| \leq J \leq L + S. \quad (4.42)$$

The spin-orbit interaction splits each of the energy levels of the non-relativistic Hamiltonian into as many sub-levels as there are possible values of J for the corresponding values of L and S . For example, the $(S = 1, L = 2)$ levels split into sub-levels corresponding to $J = 1, 2$ or 3 , whereas the $(S = 0, L = 2)$ levels do not split (J is necessarily equal to L when $S = 0$).

The combinations of the quantum numbers L , S and J characterizing the resulting sub-levels state are succinctly represented by the symbol

$$^{2S+1}L_J,$$

in which the value of J is specified as a subscript and L by the usual symbol letter. These symbols are called term symbols. For example, the $S = 1, L = 2$ states of helium can be 3D_1 , 3D_2 or 3D_3 states.

Triplet states do not readily decay to singlet states, or singlet states to triplet states, for two reasons:

- The electric dipole operator is spin-independent and therefore does not couple different spin state.
- The electric dipole operator for two-electron systems, $-e(\mathbf{r}_1 + \mathbf{r}_2)$, is symmetric in the coordinates of the two electrons. Hence, it cannot couple symmetric states to antisymmetric states (see Note 3 later in this section).

As a consequence, the spectrum of the helium atoms consists of two different series of lines, namely one arising from transitions between singlet states and one from transitions between triplet states.

Transitions between singlet and triplet states are not completely forbidden, though, because the spin-orbit interaction prevents the energy eigenstates to be purely space-symmetric singlet states or space-antisymmetric triplet states. Spectral lines corresponding to a transition between states with different values of S are called intercombination lines. These lines are normally very faint in the spectrum of helium and other light atoms. However, they can be prominent in the spectrum of heavy elements due to the greater strength of the spin-orbit interaction in these systems.

Note 3: It is easy to see why the matrix element of a space-symmetric operator between a space-symmetric state and a space-antisymmetric state is necessarily zero. Denoting the operator by $D(\mathbf{r}_1, \mathbf{r}_2)$, the wave function of the space-symmetric state by $\psi_a(\mathbf{r}_1, \mathbf{r}_2)$ and that of the space-antisymmetric state by $\psi_b(\mathbf{r}_1, \mathbf{r}_2)$, the matrix element is the integral

$$D_{ba} = \int \psi_b^*(\mathbf{r}_1, \mathbf{r}_2) D(\mathbf{r}_1, \mathbf{r}_2) \psi_a(\mathbf{r}_1, \mathbf{r}_2) d^3r_1 d^3r_2. \quad (4.43)$$

Swapping \mathbf{r}_1 and \mathbf{r}_2 gives

$$D_{ba} = \int \psi_b^*(\mathbf{r}_2, \mathbf{r}_1) D(\mathbf{r}_2, \mathbf{r}_1) \psi_a(\mathbf{r}_2, \mathbf{r}_1) d^3r_1 d^3r_2. \quad (4.44)$$

Since the operator and state a are space-symmetric, $D(\mathbf{r}_2, \mathbf{r}_1) = D(\mathbf{r}_1, \mathbf{r}_2)$ and $\psi_a(\mathbf{r}_2, \mathbf{r}_1) = \psi_a(\mathbf{r}_1, \mathbf{r}_2)$. However, since state b is anti-symmetric, $\psi_b(\mathbf{r}_2, \mathbf{r}_1) = -\psi_b(\mathbf{r}_1, \mathbf{r}_2)$. Hence,

$$D_{ba} = - \int \psi_b^*(\mathbf{r}_1, \mathbf{r}_2) D(\mathbf{r}_1, \mathbf{r}_2) \psi_a(\mathbf{r}_1, \mathbf{r}_2) d^3r_1 d^3r_2. \quad (4.45)$$

Comparing Eqs. (4.43) and (4.45) shows that $D_{ba} = -D_{ba}$, which implies that $D_{ba} = 0$.

Note 4: The energy eigenstates do no longer correspond to a well defined value of S when the spin-orbit interaction is taken into account because the Hamiltonian of this interaction contains a term proportional to $\mathbf{L}_1 \cdot \mathbf{S}_1$ and one proportional to $\mathbf{L}_2 \cdot \mathbf{S}_2$, and hence does not commute with \mathbf{S}^2 .

Much of what we saw for helium generalizes to more complex atoms. For N electrons, each with its orbital angular momentum operator L_i and its spin operator S_i , one defines a total orbital angular momentum operator

$$\mathbf{L} = \sum_{i=1}^N \mathbf{L}_i, \quad (4.46)$$

a total spin operator

$$\mathbf{S} = \sum_{i=1}^N \mathbf{S}_i, \quad (4.47)$$

and a total angular momentum operator $\mathbf{J} = \mathbf{L} + \mathbf{S}$. The corresponding quantum numbers L , S and J can be represented by the same term symbols as in the case of helium. However, S can differ from 0 and 1 when there are more than two electrons. For example, the ground state of lithium is a ${}^2S_{1/2}$ state ($S = 1/2$, $L = 0$, $J = 1/2$) and that of vanadium is a ${}^4F_{3/2}$ state ($S = 3/2$, $L = 3$, $J = 3/2$).

Note 5: The natural way of coupling the various angular momentum operators is different for atoms with a high atomic number. For helium and light elements, the spin-orbit interaction is very weak overall compared to the Coulomb interaction between electrons. It thus makes sense to describe these atoms in terms of a total orbital angular momentum quantum number and a total spin quantum number, even though the energy eigenstates are not exact eigenstates of the corresponding \mathbf{L}^2 and \mathbf{S}^2 operators in the presence of the spin-orbit interaction. This approach is called $L - S$ coupling (or Russell-Saunders coupling). For the heaviest elements, however, a better approach is to start by coupling the orbital angular momentum of each electron to its spin, so as to obtain a total angular momentum operator for each individual electron, and then couple these individual total angular momentum operators to obtain a total \mathbf{J} operator. This scheme is called $j - j$ coupling. Other schemes intermediate between $L - S$ coupling and $j - j$ coupling are also used.

4.12 One-particle states and Pauli exclusion principle

In this section: Product wave functions; Slater determinants; the Pauli exclusion principle.

Let us briefly come back to Section 4.4. As noted in that section, the Hamiltonian of helium reduces to the sum of the one-electron Hamiltonians H_1 and H_2 if the electron-electron interaction is neglected. We have seen that neglecting

this interaction is a rather poor approximation in that particular case. However, a number of other quantum systems composed of several identical particles can be understood on the basis of models in which these particles are assumed not to interact with each other, or not to interact much (for example, electrons in a metal or in a white dwarf, and ultra-cold atoms forming a Bose-Einstein condensate).

If the particles forming the system are taken to be non-interacting, each one has its own Hamiltonian, H_i , with $i = 1, \dots, N$ for N particles, and the Hamiltonian of the whole system is the sum of these one-particle Hamiltonians:

$$H = \sum_i H_i. \quad (4.48)$$

The eigenfunctions of H can then be written in terms of the one-particle wave functions $\psi_\lambda(q_i)$, where q_i is the coordinate (including spin) of the i -th particle and $\psi_\lambda(q_i)$ is an eigenfunction of its respective Hamiltonian:

$$H_i \psi_\lambda(q_i) = E_\lambda \psi_\lambda(q_i). \quad (4.49)$$

In this equation, the subscript λ stands for the entire set of quantum numbers characterizing these eigenfunctions. The product wave functions

$$\psi_{\lambda_1 \dots \lambda_N}(q_1, \dots, q_N) = \psi_{\lambda_1}(q_1) \psi_{\lambda_2}(q_2) \cdots \psi_{\lambda_N}(q_N) \quad (4.50)$$

with $\lambda_1, \dots, \lambda_N$ running over all the possible combinations of quantum numbers, are thus eigenfunctions of H , and so are any linear combination of product wave functions of a same energy.

For example, let us assume that $N = 3$ and that particle 1 could be in the eigenstate of H_1 of wave function $\psi_{\lambda=\alpha}(q_1)$ and energy E_α , particle 2 in the eigenstate of H_2 of wave function $\psi_{\lambda=\beta}(q_2)$ and energy E_β and particle 3 in the eigenstate of H_3 of wave function $\psi_{\lambda=\gamma}(q_3)$ and energy E_γ . As these particles are identical, H_1 , H_2 and H_3 are the same Hamiltonians, apart that H_1 is expressed in terms of q_1 , H_2 in terms of q_2 and H_3 in terms of q_3 . Thus H_1 has also an eigenstate of wave function $\psi_\beta(q_1)$ and energy E_β and an eigenstate of wave function $\psi_\gamma(q_1)$ and energy E_γ , and similarly for H_2 and H_3 . This gives six linearly independent product wave functions for the 3-particle system (we assume that the α , β and γ states are all different):

$$\begin{aligned} &\psi_\alpha(q_1) \psi_\beta(q_2) \psi_\gamma(q_3), \quad \psi_\alpha(q_3) \psi_\beta(q_1) \psi_\gamma(q_2), \quad \psi_\alpha(q_2) \psi_\beta(q_3) \psi_\gamma(q_1), \\ &\psi_\alpha(q_2) \psi_\beta(q_1) \psi_\gamma(q_3), \quad \psi_\alpha(q_3) \psi_\beta(q_2) \psi_\gamma(q_1), \quad \psi_\alpha(q_1) \psi_\beta(q_3) \psi_\gamma(q_2). \end{aligned}$$

These six products functions and any linear combination of these functions are eigenfunctions of the total Hamiltonian $H_1 + H_2 + H_3$, and they all have the same

energy, $E_\alpha + E_\beta + E_\gamma$. In particular, these eigenfunctions include the completely symmetric wave function

$$\begin{aligned}\psi_S(q_1, q_2, q_3) = & \mathcal{N} [\psi_\alpha(q_1)\psi_\beta(q_2)\psi_\gamma(q_3) + \psi_\alpha(q_2)\psi_\beta(q_1)\psi_\gamma(q_3) \\ & + \psi_\alpha(q_2)\psi_\beta(q_3)\psi_\gamma(q_1) + \psi_\alpha(q_1)\psi_\beta(q_3)\psi_\gamma(q_2) \\ & + \psi_\alpha(q_3)\psi_\beta(q_1)\psi_\gamma(q_2) + \psi_\alpha(q_3)\psi_\beta(q_2)\psi_\gamma(q_1)], \quad (4.51)\end{aligned}$$

and the completely antisymmetric wave function

$$\begin{aligned}\psi_A(q_1, q_2, q_3) = & \mathcal{N} [\psi_\alpha(q_1)\psi_\beta(q_2)\psi_\gamma(q_3) - \psi_\alpha(q_2)\psi_\beta(q_1)\psi_\gamma(q_3) \\ & + \psi_\alpha(q_2)\psi_\beta(q_3)\psi_\gamma(q_1) - \psi_\alpha(q_1)\psi_\beta(q_3)\psi_\gamma(q_2) \\ & + \psi_\alpha(q_3)\psi_\beta(q_1)\psi_\gamma(q_2) - \psi_\alpha(q_3)\psi_\beta(q_2)\psi_\gamma(q_1)], \quad (4.52)\end{aligned}$$

where \mathcal{N} is a normalization factor. Within an overall constant factor, there is no other completely symmetric or completely antisymmetric combination of these six products functions. It follows from Section 4.10 that amongst all the different possibilities, only $\psi_S(q_1, q_2, q_3)$ or $\psi_A(q_1, q_2, q_3)$ could represent a physically realizable state, i.e., $\psi_S(q_1, q_2, q_3)$ if the three particles are identical bosons and $\psi_A(q_1, q_2, q_3)$ if they are identical fermions.

More generally, there are $N!$ different ways of assigning N identical particles to N different one-particle functions. Each energy level of the total Hamiltonian may thus correspond to a huge number of linearly independent eigenfunctions. However, only *one* of these eigenfunctions is physically admissible, namely the one which is completely symmetric in all the coordinates q_i if the particles are bosons or the one which is completely antisymmetric if the particles are fermions.

The N -particle states considered so far are build from N different one-particle states. Coming back to Eq. (4.52), let us now assume that the α state is exactly the same as the β state, so that $\psi_\alpha(q) \equiv \psi_\beta(q)$ for $q = q_1, q_2$ and q_3 . Eq. (4.52) then becomes

$$\begin{aligned}\psi_A(q_1, q_2, q_3) = & \mathcal{N} [\psi_\alpha(q_1)\psi_\alpha(q_2)\psi_\gamma(q_3) - \psi_\alpha(q_2)\psi_\alpha(q_1)\psi_\gamma(q_3) \\ & + \psi_\alpha(q_2)\psi_\alpha(q_3)\psi_\gamma(q_1) - \psi_\alpha(q_1)\psi_\alpha(q_3)\psi_\gamma(q_2) \\ & + \psi_\alpha(q_3)\psi_\alpha(q_1)\psi_\gamma(q_2) - \psi_\alpha(q_3)\psi_\alpha(q_2)\psi_\gamma(q_1)]. \quad (4.53)\end{aligned}$$

We see that in this case $\psi_A(q_1, q_2, q_3) \equiv 0$, which means that this wave function does not represent a physically realizable state. The same result would of course also be found if the α was identical to the γ state or the γ state to the β state, and for any number of particles. This establishes the Pauli exclusion principle: two (or more) identical fermions cannot be simultaneously in the same state.

By contrast, any number of identical bosons can be in the same state. For example, upon taking $\psi_\alpha(q) \equiv \psi_\beta(q) \equiv \psi_\gamma(q)$, Eq. (4.51) reduces to

$$\psi_S(q_1, q_2, q_3) = \psi_\alpha(q_1)\psi_\alpha(q_2)\psi_\alpha(q_3), \quad (4.54)$$

which is an unproblematic wave function.

In general, the completely antisymmetric N -particle wave function which can be constructed from a set of N one-particle states $\psi_\alpha(q)$, $\psi_\beta(q)$, \dots , $\psi_\nu(q)$ is given by the following equation:

$$\psi_A(q_1, q_2, \dots, q_N) = \mathcal{N} \begin{vmatrix} \psi_\alpha(q_1) & \psi_\beta(q_1) & \cdots & \psi_\nu(q_1) \\ \psi_\alpha(q_2) & \psi_\beta(q_2) & \cdots & \psi_\nu(q_2) \\ \vdots & \vdots & & \vdots \\ \psi_\alpha(q_N) & \psi_\beta(q_N) & \cdots & \psi_\nu(q_N) \end{vmatrix},$$

where \mathcal{N} is a normalization coefficient. The right-hand side of this equation is called a Slater determinant. This wave function is indeed completely antisymmetric in the coordinates q_1, \dots, q_N since swapping two of these coordinates means swapping two rows in the determinant, which amounts to multiplying it by -1 .

4.13 The Hartree Fock method and the periodic table

In this section: Introduction to the Hartree Fock method; spin-orbitals; self-consistency; the ground state configuration of complex atoms.

The Hartree Fock method is a powerful computational approach for calculating the ground state energy of many-electron atoms and other complex quantum systems. At the basis of this and related methods is the idea of representing the complicated interaction of each electron with the nucleus and with the other electrons by an average effective potential.

In the Hartree-Fock approach, this is done by assuming that each electron is in a one-particle state, called a spin-orbital. Each of these spin-orbitals is a product of a spatial wave function $u_\lambda(\mathbf{r})$ and a spin state $\chi_{1/2, m_s}$, where λ represents the set of all the quantum numbers identifying this one-electron state. For electron i ,

$$\psi_\lambda(q_i) = u_\lambda(\mathbf{r}_i) \chi_{1/2, m_s}(i). \quad (4.55)$$

The complete wave function of the N -electron atom is a Slater determinant constructed from a set of N different spin-orbitals (see Section 4.12). The spin-orbitals are then obtained by minimizing the energy functional of the Rayleigh-Ritz variational method. More precisely, one finds that each of the orbitals $u_\lambda(\mathbf{r})$ must satisfy a Schrödinger-like equation of the form

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + \mathcal{V}_\lambda \right] u_\lambda(\mathbf{r}) = E_\lambda u_\lambda(\mathbf{r}), \quad (4.56)$$

where the operator \mathcal{V}_λ accounts for the interaction of the electron with the nucleus and with all of the other electrons. The effect of this operator on the

orbital $u_\lambda(\mathbf{r})$ can be calculated once the spin orbitals occupied by the other $N - 1$ electrons are known.²

The problem of calculating the ground state energy of the N -electron atom is thus reduced to obtaining the operators \mathcal{V}_λ and to solving the one-electron equations (4.56). Since the operators \mathcal{V}_λ depend on the orbitals, it may seem that the procedure is circular: one cannot obtain the orbitals without knowing the operators \mathcal{V}_λ , and one cannot obtain the operators \mathcal{V}_λ without knowing the orbitals. The solution is to proceed by iterations: The trick is to start with a guess for the N spin-orbitals, obtain the corresponding operators \mathcal{V}_λ , then use these to calculate the corresponding orbitals $u_\lambda(\mathbf{r})$. Having found those, one repeats the operation: the corresponding operators are obtained again, then the orbitals are re-calculated, and one continues in this fashion until a self-consistent solution is found.

As in the case of a hydrogenic system, each spin-orbital can be labelled by a principal quantum number n ($n = 1, 2, \dots$), an orbital angular momentum l ($0 \leq l \leq n - 1$), an orbital magnetic quantum number m_l ($-l \leq m_l \leq l$), and a spin magnetic quantum number m_s ($m_s = \pm 1/2$). The ground state of the atom is obtained by populating these various orbitals in such a way as to keep the total energy as low as possible. This gives the ground state configuration of the atom, i.e., the set of orbitals occupied by the N electrons.

One can have up to two electrons in a $l = 0$ orbital — one with spin up ($m_s = 1/2$) and one with spin down ($m_s = -1/2$) — up to six electrons in a $l = 1$ orbital (m_l can be $-1, 0$ or 1 , and for each of these possibilities m_s can be $1/2$ or $-1/2$), up to ten in a $l = 2$ orbital, etc.

For example, the ground state configuration of helium is $1s^2$, which means two electrons in a ($n = 1, l = 0$) spin-orbital. The ground state configuration of lithium is $1s^2 2s$, that of neon is $1s^2 2s^2 2p^6$, etc. What these configurations are, and in particular what the highest energy orbitals are, determine the chemical properties of the elements.

Note 1: Please refer to Young and Freedman or other introductory textbooks for more information about the resulting shell structure of complex atoms.

Note 2: Strictly speaking, values of l and m_l corresponding to eigenvalues of one-electron \mathbf{L}^2 and L_z operators can be unambiguously assigned to the orbitals $u_\lambda(\mathbf{r})$ only if the operators \mathcal{V}_λ are effectively spherically symmetric. There are departures from spherical symmetry for many atoms, but not to the point of making it impossible to label the states by these quantum numbers.

² \mathcal{V}_λ is not a simple multiplicative operator whose effect would merely be to multiply $u_\lambda(\mathbf{r})$ by a potential function.

Note 3: The Hartree-Fock method is considerably more accurate than the perturbative method outlined in Section 4.6. For example, while the latter gives the ground state energy of helium to be -75 eV, compared to the exact value of -79 eV, the Hartree Fock method yields -78 eV. While this last result does not compare well with those of the best variational calculations of this quantity, the Hartree-Fock method is applicable to a large variety of systems and is also the starting point of better and more sophisticated calculations.