

Second Year Atomic Physics 2019/20

Part III – Helium

Richard Thompson

January 13, 2020

7 Two-electron systems

In this lecture we will examine how to write wavefunctions for two-electron systems in a way that takes account of the symmetry requirements for identical particles. This will lead into a discussion of quantum numbers in helium.

7.1 Introduction

Once we move from hydrogen to the consideration of more complicated atoms, we have to tackle the question of how we can write wavefunctions for systems of more than one identical particle. As we will see, this has fundamental implications for the possible states of an atom like helium, which has a nucleus of charge $Z = 2$ and two electrons.

We shall find that because of symmetry requirements, there are states in helium that we might expect to observe which in fact are not allowed. We will also find the unexpected result that symmetry requirements lead to changes in the energies of atomic states in multi-electron atoms like helium. The reason for all this is that for any two identical particles the total wavefunction for the system, $\Psi(1,2)$, must have a definite symmetry when the particles are exchanged, i.e. $\Psi(2,1) = \pm\Psi(1,2)$. Otherwise the particles could be distinguished from a physical measurement of the system. Quantum mechanics does not allow us to label individual particles.

7.2 Symmetry considerations

Fundamental particles like electrons are identical to each other, and in quantum mechanics this means that any measurements of the system cannot distinguish between the particles. This leads in general to strict requirements about the symmetry of the wavefunctions when particles are exchanged. For *fermions*, which have a spin of $\frac{1}{2}$, the total wavefunction must be antisymmetric with respect to exchange of the particles (i.e. it changes sign when two particles are exchanged). This is strongly related to the Pauli exclusion principle, which says that no two fermions may occupy the same quantum state (i.e. have identical quantum numbers). Pauli formulated this principle in the 1920s in explaining why atoms seemed to have a shell structure. We say that fermions follow *Fermi-Dirac statistics*.

The exclusion principle actually applies to all particles with half-integer spin, including electrons, protons and neutrons along with more exotic fundamental particles. It also applies to composite particles such as atoms that have an overall spin of $\frac{1}{2}$. It does not apply to particles such as photons and atoms with an integer overall spin. These *bosons* follow *Bose-Einstein statistics* which require the total wavefunction to be symmetric with respect to exchange of particles.

Mathematically, we might try to write the wavefunction of a system of two electrons as

$$\Psi = \psi_a(1)\psi_b(2) \tag{7.1}$$

where a stands for the set of quantum numbers of particle 1 and b stands for the set of quantum numbers for particle 2. Each of these single particle states would be written as $\psi = \phi \times \chi$ where ϕ is the space part of the wavefunction and χ is the spin part. Now if we exchange particles 1 and 2 in equation 7.1 we obtain a *different* wavefunction, namely $\Psi' = \psi_b(1)\psi_a(2)$. A measurement made on this wavefunction would give different results than a measurement made on the original wavefunction Ψ . The laws of quantum mechanics say that this is wrong because the particles are identical, so exchanging them should have no measurable consequence. Instead we have to write a wavefunction such as

$$\Psi = \frac{1}{\sqrt{2}}[\psi_a(1)\psi_b(2) - \psi_b(1)\psi_a(2)]. \quad (7.2)$$

This has the property that if we now exchange particles 1 and 2, we just find that the sign of the wavefunction changes, i.e. it is *antisymmetric*. This wavefunction therefore satisfies the Pauli exclusion principle. The results of a measurement are now the same when the particles are exchanged.

In fact we will see in the next lecture that the overall wavefunction for the electrons in the helium atom is best written in a different way, as $\Psi = \Phi \times \chi$ where now Φ is the space part of the wavefunction for both particles and χ is the spin part of the wavefunction for both particles. This is because the Coulomb interaction causes the spatial wavefunctions of the two electrons to be coupled together and separately causes the spin parts to couple together.

Now if the above expression for Ψ has to be antisymmetric with respect to particle exchange, there are only two ways to do this: either Φ is symmetric and χ is antisymmetric or Φ is antisymmetric and χ is symmetric.

We will come back to these ideas when we have considered the principles of how energy levels work in helium.

7.3 Schrödinger equation for helium

In this part of the course I am going to use atomic units, simply because it makes writing the equations much more straightforward. It has no effect on the physics of the situation.

So we set $e = m_e = \hbar = 4\pi\epsilon_0 = 1$. This means that we can write the Schrödinger equation as

$$\mathcal{H}\Phi(\mathbf{r}_1, \mathbf{r}_2) = \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \Phi(\mathbf{r}_1, \mathbf{r}_2) = E\Phi(\mathbf{r}_1, \mathbf{r}_2), \quad (7.3)$$

where $\Phi(\mathbf{r}_1, \mathbf{r}_2)$ is the total spatial part of the wavefunction. Here ∇_1^2 acts only on the coordinates of particle 1, ∇_2^2 acts only on the coordinates of particle 2, \mathbf{r}_1 and \mathbf{r}_2 are the position vectors for the two electrons, and r_{12} is their separation (given by $r_{12}^2 = |\mathbf{r}_1 - \mathbf{r}_2|^2$). The first two terms in the Hamiltonian represent the kinetic energy of particles 1 and 2, the second two terms represent the potential energy of the particles in the electric field of the nucleus (which in helium has $Z = 2$), and the final term represents the Coulomb interaction between the electrons.

Our aim is to solve this equation in order to find the energy levels and wavefunctions for the helium atom. However, this equation cannot be solved analytically. This is because of the presence of the term in r_{12} . This couples the motions of the two electrons. In the absence of this term, the equation could be separated into a part to do with particle 1 and a part to do with particle 2. Moreover, this term $1/r_{12}$ is not small – you can see that since $Z = 2$, it is going to be of the same order of magnitude as the other terms, so we cannot apply it as a small perturbation if we want to get accurate results.

7.4 The independent particle model

We now come to one of the key approximations that is made in order to be able to describe multi-electron atoms mathematically. Focussing on helium, we assert that the two electrons

move *independently* in the atom. This will allow us to write the spatial part of the wavefunction for the two electrons as a product wavefunction $\Phi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$. This approximation does *not* mean that the electrons do not have an effect on each other, but in effect it means that each electron moves in a potential that is no longer the pure nuclear potential, but is modified because of the electron-electron Coulomb interaction. We can say that each of the electrons sees the nuclear potential modified by the *averaged* probability density distribution of the other electron. The motions of the two electrons are therefore not correlated in this approximation. A consequence of the independent particle model is that when we want to specify the state of the atom, we can start by specifying the state that each of the electrons is in.

7.5 The central field approximation

Now we come to the second approximation, which tells us about the form of the modified potential. The term in r_{12} depends on all the coordinates of the electrons, and the instantaneous force from one electron on the other one can therefore be in any direction. However, we can say that *on average* the force from each electron on the other is directed along the radius vector, i.e. it is a radial force (reducing the force of attraction to the nucleus). This means that the potential seen by each electron is a *central potential*, i.e. it only depends on the radial coordinate r and not on the angular coordinates θ and ϕ . The components of the force perpendicular to the radius vector averages out to zero.

Now when you studied the quantum mechanics of a particle in a central potential you learnt that the angular properties of the wavefunction are always the same and are described by the spherical harmonics. Therefore once we know that the electrons in helium each see a central potential, we can immediately write down the angular properties of the states and define the relevant quantum numbers. All the angular properties of the states (and the quantum numbers used to describe them) are the same as they are in hydrogen. What we *can't* do yet is to write down the energies of the states. This is because we no longer have an exact Coulomb potential, so the radial wavefunctions are not known and therefore the energies cannot be calculated exactly.

The states of the helium atom are therefore labelled by the quantum numbers n_1, l_1, m_{l1} for electron 1 and n_2, l_2, m_{l2} for electron 2, i.e. the spatial part of the wavefunction is written

$$\Phi(\mathbf{r}_1, \mathbf{r}_2) = \phi_{n_1, l_1, m_{l1}}(\mathbf{r}_1)\phi_{n_2, l_2, m_{l2}}(\mathbf{r}_2). \quad (7.4)$$

The ground state of helium is therefore going to have both electrons in the 1s state, and we write that as $1s^2$. As shorthand we will write the spatial part of the wavefunction as $\phi_{1s}(1)\phi_{1s}(2)$.

The first excited state will have one electron still in the 1s state and the second one in the $n = 2$ state. It turns out that the 2s state is significantly lower in energy than the 2p state (we'll see why later), so the first excited state of helium is written as $1s2s$. As shorthand we will write this spatial wavefunction as $\phi_{1s}(1)\phi_{2s}(2)$ for the moment (and we will return to the symmetry considerations later). Note that we do not know the exact form of the radial part of the ϕ_{nl} but this does not prevent us from making general statements about how the total wavefunction for the helium atom should be written.

7.6 The total wavefunction of the helium ground state

Before we try to calculate the energies of these states, we will return to the issue of the symmetry of the wavefunctions.

Consider first the $1s^2$ state. If we exchange the particles, the spatial wavefunction $\phi_{1s}(1)\phi_{1s}(2)$ is unchanged, so this is said to be symmetric with respect to particle exchange. As we saw earlier, this means that the spin part of the wavefunction must be antisymmetric.

We'll use Dirac notation to write these spin wavefunctions as it makes the labelling more clear. We write 'spin-up' ($m_s = +\frac{1}{2}$) for a single electron as $|\uparrow\rangle$ and 'spin-down' ($m_s = -\frac{1}{2}$)

as $|\downarrow\rangle$. For two electrons, we can write for example $|\uparrow\downarrow\rangle$ where the first symbol (up) refers to electron 1 and the second (down) refers to electron 2.

A spin wavefunction like $|\uparrow\uparrow\rangle$ or $|\downarrow\downarrow\rangle$ is *symmetric* because it is unchanged if I exchange the electrons. However, the wavefunction $|\uparrow\downarrow\rangle$ is neither symmetric nor antisymmetric because on exchanging the electrons I get $|\downarrow\uparrow\rangle$ which is just a different wavefunction. I can make a symmetric wavefunction by forming the superposition

$$\chi_S = \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle], \quad (7.5)$$

which is unchanged when the particles are exchanged, as you can easily verify for yourself. On the other hand, the superposition

$$\chi_A = \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle] \quad (7.6)$$

is antisymmetric, because it changes sign when I exchange the particles. So this is the spin wavefunction that I need to use for the ground state of helium. The total wavefunction for the ground state can therefore be written as $\Psi = \phi_{1s}(1)\phi_{1s}(2)\chi_A$.

Note that loosely speaking we can say that in this state one electron is ‘spin-up’ and one electron is ‘spin-down’: in other words, the spin states of the two electrons are different. The states where the spins are the same ($|\uparrow\uparrow\rangle$ and $|\downarrow\downarrow\rangle$) are both symmetric states and therefore they cannot be combined with the $1s^2$ spatial wavefunction. This is an example of the Pauli exclusion principle affecting the allowed states of the system: if the spatial states are the same (i.e. they are both in the $1s$ state) then the spin states must be different.

7.7 Excited states of helium

All the excited states of helium have the electrons in different electronic states: one of them in the ground state ($1s$) and one in an excited state (nl). The spatial wavefunction has to be correctly symmetrised, so it is either antisymmetric (Φ_A) or symmetric (Φ_S) on exchange of particles. These two wavefunctions are written as:

$$\Phi_S = \frac{1}{\sqrt{2}}[\phi_{1s}(1)\phi_{nl}(2) + \phi_{nl}(1)\phi_{1s}(2)] \quad (7.7)$$

$$\Phi_A = \frac{1}{\sqrt{2}}[\phi_{1s}(1)\phi_{nl}(2) - \phi_{nl}(1)\phi_{1s}(2)]. \quad (7.8)$$

The symmetric one, Φ_S , has to be paired with χ_A to give an overall wavefunction that is antisymmetric, and the antisymmetric one, Φ_A , has to be paired with a symmetric spin part. There are three possible symmetric spin wavefunctions:

$$|\uparrow\uparrow\rangle, \quad |\downarrow\downarrow\rangle, \quad \frac{1}{\sqrt{2}}[|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle]. \quad (7.9)$$

Now we should think about the quantum numbers to apply to these spin wavefunctions. Because the wavefunctions have been symmetrised, it is no longer possible to assign quantum numbers m_l and m_s to each individual particle. So we should use quantum numbers that apply to the whole system. These quantum numbers are always written with capital letters.

We define the total spin operator $\hat{\mathbf{S}} = \hat{\mathbf{s}}_1 + \hat{\mathbf{s}}_2$ and the operator for the total z -component of spin $\hat{S}_z = \hat{s}_{1z} + \hat{s}_{2z}$. By analogy with other angular momentum operators, the expectation value of $\hat{\mathbf{S}}^2$ is equal to $S(S+1)\hbar^2$ and the expectation value of \hat{S}_z is equal to $M_S\hbar$. Since the spins of the electrons are both $\frac{1}{2}$, the total spin of the system of two electrons can only have a value of $S = 0$ or $S = 1$. Since $\hat{\mathbf{S}}$ is equal to $\hat{\mathbf{s}}_1 + \hat{\mathbf{s}}_2$, and \hat{S}_z is equal to $\hat{s}_{1z} + \hat{s}_{2z}$, it is easy to see that the three wavefunctions in equation 7.9 have spin projections of $M_S = +1, -1$ and 0 respectively. They therefore correspond to the three possible states of a spin of $S = 1$. On the other hand, the spin wavefunction χ_A in equation 7.6 has $S = 0$ and $M_S = 0$, as can be verified using the definitions of $\hat{\mathbf{S}}$ and \hat{S}_z .

Because there are three spin wavefunctions associated with $S = 1$, this is called a *triplet state*, and the single spin wavefunction associated with $S = 0$ is called a *singlet state*. As a general rule, every excited state in helium has both a triplet state (with $S = 1$) and a singlet state (with $S = 0$) associated with it. As we will see later, these always have different energies, and the triplets are always lower in energy (more tightly bound).

Note that states where both electrons are excited (e.g. $2s^2$) all have energies above the first ionisation energy of helium, i.e. they are unstable and will eject an energetic electron, leaving a helium ion (He^+) behind. We therefore do not consider these states any further.

7.8 Summary

- The independent particle model and the central field approximation allow us to ascribe quantum numbers to individual electrons in helium
- The angular properties of the wavefunctions for the electrons are identical to those for hydrogen wavefunctions, because the potential is central
- To satisfy the Pauli exclusion principle, all wavefunctions for helium must be antisymmetric overall with respect to exchange of particles
- Symmetric spatial wavefunctions are always paired with antisymmetric spin wavefunctions (a singlet state with $S = 0$)
- Antisymmetric spatial wavefunctions are always paired with symmetric spin wavefunctions (a triplet state with $S = 1$)
- The ground state ($1s^2$) only has a singlet state

8 Helium – gross structure

In the previous lecture we looked at the restrictions on the allowable states of helium due to symmetry considerations. Now we will see how to calculate the energies of these states.

8.1 Ground state energy

The Schrödinger equation for the spatial part of the wavefunction in helium is, in atomic units (a.u.),

$$\mathcal{H}\Phi(\mathbf{r}_1, \mathbf{r}_2) = \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}} \right) \Phi(\mathbf{r}_1, \mathbf{r}_2) = E\Phi(\mathbf{r}_1, \mathbf{r}_2). \quad (8.1)$$

If we want to find the ground state energy, the easiest thing to do is just to forget the inter-electron Coulomb interaction $1/r_{12}$ and apply it later as a perturbation. This is a very poor approximation but it's a useful start.

If we ignore that term, the equation separates into a part to do with electron 1 and a part to do with electron 2, so we can write the wavefunction as a product $\Phi(\mathbf{r}_1, \mathbf{r}_2) = \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)$, where $\phi(\mathbf{r}_1)$ and $\phi(\mathbf{r}_2)$ are solutions of

$$\left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} \right) \phi(\mathbf{r}_i) = E_i\phi(\mathbf{r}_i). \quad (8.2)$$

and $E = E_1 + E_2$.

The ground state is $1s^2$, i.e. $n_1 = n_2 = 1$, $l_1 = l_2 = 0$. Setting $Z = 2$ for helium, we find $E = -2 \times 2^2 \times 13.6 \text{ eV} = -108.8 \text{ eV}$ (or 4 atomic units). This means that in this approximation it takes 54.4 eV to remove the first electron in helium and another 54.4 eV to remove the second one.

Given this zero-order wavefunction, we can now make an estimate of the effect of the ignored electron-electron interaction on the energy. If the perturbation is $\mathcal{H}' = 1/r_{12}$, then the expectation value of the perturbation can be calculated and this gives the result:

$$\Delta E = \langle 1s^2 | \mathcal{H}' | 1s^2 \rangle = \langle 1s^2 | \frac{1}{r_{12}} | 1s^2 \rangle = \frac{5}{4} \quad (8.3)$$

in atomic units. This calculation uses the hydrogenic wavefunctions (with $Z = 2$) and the calculation itself is quite lengthy. So this raises the energy from -4 to -2.75 a.u. (-79.0 eV). The actual value is -2.904 a.u. so despite the approximation being very poor, we obtain a value for the energy that is getting quite close to the true value. Higher-order perturbation theory would of course get us closer.

Now we know that the binding energy of the single electron in He^+ is exactly equal to 2 a.u., so this means that the energy it takes to remove one of the two electrons in neutral helium must be 0.904 a.u., which is equal to 24.6 eV.

We might have taken a different approach to this problem and postulated that the first electron shields the second electron from the nuclear charge of $Z = 2$, reducing it to an effective value of $Z = 1$. Then the binding energy of the second electron should be the same as for hydrogen and therefore equal to 13.6 eV. You can see that the actual binding energy of the second electron is somewhere between that corresponding to a nuclear charge of $Z = 2$ and $Z = 1$, so there *is* a shielding effect, but it is only partial.

Non-examinable comment: An alternative way to calculate the ground state energy is by the use of the *variational theorem*. This involves writing down a trial wavefunction with some variable parameters, and calculating the total energy (i.e. evaluating $\langle \mathcal{H} \rangle$) as a function of those variables. If the energy is then minimised with respect to variation in those parameters, it can be shown that this gives the best approximation to the true ground state energy. The more sophisticated the trial wavefunctions, the closer the energy will be to the true value. The best calculations give

$$E_{1s^2} = -2.903\,724\,377\,03 \text{ a.u.}, \quad (8.4)$$

which corresponds exactly to the measured value.

8.2 Excited state energies

We can use the same first order perturbation theory approach to make rough estimates of the excited state energies in helium, starting again from the zero-order wavefunctions where we ignore the electron-electron interaction $1/r_{12}$. Consider the state where one electron is in the $1s$ state and the other is in the nl state. Then we can write the correctly symmetrised spatial part of the wavefunction in the form

$$\Phi_S = \frac{1}{\sqrt{2}} [\phi_{1s}(1)\phi_{nl}(2) + \phi_{nl}(1)\phi_{1s}(2)] \quad (8.5)$$

$$\Phi_A = \frac{1}{\sqrt{2}} [\phi_{1s}(1)\phi_{nl}(2) - \phi_{nl}(1)\phi_{1s}(2)]. \quad (8.6)$$

Remember that the wavefunctions have to have this form so that the electrons remain indistinguishable. The symmetric state Φ_S goes with the antisymmetric spin state, which has total spin $S = 0$ (singlet state). The antisymmetric state Φ_A goes with the symmetric spin state, which has total spin $S = 1$ (triplet state).

The first order perturbation energy shift is

$$\Delta E = \langle \Phi | \mathcal{H}' | \Phi \rangle = \langle \Phi | \frac{1}{r_{12}} | \Phi \rangle. \quad (8.7)$$

Substituting the two possible expressions for Φ we find

$$\Delta E_{\pm} = \langle 1s nl | \frac{1}{r_{12}} | 1s nl \rangle \pm \langle 1s nl | \frac{1}{r_{12}} | nl 1s \rangle, \quad (8.8)$$

which we write as

$$\Delta E_{\pm} = J \pm K \quad (8.9)$$

where $+$ refers to the singlet state (S) and $-$ refers to the triplet state (A).

Here J , given by

$$J = \langle 1s n l | \frac{1}{r_{12}} | 1s n l \rangle, \quad (8.10)$$

is called the *direct integral*, and it is a measure of the energy shift due to screening of the nuclear charge by the electrons (note that this J is not a quantum number!). This reduces the binding energy of the system. K , defined by

$$K = \langle 1s n l | \frac{1}{r_{12}} | n l 1 s \rangle, \quad (8.11)$$

is referred to as the *exchange integral* because it is in this integral that the two particles are exchanged. This change of energy is a direct result of the requirement for an antisymmetric total wavefunction for the system. So although the Coulomb interaction does not directly depend on the spin wavefunction, the symmetry restrictions lead to a change of energy of the system depending on the value of S . Note that K is a weighted measure of the degree of overlap of the single particle wavefunctions. If the electrons are well separated, its value is small. There is no obvious classical interpretation of the K integral as it describes a purely quantum mechanical effect.

Some other general points to note:

- J and K are both always positive
- J is always greater than K
- For large values of n and l , the values of J and K both reduce, but K reduces faster than J .

If we examine the symmetrised wavefunctions, we find that in the triplet state the electrons are on average further apart from each other and for the singlet state they are on average closer to each other. You can think of this loosely in terms of the exclusion principle. If the spins are the same (triplet) then the electron wavefunctions must not overlap strongly because then you would have electrons with the same spin state in the same location. This effectively pushes them apart so their Coulomb energy is lower. If the spins are different (singlet) then there is no restriction on overlap of the wavefunctions, so on average they are closer to each other and the energy is higher.

When n and l are large, we can take a different approach to calculating the energy levels. In this case, the $1s$ electron wavefunction is concentrated close to the nucleus, while the wavefunction of the other electron (the valence electron) is mainly at larger radii. The $1s$ (*core*) electron then shields the nuclear charge such that the other electron sees an effective nuclear charge close to 1. The energies of these states then approach those of a hydrogen atom, which has $Z = 1$. For a given value of n , the validity of this approximation is best for high values of l . For $l = 0$ it is not a very good approximation and the result is that the energies of the s states are lower than the corresponding hydrogen values. This is because the s state wavefunctions have higher amplitude close to the origin than those for states with higher l , so these wavefunctions see a higher effective nuclear charge (this is referred to as *core penetration*).

8.3 Quantum numbers in two-electron atoms

We made the approximation earlier that the overall potential seen by the electrons is central (i.e. it depends on r only). This allowed us to assume that all the angular properties of the wavefunctions were the same as in hydrogen, so we could write down the angular momentum

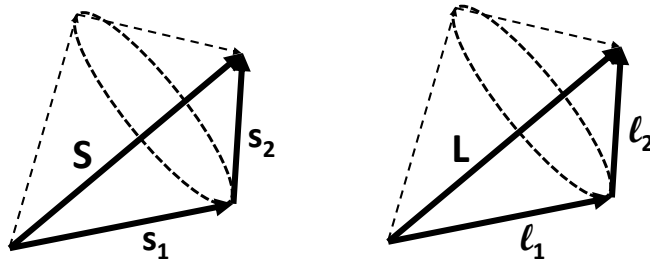


Figure 1: Coupling of the angular momenta of individual electrons to give resultant angular momenta for the whole atom.

quantum numbers l and m_l for each electron. We also said that the electrons move independently. Of course in reality the potential is not going to be purely central, and there will be some correlation between the motions of the electrons. These approximations will therefore not be perfect and there will be some effects on the energies of the atomic states arising as a result.

We have already seen this in the previous section when we discussed the effect of spin in helium. We showed that the individual spin angular momenta \hat{s}_1 and \hat{s}_2 couple together to form a resultant total spin \hat{S} and that states having different values of S have different energies. (Remember that we will always use capital letters for operators and quantum numbers that describe the whole atom and lower case letters for single-electron operators and states.) We can represent this diagrammatically using the ‘vector model’ as shown in figure 1. It is the residual (non-central) electrostatic interaction that leads to the energy difference between the states with $S = 0$ and $S = 1$, which in helium is represented by the exchange integral, K .

In fact in general in multi-electron atoms the effect of the residual electrostatic interaction is also to raise the degeneracy between states specified by the values of l_i . The end result is that the orbital angular momenta \hat{l}_i of each electron in an atom are coupled together to form a resultant total angular momentum \hat{L} for the whole atom (see figure 1). In an exactly analogous way to the spin operators, we define the total orbital angular momentum operator $\hat{L} = \hat{l}_1 + \hat{l}_2$ and the operator for the z -component of the total orbital angular momentum $\hat{L}_z = \hat{l}_{1z} + \hat{l}_{2z}$. The eigenvalue of \hat{L}^2 is equal to $L(L+1)\hbar^2$ and the eigenvalue of \hat{L}_z is equal to $M_L\hbar$.

The residual electrostatic interaction between the electrons leads to the coupling between the individual angular momenta and hence to energy splittings. It gives rise to a torque on each \hat{l}_i that causes them both to precess about their resultant, \hat{L} . This has to be a constant of the motion because there is no external torque on the atom. We started with individual single-electron spatial quantum numbers $l_1, m_{l_1}, l_2, m_{l_2}$ but m_{l_1}, m_{l_2} no longer represent constants of the motion so the new quantum numbers to describe the system are l_1, l_2, L, M_L , where M_L is the quantum number corresponding to the z -component of total angular momentum of the atom, \hat{L}_z . The residual electrostatic interaction therefore leads to states with different values of L having different energies.

However, in helium it is actually more simple than this: one electron is always in the $1s$ state with $l = 0$ so for this particular example L is always equal to the value of l for the second electron.

8.4 Nomenclature

Now we can extend the spectroscopic notation that we introduced earlier. For individual electrons we use lower case letters as before. For the whole atom we have the following quantum numbers: L represents the total orbital angular momentum of the atom and in helium it is always equal to the value of l for the second electron, since the first electron is in the $1s$ state with $l = 0$. The total spin angular momentum quantum number is S , which can take the value 1 (triplet state) or 0 (singlet state) in helium. The triplet states always have the lower energy

(but there is no triplet state for the ground state $1s^2$).

We call the list of values of n and l for each electron the *configuration* of the atom. Each configuration splits into a number of *terms* corresponding to different values of L and S . The terms are written in the form ^{2S+1}L where L has the same code as for single electron states (S, P, D, F, ...) but using capital letters.

The ground term of helium is therefore $1s^2\ ^1S$ (pronounced “1s squared singlet S”) and the first excited terms are $1s2s\ ^1S$ and 3S (pronounced “triplet S”) and then $1s2p\ ^1P$ and 3P .

8.5 Summary

- We can get very approximate energies for the states of helium by assuming that both electrons move independently and see the full nuclear charge
- The electrons are then described by single particle quantum numbers as in hydrogen
- We can then apply the electron-electron interaction $1/r_{12}$ as a perturbation to get us closer to the actual energies of the states
- The residual (non-central) electrostatic interaction couples the electrons so that their orbital and spin angular momenta add to give resultant angular momenta $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$
- In helium S can take the value 0 (singlet) or 1 (triplet)
- The perturbation $1/r_{12}$ gives expressions for the energies of excited states in the form $\Delta E_{\pm} = J \pm K$, where J is the direct integral and K is the exchange integral
- Because K is always positive, the triplet states are always lower in energy (more tightly bound) than the corresponding singlet states.
- For high values of n and l the energy levels approach those of hydrogen, due to shielding of the nuclear charge by the 1s electron.

9 Helium: fine structure and spectrum

In this lecture we look at fine structure effects in helium and discuss the main characteristics of the helium spectrum.

9.1 The term diagram of helium

A term diagram (sometimes called a *Grotrian diagram*) is a diagram that shows the energies of the different states that an atom can exist in. In most atoms there is only one electron that changes its n and l quantum numbers because usually if more than one electron is excited, the atom will have enough energy to ionise and those states will therefore not be bound. Therefore the energy levels are usually set out in the term diagram according to the values of l of this *valence electron*. This is what we used to show the energy levels of hydrogen in earlier lectures.

The helium term diagram (see figure 2) has two halves: one side showing the singlet terms (including the ground state $1s^2$), and the other showing the triplet terms. As we will see later, there are no radiative transitions between the singlet and triplet states, so all optical transitions are seen as diagonal lines on one side of the diagram or the other (they are diagonal because, as we have already seen, the value of l for the valence electron must change by ± 1). Because of this separation of the atomic states and their spectra, there are effectively two different helium atoms, referred to as *parahelium* for the singlet states and *orthohelium* for the triplet states.

In general every configuration in helium (except the ground state $1s^2$) gives rise to one singlet term and one triplet term. So for example the configuration $1s2p$ gives rise to a term 1P

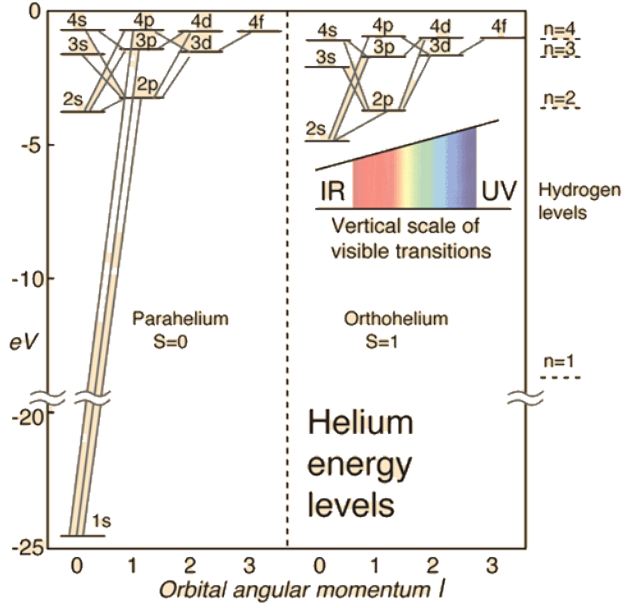


Figure 2: Energy levels and allowed transitions of the helium atom.

($L = 1, S = 0$) and a term 3P ($L = 1, S = 1$). Note that the triplets are always lower in energy (more tightly bound).

9.2 Fine structure in multi-electron atoms

We now have to consider the interaction between $\hat{\mathbf{S}}$ and $\hat{\mathbf{L}}$ which leads to fine structure. Just as in hydrogen, there is always an interaction between the spin angular momentum of an atom and its orbital angular momentum. This leads to a splitting of terms into levels labelled by the value of the total angular momentum of the atom, J . The only exceptions to this are when either $S = 0$ or $L = 0$. So in helium it is only the triplets that show a fine structure splitting.

We define the total angular momentum operator $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ and its projection $\hat{J}_z = \hat{L}_z + \hat{S}_z$. As with other angular momentum operators, the eigenvalues of $\hat{\mathbf{J}}^2$ are of the form $J(J+1)\hbar^2$. In general, J will take values specified by $J = |L - S|, |L - S| + 1, \dots, L + S - 1, L + S$, that is, either $2L + 1$ or $2S + 1$ values in integer steps between $|L - S|$ and $L + S$. For helium triplet terms, $J = L + 1, L$ or $L - 1$ for $L > 0$.

The principal physical origin of the splitting in multi-electron atoms is again the spin-orbit interaction, i.e. the interaction between the magnetic field seen by the electrons and the magnetic moment due to their spin, just like in hydrogen. Since this is generally a weaker interaction than the residual electrostatic interaction that gives rise to the energy differences between terms, it is the *total* orbital angular momentum and the *total* spin angular momentum that interact, rather than the *individual* orbital and spin angular momenta of each electron. As we have seen with other examples, we apply the larger perturbation (the residual electrostatic interaction) first, and the weaker perturbation (the spin-orbit interaction) second. This situation is referred to as *LS-coupling* and it applies in most small to medium-sized atoms.

It is worth noting that spin-orbit splittings become much bigger in atoms with large numbers of electrons than they are in smaller atoms. We don't usually need to worry about the other relativistic effects in the fine structure of multi-electron atoms because they are generally much smaller than the spin-orbit interaction. However, it turns out that this is not the case for helium so we will not attempt to make any calculations of the magnitude of the fine-structure splitting in helium because it is too complicated and does not follow the usual rules.

We can describe the new energy levels in terms of their wavefunctions and quantum numbers. We start with the single-electron spatial wavefunctions described by the quantum numbers

n_i, l_i, m_{li} for each electron. This is the configuration of the atom. At this stage there is a lot of degeneracy as the energy does not depend on the values of the m_{li} , and there is also degeneracy associated with the different values of the spin projections m_{si} . The residual electrostatic interaction is the strongest perturbation and that mixes spatial states with different values of m_{li} . They form new wavefunctions which are linear combinations of the single electron wavefunctions, but these new wavefunctions have different energies and are now characterised by the value of the total orbital angular momentum L and its projection M_L rather than the individual m_{li} for each electron. The m_{li} quantum numbers do not now represent constants of the motion so they are no longer good quantum numbers (see section 8.3).

The residual electrostatic interaction also couples the individual electron spins to form states characterised by different values of the total spin S and its projection M_S rather than the individual m_{si} . The Coulomb interaction affects the energies of different spin states indirectly because of the requirements for the symmetry of the wavefunctions.

Now we think about the effect of the spin-orbit interaction on the wavefunctions in a two-electron atom. This time we start with the wavefunctions labelled with $n_1, l_1, n_2, l_2, L, M_L, S, M_S$. There is still a lot of degeneracy because M_L can take $2L + 1$ different values and M_S can take $2S + 1$ different values. Again, the spin orbit interaction forms new linear combinations of these wavefunctions which have different energies and are characterised by the value of J . The M_L and M_S quantum numbers are no longer good quantum numbers and are replaced by J and its projection M_J . You can check for yourself that the total degeneracy is unchanged, by adding up the degeneracy of all the new J levels and comparing it to the previous degeneracy $(2L + 1)(2S + 1)$.

9.3 Fine structure in helium

We now focus on helium. In helium all stable configurations are of the form $1s nl$, so one electron always has $l = 0$. Therefore in helium L is always equal to l , the orbital angular momentum of the valence electron.

For the singlet states there is no fine-structure splitting because $S = 0$, so $J = L$ only, and the levels are labelled as $^1S_0, ^1P_1, ^1D_2$, etc (the subscript is the value of J). For the triplets, there will nearly always be three different values of J , namely $L - 1, L$ and $L + 1$. The exception is for S terms, where only $J = 1$ is possible. The levels for triplet states are therefore written as 3S_1 for an S term, $^3P_0, ^3P_1, ^3P_2$ for a P term and $^3D_1, ^3D_2, ^3D_3$ for a D term, etc. Note that (bizarrely) we still say “triplet” for 3S , even though there is only one level in this case (i.e., only one value of J).

The magnitude of the fine-structure splitting is hard to calculate in helium and we won’t go into that at all here.

9.4 The Zeeman effect

The interaction of an atomic energy level with an external magnetic field $\mathbf{B} = B\hat{\mathbf{z}}$ (the Zeeman effect) is just determined by the quantum numbers of the level. When we discussed hydrogen we showed that a level j split into $2j + 1$ states labelled by m_j , with energy shifts given by $\Delta E_{m_j} = g_j \mu_B B m_j$. The g -factor is calculated using the equation

$$g_j = \frac{3j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}. \quad (9.1)$$

In the case of helium the calculation is exactly the same except it is now the angular momenta for the whole atom (L, S and J) that are used, rather than those for a single electron (l, s and j). We therefore find that a level with total angular momentum J splits into $2J + 1$ states with

$\Delta E_{M_J} = g_J \mu_B B M_J$, where

$$g_J = \frac{3J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}. \quad (9.2)$$

Note that if $S = 0$, then $g_J = 1$ because the magnetic moment all comes from the orbital angular momentum. Similarly, if $L = 0$, then $g_J = 2$ because the magnetic moment is all due to the spin.

9.5 The spectrum of helium

Now we turn to how helium interacts with light to give us the spectrum that we see. As we saw earlier, all the bound states of helium have one electron in the 1s state and the other in an excited state nl . This means that when helium absorbs or emits light, it is just one of the electrons that changes its state. In turn this means that all the selection rules that applied when we considered the interaction of the hydrogen atom with light also apply here to the quantum numbers n and l for the valence electron. The rules for electric dipole radiation (the only case we will consider) are the following:

- There is no restriction on the value of Δn
- Δl has to be ± 1 (this arises from consideration of the parity of the single-electron states and the single unit of angular momentum carried by the photon).

We also have to consider the possible changes for the quantum numbers that describe the atom as a whole: L, S, J and M_J .

- Since the electric dipole operator, which drives the transition, only interacts with the spatial part of the wavefunction, and not the spin part, there can be no change to the spin state, so in all allowed transitions $\Delta S = 0$. This is a strong selection rule and leads to a complete separation of the helium spectrum into a set of transitions between singlet states and a set of transitions between triplet states.
- The electric dipole operator does act on the spatial part of the wavefunction so L can change in multi-electron atoms, but its change is again limited by the amount of angular momentum carried away by the photon (the *triangle rule*). As a result we find that ΔL can in general take the values 0 or ± 1 but a transition from $L = 0$ to $L = 0$ is forbidden due to angular momentum conservation. However, in helium we *always* have that L is equal to the value of l for the valence electron, so the rule in this case is always $\Delta L = \Delta l = \pm 1$ only.
- Similarly, ΔJ is restricted to the values 0 and ± 1 with $J = 0 \rightarrow J = 0$ forbidden.
- The final quantum number is M_J . When this changes by ± 1 the light is said to be σ -polarised and when it changes by 0 the light is said to be π -polarised (see below).

Although singlet transitions only have one component, because each term only has one level, triplet transitions will be more complicated. For example, a transition between a 3P term ($J = 0, 1, 2$) and a 3S term ($J' = 1$ only) will have three components that satisfy the selection rules. Others, for example, 3D term ($J = 1, 2, 3$) to 3P term ($J' = 0, 1, 2$) will have six components. In general these components will all have different amplitudes and frequencies. Because the angular momentum properties of the atomic states are well understood and only depend on the quantum numbers involved, it is possible to calculate the relative amplitudes of different components of a transition from first principles, and the results will apply to all states in all atoms having those quantum numbers. We will not go into these calculations at all but it is sufficient to note that there are characteristic patterns that emerge, and these patterns can be used to help interpret and identify atomic spectra.

9.6 Polarisation of light emitted by atoms

Light is an electromagnetic wave and it can be polarised in two different directions. We have to distinguish between the direction of propagation of the light (say \mathbf{k}) and the direction of polarisation (i.e., the direction of the electric field vector \mathbf{E} , which is always at right angles to \mathbf{k}).

Let us take the quantisation axis of our atom to be the z -direction, and let us first consider light that is emitted in the x - or y -direction. Light that is linearly polarised in the z -direction (i.e. the electric field is in the z -direction) is called π -polarised light. This is associated with $\Delta M_J = 0$. Alternatively, the electric field can be in the plane perpendicular to the z -direction, in which case it is referred to as σ -polarisation. This corresponds to $\Delta M_J = \pm 1$. Light from $\Delta M_J = \pm 1$ transitions can also be emitted in the z -direction, in which case it's circularly polarised. However, $\Delta M_J = 0$ transitions do not radiate in the z -direction because of the orientation of the atomic dipole in that case.

These considerations about polarisation only become important when there is a magnetic field present, because then all these different polarisations correspond to different frequencies of the light. If there is no magnetic field present, the quantisation axis is not defined, so all the M_J states are degenerate and the emitted light does not have a well-defined polarisation.

9.7 Metastable states in helium

Helium has two metastable states, i.e. states from which there is no allowed electric dipole transition to a lower level. The first is the $1s2s\ ^1S_0$ level, which has a lifetime of about 20 ms. The $1s2s\ ^3S_1$ state is the lowest triplet state and that has a lifetime of around 8000 seconds – the longest lifetime of any atomic state in a neutral atom. The transition from this state to the ground state $1s^2\ ^1S_0$ is highly forbidden because it violates several of the selection rules, especially the rule that S cannot change. We will talk about the practical importance of metastable states in helium when we discuss lasers during the lecture.

9.8 Summary

- The *configuration* of an atom is specified by the values of the individual electron quantum numbers $l_i\ m_{li}$. The *term* is specified in addition by the values of L and S . Finally, the *level* is specified by the value of J .
- A term diagram shows the energies of the different states of an atom defined by the values of L and S . In helium the term diagram separates the singlet terms (parahelium) from the triplet terms (orthohelium)
- In helium all excited states are of the form $1snl$, so helium always has $L = l$ (the angular momentum quantum number of the valence electron)
- The spin-orbit interaction splits triplet terms in helium into three levels with $J = L + 1, L, L - 1$ unless $L = 0$, in which case $J = 1$ only
- The spectrum of helium is determined by selection rules similar to those for hydrogen, with additional rules for L and J , which must satisfy the triangle rule. S cannot change because the electric dipole operator does not interact with the spin state of the atom
- The change in the value of M_J determines the polarisation of the light

10 Many-electron atoms

The detail of the material in this lecture is not examinable – only the general principles.

In the final lecture we look very briefly at how the principles that we developed in the discussions of hydrogen and helium are extended to the case of atoms with several electrons. We will conclude the course with a survey of a current experimental atomic physics research project where many of the concepts we have discussed in this course can be seen in action.

10.1 Approximations

The Schrödinger equation for a many-electron atom with atomic number Z is hopelessly complicated and can't be solved analytically. One possible approach is of course to solve it numerically, but even this is very complicated because for every electron there are three spatial coordinates, and spin has to be taken into account too. The other approach is to think again about what approximations can be made that allow the equation to be solved. It turns out that we can apply the same approximations as we discussed for helium.

- *The independent particle model.* It is a reasonable approximation to assume that each electron sees a potential that consists of the nuclear potential ($-Ze^2/4\pi\epsilon_0 r$) modified by the screening effect of all the other electrons. Each electron can then be treated as moving independently in a potential that depends on the states of all the other electrons, but the motions of individual electrons are not correlated. This approximation allows us to separate the Schrödinger equation for Z electrons into Z single-electron Schrödinger equations.
- *The central field approximation.* Next we assume that the potential seen by each electron is central, i.e. it depends on the distance from the origin only and does not have any angular dependence. This allows us to separate the Schrödinger equation for each electron into an angular part and a radial part.
- *Angular behaviour.* It follows from the previous two points that the angular part of the wavefunctions of all the electrons is described by the spherical harmonics.

10.2 The Pauli exclusion principle

We now need to consider the Pauli exclusion principle. If this principle did not apply, all the electrons could go into the lowest energy state (1s). However, because electrons are identical fermions and the total wavefunction must therefore be antisymmetric with respect to exchange of any two particles, it can be shown that they must all occupy different single-particle states. In other words, each electron must have a different set of quantum numbers.

Consider the 1s spatial state ($n = 1, l = 0$). This only has one possible value of $m_l = 0$. There are two possible spin states ($m_s = \pm\frac{1}{2}$) so at most two electrons can occupy the 1s state (i.e. the degeneracy of the 1s state is 2). Lithium has $Z = 3$ (i.e. three electrons) so it therefore has the configuration $1s^2 2s$ (since 2s is the next highest state in energy). Since 2s also has $l = 0$, it can also take a maximum of 2 electrons. Beryllium ($Z = 4$) therefore has the configuration $1s^2 2s^2$. When we get to $Z = 5$, the electrons start to occupy states with $l = 1$ (the 2p state).

In general each value of l gives rise to $2 \times (2l + 1)$ possible states, and these are referred to as 'orbitals'. An s orbital has a degeneracy of 2, so it can accommodate 2 electrons, a p orbital has a degeneracy of 6, a d orbital has a degeneracy of 10, etc. The way that we build multi-electron atoms by filling these orbitals in turn is called the 'Aufbau principle', and it gives rise to the periodic table and the chemical properties of the elements.

This is one of the topics that will be dealt with in the *Light and Matter* course next year. All we do here is to point out a couple of important points.

10.3 The chemical elements

- *The noble gases.* When the energies of the various single-particle states are evaluated in multi-electron atoms, we find that there is always a large gap in energy before a new s orbital starts to be filled. This means that the elements that have all the states filled up to that point are particularly strongly bound and it therefore takes a lot of energy to excite one of the electrons into a higher state. These elements are referred to as the noble gases. The first two are helium ($Z=2$, $1s^2$) and neon ($Z=10$, $1s^2 2s^2 2p^6$). They are chemically unreactive because it takes a lot of energy to excite one of the electrons to a higher state. We say that they have ‘closed shells’, i.e. for each value of n and l , all possible m_l and m_s states are occupied.
- *The alkalis.* If you go to the case where you add one more electron to a noble gas, the additional electron goes into the next highest state, which will be an s orbital and is much less tightly bound than the previous electron. It is therefore easier to excite this final electron and that means that these elements are chemically reactive. The first two alkalis are lithium ($Z=3$, $1s^2 2s$) and sodium ($Z=11$, $1s^2 2s^2 2p^6 3s$). We say that these elements have one electron outside closed shells. The final electron is loosely bound and can typically be excited with photons in the visible region of the spectrum.
- In general we find that the order in which the orbitals are filled is not quite the same as they appear in the excited states of hydrogen. This is because of the effect of the shielding of the nuclear charge by the electrons. The order in which the orbitals are filled is: $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $3d$, ... The large gaps referred to earlier occur before $2s$, $3s$ and $4s$.
- We can now return to the central field approximation. Since most of the electrons in an atom are in filled shells, the electron distribution is *exactly* spherically symmetric because we showed that the sum of all the spherical harmonics for a given value of l has no angular dependence. Therefore the central field approximation is a very good approximation, especially for the alkalis where there is only one electron that is not in a filled shell. We can also see that because all m_l and m_s states are occupied in filled shells, the overall orbital and spin angular momenta for the filled shells are both zero.
- The residual electrostatic interaction leads to coupling of the orbital angular momenta of electrons that are outside closed shells to form a total orbital angular momentum \mathbf{L} . Similarly, their spins are coupled to give a total spin \mathbf{S} . Then the weaker spin-orbit coupling causes these to interact to give a total angular momentum \mathbf{J} for the atom as a whole. This scheme is referred to as LS -coupling and applies to most small and medium-sized atoms.

10.4 Summary

- The Schrödinger equation for many-electron atoms is too complicated to solve directly so we have to use approximation techniques
- The independent particle model and the central field approximation allow us to make general predictions about the angular properties of the single-particle states
- The Pauli exclusion principle requires each electron to be in a different single-particle state, i.e. to have a different set of quantum numbers
- The single-particle states fill in a well-defined order and this gives rise to the periodic table, which demonstrates how and why some elements have similar properties
- The atom as a whole is described by the quantum numbers L , S and J in the LS -coupling scheme.