LECTURE 7

Content

In this lecture we will begin to discuss atoms with more electrons than hydrogen. Unfortunately this problem becomes very complicated very quickly — even for helium with just two electrons. Rather than attempting an analytical solution we will concentrate on devising a model to help us understand the physics. We will consider first the **independent particle model** which is rather unrealistic as it neglects the Coulomb interactions between electrons, before examining the **central field approximation**.

Outcomes

At the end of this lecture you will:

- know that a many electron atom is much more complicated than hydrogen

- know, and appreciate why, approximate methods are needed

- know and be able to criticise the independent particle model

- know and be able to use the central field approximation

LECTURE 7 SUMMARY

- An atom with more than one electron is too complicated to solve analytically

- Simple models can help us understand the fundamental physics without a great deal of mathematical complexity

- The independent particle model neglects $e^- - e^-$ interactions but produces poor solutions

- The central field model includes the averaged effect $e^- - e^-$ interactions as a screened potential

- It preduces reasonable solutions, especially for alkali-metal-like atoms

- Modifying the potential lifts the degeneracy with respect to l

LECTURE 8

Content

In this lecture we will introduce two ways of parameterising the energy levels of multi-electron atoms, namely **quantum defects** and **screening constants**. We will then move on to discuss the Pauli Exclusion Principle and its effects on the symmetry of the wavefunction. This will be in preparation for a discussion of the Helium atom in later lectures.

Outcomes

At the end of this lecture you will:

- know the definition of the quantum defect, Δ_{nl} and...

- describe and justify its variation with n and l.

- be able to calculate Δ_{nl} from data

- know the definition of the screening constant

- know the Pauli Exclusion Principle

LECTURE 8 SUMMARY

- the quantum defect characterises the departure from hydrogenic behaviour

- it is especially useful for atoms with a single optically active electron

- a screened charge may be used to parameterize a non-hydrogenic atom

- the Pauli Exclusion Principle states that the wavefunction of a system of identical fermions must be anti-symmetric with respect to exchange

- an alternative formulation is that the electrons must have different sets of quantum numbers.

LECTURE 9

Content

In this lecture we will begin to study the Helium atom and determine the consequences of the Pauli Exclusion Principle on the wavefunction of the ground state

Outcomes

At the end of this lecture you will:

- know and be able to construct wavefunctions that are symmetric and antisymmetric under exchange

- know the Helium wavefunction is separable into spatial and spin parts

- know the Pauli Exclusion Principle requires that the total wavefunction of Helium must be antisymmetric

- be able to demonstrate the restrictions this places on the form of the wavefunction

LECTURE 9 SUMMARY

- The Helium atom wavefunction consists of a space part and a spin part

- The total wavefunction must be antisymmetric overall with respect to exchange

- For a non-vanishing wavefunction we then require the space part to be symmetric and the spin part to be antisymmetric

- The result is a singlet state

LECTURE 10

Content

In this lecture we will examine the quantum mechanical phenomenon of the **exchange interaction**, taking the helium atom as an example of where this is important. We will see how this arises from the symmetries of the wavefunctions and the effect it has on the energies of the states.

Outcomes

At the end of this lecture you will:

- know and be able to explain the causes of the exchange interaction

- be able to apply this knowledge to the case of the helium atom

- evaluate the effect on the singlet and triplet states of a two electron atom

- describe how exchange causes a splitting of energy levels

LECTURE 10 SUMMARY

- exchange is a quantum mechanical phenomenon for which there is no classical analogue

- it arises from the spin-dependent properties of the wavefunction

- as a result of the Pauli Exclusion Principle space and spin states are coupled

- the exchange interaction modifies the energies of the states according to the symmetry of the wavefunction

- it splits the energies of the singlet and triplet states

- excited helium may exist in two states - parahelium and orthohelium - with different energies

LECTURE 11

Content

In this lecture we will introduce electron configurations and term notation. We will see how the electron configuration of shells and sub-shells affects properties such as the ionisation energy. The method for deducing allowed spectroscopic terms will be examined.

Outcomes

At the end of this lecture you will:

- be able to use electron configuration and term notation

- be able to describe electronic structure in terms of the filling of shells and sub-shells

- be able to calculate the allowed terms from a given electronic configuration

LECTURE 11 SUMMARY

- electronic structure can be described in terms of filled and unfilled shells and subshells

- the filling of the shells determines physical properties

- spectroscopic terms give the allowed angular momentum states of an electron configuration

LECTURE 12

Content

In this lecture we will finish our discussion of spectroscopic terms by introducing **Hund's Rules** for the ordering (in energy) of terms. We will then commence a study of the **magnetic moment** of an electron arising from orbital and intrinsic angular momentum that will be needed when we discuss the **spin-orbit interaction** in later lectures which separates (splits) the terms into energy **levels**.

Outcomes

At the end of this lecture you will:

- know and be able to apply Hund's Rules to order terms

- be able to explain the origin of the magnetic moment of an orbiting electron in terms of angular momenta

- be able to describe the interaction between a magnetic field and the magnetic moment using the vector model

LECTURE 12 SUMMARY

- Hund's Rules provide guidelines for the ordering (in energy) of terms.

- Terms are split into levels by the spin-orbit interaction

- A magnetic moment $\underline{\mu}_X$ is associated with an angular momentum $\underline{X}$

- Both spin and orbital angular momenta ive rise to magnetic moments

LECTURE 13

Content

in this lecture we will examine the effect on the energy of the system of the interaction between the spin magnetic moment of the electron and the internal magnetic field of the atom - the **spin-orbit interaction**. we will introduce the **total** angular momentum J, and see that the terms are split into energy levels according to their value of J. A third Hund's Rule will be required for the ordering of energy levels.

Outcomes

At the end of this lecture you will:

- be able to derive the form of the spin-orbit interaction

- know that the coupling of $\underline{S}$ and $\underline{L}$ requires the total angular momentum $\underline{J} = \underline{S} + \underline{L}$ to be introduced.

- be able to identify the LS-coupling and jj-coupling limits for the spin-orbit interaction in a multi-electron atom

- know and be able to apply the third Hund's Rule for ordering of energy levels with respect to J

- know and be able to use the Landé interval rule

- be able to identify the parity of an energy level from the angular momentum

LECTURE 13 SUMMARY

- the spin-orbit interaction arises from the interaction between the electron spin magnetic moment and the magnetic field due to the apparent motion of the nuclear charge

- the interaction energy depends on the relative orientation of $\underline{L}$ and $\underline{S}$

- the spin-orbit interaction splits terms into energy levels according to their total angular momentum

- in multi-electron atoms the two extreme regimes are LS-coupling and jj-coupling, depending on the size of the interaction

- the energy levels can be ordered using a third Hund's Rule

- the separation of the energy levels can be found from the Landé interval rule

- the parity of an N electron wavefunction is $(-1)^{\sum l_i}$