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

3 MANY ELECTRON ATOMS

While the Schrödinger equation for hydrogen can be solved analytically to yield an expression for the quantum energy levels $E_n = -1/(2n^2)$, more complicated atoms require **numerical solutions**. But we can develop simple models to estimate and classify (roughly) the energy levels of more complicated atoms.

These models help our **physical understanding** far more than getting a bunch of numbers from a solution of Schrödinger's equation using a powerful computer. So for instance we can give an **approximate** expression for alkali atoms where the electrons are all arranged in a tight spherical core except the outer one which is loosely bound.

3.1 MANY ELECTRON HAMILTONIAN

For atoms with more than one electron we cannot solve the Schrödinger equation analytically, as we did with the hydrogen atom. We have to use approximate methods to infer the properties of atoms like helium, lithium etc... For a one-electron atom, the Hamiltonian (in atomic units) is:

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \tag{1}$$

For an N-electron atom we might expect the Hamiltonian, in atomic units, to be:

$$\begin{aligned} \hat{H} &= \underbrace{\sum_{i=1}^{N}\left[-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right]}_{\text{KE + attraction of nucleus and } i\text{ th } e^-} + \underbrace{\sum_{\substack{i,j\\ i>j}} \frac{1}{r_{ij}}}_{e^-\text{–}e^-\text{ Coulomb repulsion, non-central}} \\ &= \sum_{i=1}^{N} \hat{h}(\mathbf{r}_i) + \sum_{\substack{i,j\\ i>j}} \frac{1}{r_{ij}} \end{aligned} \tag{2}$$

with $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$.

The **Coulomb repulsion term** means the Hamiltonian is *no longer analytically solvable* since we cannot use separation of variables.

NOTE: We have to write the $1/r_{ij}$ (Coulomb) term carefully to avoid 'double-counting'.

For example:

For He: $1/r_{12}$.

For Li: $1/r_{12} + 1/r_{13} + 1/r_{23}$.

So for a N electron atom, we have $\frac{1}{2}N(N-1)$ such terms.

3.2 APPROXIMATE SOLUTIONS

For the next few lectures we will 'deconstruct' multi-electron atoms. We begin with a completely unrealistic model, by neglecting the e^-– e^- Coulomb repulsion term entirely (**the independent particle model**).

Then we gradually 'rebuild' a realistic atom, by adding the neglected interactions. We begin with the spherically averaged part of $1/r_{ij}$ (we get central potentials, screening, Quantum defects).

Then we include the non-central part as well as spin and spin-orbit effects. **Configurations**, **terms** and **levels** is the hierarchy which emerges as we consider these more realistic multi-electronic atomic energy levels.

This replaces the very simple, spin-free Bohr atom energy ladder which depends only on the n quantum number.

3.2.1 INDEPENDENT PARTICLE MODEL

As a first approximation, we **neglect** $1/r_{ij}$ **entirely**. Then the N electron Hamiltonian of equation 3.1 becomes:

$$\hat{H}(\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N) = \sum_{i=1}^{N} \hat{h}(\underline{r}_i) \ . \tag{3}$$

Each term i in the series depends only on the position of the i-th electron — there are no electron-electron interactions, or "cross-terms", so $\hat{H}$ separates into the sum of N one-electron Hamiltonians $\hat{h}$, with eigenstates $\psi(\underline{r}_i)$ (and eigenvalues E_i):

$$\hat{h}(\underline{r}_i)\psi(\underline{r}_i) = E_i\psi(\underline{r}_i) \tag{4}$$

which in turn are separable in coordinates (r, θ, ϕ).

We thus have N *hydrogen-like* solutions, $\psi(\underline{r}_i)$.

Example:

For $N = 2$, the helium ground state (remembering that $Z = 2$):

$$E = E_{n=1} + E_{n=1} = -\frac{Z^2}{2n^2} - \frac{Z^2}{2n^2} = -4\,\text{a.u.} \tag{5}$$

Where the $E_{n=1}$ are the *hydrogen-like* solutions we obtained in Lecture 4 (via the Bohr model) and Lecture 6 (via the Schrödinger equation).

The measured ground state energy is $E = -2.9\,\mathrm{a.u.}$ The neglect of the inter-electron repulsion yields a value which is **too negative**.

One can roughly estimate the magnitude of this repulsive term. The average separation of the helium $n = 1$ electrons is $1\,\mathrm{a.u.}$; hence the average repulsive energy is

$$E_r = \int \Psi^* \frac{1}{r_{12}} \Psi d\tau \approx \frac{1}{\langle r_{12} \rangle} \approx 1\mathrm{a.u.} \tag{6}$$

$$E + \frac{1}{\langle r_{12} \rangle} \sim -3\,\mathrm{a.u.}\ .$$

This is better but still crude. Neglects effects due to Pauli principle, as we will see later.

3.2.2 CENTRAL FIELD APPROXIMATION

An alternative approach which takes into account the other electrons.

We take the same separable Hamiltonians, $\hat{h}(\underline{r}_i)$, as above, but now we add, to each one, a central potential $V_c(r_i)$ which represent the *average interaction* of the ith e$^-$ with the nucleus *screened by the other electrons.* In other words:

$$\begin{aligned} \widehat{H}(\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N) &= \sum_{i=1}^{N} \hat{h}'(\underline{r}_i) & (7) \\ \hat{h}'(\underline{r}_i) = \hat{h}(\underline{r}_i) + V_c(r_i) &= -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i} + V_c(r_i) & (8) \end{aligned}$$

i.e. the N-electron Hamiltonian is the sum of N one-electron Hamiltonians, $\hat{h}'(\underline{r}_i)$, each of which depends **only** on the position of the i-th electron.

The additional term in $\hat{h}'(\underline{r}_i)$ is the central potential $V_c(r_i)$, where

$$V_c(r_i) = \langle \sum_j \frac{1}{r_{ij}} \rangle \ . \qquad (9)$$

The brackets indicate that we have *averaged out* the effect of the other electrons over a sphere.

The important fact is that V_c depends only on r **not** $\underline{r}$, and so has no angular (ϕ,θ) dependence: it is spherically symmetric, **isotropic**. (In case you're worried, we'll treat spin separately later.)

We can then solve the N one-particle equations:

$$\hat{h}'\Phi(\underline{r}_i) = \epsilon_i \Phi(\underline{r}_i) \tag{10}$$

and the total energy is

$$E = \sum_{i=1}^{N} \epsilon_i \ . \tag{11}$$

The $\Phi(\underline{r}_i)$ are one-particle **orbitals**.

The resulting **total** wavefunction has a **product-form**:

$$\Psi(\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N) = \Phi(\underline{r}_1)\Phi(\underline{r}_2)\ldots\Phi(\underline{r}_N) \ . \tag{12}$$

So what form do these one-particle orbitals take ? We know that they are, like hydrogen, a product of a radial and an angular part (we insisted on separable solutions):

$$\Phi(\underline{r}_i) = F_{nl}(r_i) Y_{lm}(\theta, \phi) \ . \tag{13}$$

The **angular** part of the one-electron Hamiltonian $\hat{h}'(r_i)$ is exactly the same as hydrogen so we still get a spherical harmonic. The s, p, d, f terminology we introduced in Lecture 6 for angular momentum is still useful.

The form of the **radial** part F_{nl}, though, can be quite complicated and is not like hydrogen.

Remember I warned you about "accidental" degeneracy with respect to the quantum number l arising from the $(1/r)$ potential in Lecture 6? Introducing the central field has modified the potential and so *lifted this degeneracy.*

Now the energies $\epsilon_i \rightarrow \epsilon_{nl}$ depend on both n as well as l, unlike hydrogen. An analogy here could be the precession of planetary orbits around the sun, due to the perturbations arising from the gravitational effects of the other planets.

We label the orbitals $1s, 2s, 2p, 3s, 3p, 3d \ldots$ etc.

To indicate the number of electrons which occupy a given orbital we put right-hand superscript: $1s^2 2s^2 2p^1$ etc.

Question

When does the central field model make most sense?

Answer

Mostly for alkali-atoms (that is in Group I of the periodic table Li, Na, K,...) or similar ones. Consider an alkali atom with N electrons ($Z = N$ since the atom is neutral).

There is a tightly bound *inner core* of $N - 1$ electrons, and a single outer, loosely bound electron. The central field model is good for the energy levels of the outer **'optically active'** electron, especially when it is excited to a high lying state.

The inner core of electrons *'screens'* the charge of the nucleus. We know the limiting forms of the interaction felt by the outer electron:

$$-\frac{N}{r_i} + V_c(r_i) \rightarrow -\frac{N}{r_i} \qquad \text{as} \;\; r_i \rightarrow 0 \tag{14}$$

that is, right up close to the nucleus the Coulomb attraction of N protons dominates, and:

$$-\frac{N}{r_i} + V_c(r_i) \rightarrow -\frac{1}{r_i} \qquad \text{as} \;\; r_i \rightarrow \infty \tag{15}$$

that is, well away from the nucleus it and the inner core of electrons appear like a single positive charge.

The extent to which the outer electron samples the screened charge ($V \sim -1/r$) relative to the bare nuclear charge ($V \sim -N/r$) depends most strongly on the value of l. For intermediate distances it is much more difficult, need to use, for instance, the **Hartree-Fock method** to find $V_c(r_i)$.

Previously we looked at the radial dependence of hydrogenic orbitals (the same qualitative picture applies here) For example, compare $n = 3$, $l = 0$ (3s) and $n = 3$, $l = 2$ (3d) (see diagrams used in **Lecture 6**).

The 3d orbitals overlap weakly with the inner region (defined by the 1s orbital here), but the 3s orbitals were described as 'penetrating' since they overlap more strongly with the inner region and hence with the inner structure of the atom (the 1s, 2s, 2p electrons).

- LOW-l orbitals experience more of the bare nuclear charge. Since $E_n \propto -Z^2/n^2$, their energy is more negative, they are more tightly bound. Although multi-electron atoms have different radial functions, similar *qualitative* behaviour to hydrogen applies (i.e., low l means stronger overlap with small r).
- Conversely HIGH-l avoid nuclear charge so 'feel' only completely screened charge $Z = 1$ so behaviour is more hydrogen-like. Energy is less negative.

So, whereas for hydrogen we had the degeneracy with respect to l,

$$E(1\mathrm{s}) < E(2\mathrm{s}) = E(2\mathrm{p}) < E(3\mathrm{s}) = E(3\mathrm{p}) = E(3\mathrm{d}) \ ,$$

for a multi-electron atom it is lifted,

$$E(1\mathrm{s}) < E(2\mathrm{s}) < E(2\mathrm{p}) < E(3\mathrm{s}) < E(3\mathrm{p}) < E(3\mathrm{d}) \ .$$

ENERGY LEVEL SPECTRUM OF LITHIUM

See the diagram available from the website for **Lecture 7**.

Note that Li 2s is lower in energy than 2p.

Li 2s is approx. 1.7 eV lower in energy than the $n = 2$ level of hydrogen.

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

3.2.3 QUANTUM DEFECTS AND SCREENING CONSTANTS

For multi-electron atoms with a core plus a single optically active outer electron, we can give an analytical expression for the energy in (a. u.) of the outer electron:

$$E_{nl} = -\frac{Z_{\text{eff}}^2}{2(n - \Delta_{nl})^2} \ , \tag{16}$$

in terms of:

1. an effective charge, Z_{eff} (Nuclear charge + charge of inner core electrons)
2. a set of parameters Δ_{nl} called the **quantum defects** which quantify the departure from hydrogenic behaviour.

NOTE: Equation (16) can be derived rigorously from the Schrödinger equation by considering a potential which deviates from pure Coulomb $1/r$ only for small r. Remember that when we solved the hydrogen atom, an unphysical solution which blows up at the origin had to be discarded. QDT in fact makes use of that solution !

The quantity $n - \Delta_{nl}$ can be considered to be an *effective* quantum number, but **BEWARE:** in general it will **not** be an integer.

Properties of quantum defects

	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$
$l = 0$	1.63	2.64	3.65	4.65	5.65
$l = 1$	2.12	3.14	4.14	5.14	6.14
$l = 2$	2.99	3.99	4.99	5.99	6.99
$l = 3$	-	4.00	5.00	6.00	7.00

The table shows the effective quantum number $n - \Delta_{nl}$ for sodium. Note that in general the Δ_{nl} are positive. To a good approximation they depend only on l

$$\Delta_{nl} \to \Delta_l \tag{17}$$

For high l the quantum defects tend rapidly to zero, of course. **Why ?**

Electrons in orbits with small l are more penetrating, and so experience, for at least part of their orbit, a greater effect from the nucleus. The outer electrons which do not penetrate near the nucleus will move in a hydrogen-like Coulomb field due to the nuclear charge $+Ze$ screened by the innner electrons carrying charge $-(Z - 1)e$. This is shown in the diagrams from **Lecture 6** and **Lecture 7** of the radial distribution functions for $(n, l) = (3, 0)$ and $(n, l) = (3, 2)$.

EXAMPLE 1. Values of Δ_{nl}

l	0	1	2	3
Li	0.40	.04	0.00	0.00
Na	1.35	0.85	0.01	.0.00

EXAMPLE 2

The atom Na has $Z = 11$. What is Z_{eff} ?

EXAMPLE 3

The atomic ion C^{3+} is an alkali-like ion. Its outer electron is seen to have the following energies in its ‘s’ states:

2s	$-520178.4\,\text{cm}^{-1}$
3s	$-217329.4\,\text{cm}^{-1}$
4s	$-118830.3\,\text{cm}^{-1}$
5s	$-74809.9\,\text{cm}^{-1}$

What are the quantum defects for these states ?

3.2.4 ALTERNATIVE TO QUANTUM DEFECTS: THE SCREENING CONSTANT

Another way of parametrizing the behaviour of a non-hydrogenic atom is to keep n as an integer but to introduce a variable ‘screened charge’, detonted Z^*. Instead of Eq. (16) we have:

$$E_{nl} = -\frac{(Z - \sigma_{nl})^2}{2n^2} = -\frac{(Z^*)^2}{2n^2} \tag{18}$$

where σ_{nl} is the **screening constant**.

N.B. In Eq. (16), the quantum defect expression, Z_{eff} is always integer. In the screening constant equation, Z^* is non-integer in general.

3.3 THE PAULI PRINCIPLE AND ITS EFFECTS

In multi-electron atoms, an additional effective 'interaction' called **exchange** appears as a consequence of the spin and Pauli exclusion principle.

3.3.1 THE PAULI EXCLUSION PRINCIPLE (PEP)

Atomic spectroscopy suggested that, in fact, two electrons occupied each nlm combination but **no more than 2**: something that the Bohr model couldn't explain! Pauli suggested that a new quantum property with 2 values could account for this. It turned out to be the spin $S = 1/2$ with components along the z-axis $S_z = +1/2$ 'spin up' or $S_z = -1/2$ 'spin down'.

He first formulated his principle in the following way: **in a multielectron atom there can never be more than one electron in the same quantum state** (that is there can never be two or more electrons with all their quantum numbers the same).

He then discovered that this was a much more general behaviour that applied to all particles with half-integer spin such as electrons, neutrons, protons... These particles are called **fermions** and they obey *Fermi-Dirac* statistics. 'Particles' of integer spin, such as the photon, some atoms etc are called **bosons** and they obey *Bose-Einstein* statistics.

The generalized Pauli Exclusion Principle can be reformulated as a stronger condition:

> Quantum wavefunctions of a system of identical fermions must be **anti-symmetric** with respect to the exchange of any two sets of space and spin variables

Anti-symmetric wavefunctions fullfil the condition that no two electrons can be in the same quantum state, specified by n, l, m_l, and m_s.

Experimental evidence for the existence of spin (or *intrinsic angular momentum*) came from experiments such as those of Stern and Gerlach.

3.3.2 INDISTINGUISHABLE PARTICLES

Consider two indistinguishable (by any physical measurement) particles, labelled ‘1’ and ‘2’, and define an operator $\hat{P}_{12}$ which we will call the “particle interchange operator” which swaps the labels of the particles.

Operating with $\hat{P}_{12}$ we can write:

$$\begin{aligned} \hat{P}_{12}\hat{H}(1,2)\psi(1,2) &= \hat{H}(2,1)\psi(2,1) \qquad (19) \\ &= \hat{H}(1,2)\hat{P}_{12}\psi(1,2) \qquad (20) \end{aligned}$$

since $\hat{H}(1,2) = \hat{H}(2,1)$ (where $\hat{H}$ is the Hamiltonian) as the particles are indistinguishable.

We may rearrange this to show that:

$$\left(\hat{P}_{12}\hat{H}(1,2) - \hat{H}(1,2)\hat{P}_{12}\right)\psi(1,2) = 0 \tag{21}$$

i.e. the particle interchange operator and the Hamiltonian **commute**. The same is true of any operator resresenting a physical quantity, and so whatever measurement is made on the system the resulting wavefunction will be an eigenstate of $\hat{P}_{12}$.

The implication of this is that if $\psi(1,2)$ is an eigenfunction then:

$$\hat{P}_{12}\psi(1,2) = p\psi(1,2) = \psi(2,1) \tag{22}$$

where p is the corresponding eigenvalue. Operating again tells us:

$$\begin{aligned} \hat{P}_{12}\psi(2,1) &= p\hat{P}_{12}\psi(1,2) && (23)\\ &= p^2\psi(1,2) \\ &= \psi(1,2). \\ & && (24) \end{aligned}$$

This means that $p^2 = 1$ and so $\psi(1,2) = \pm\psi(2,1)$, and we conclude that any physically acceptable wavefunction representing two indistinguishable particles *must* be either **symmetric** or **antisymmetric** with respect to exchange of the particles.

The former type of particles are called **bosons**, the latter type are **fermions**. The Pauli Exclusion Principle applies to the latter.

Now consider the case where the particles are fermions, but non-interacting. We denote an unsymmetrised eigenfunction by $\psi(1,2)$ and make the linear combinations that are symmetric and antisymmetric under exchange:

$$\Psi_{\pm}(1,2) = \frac{1}{\sqrt{2}}\left(\psi(1,2) \pm \psi(2,1)\right) \tag{25}$$

where '+' is the symmetric combination and '-' the antisymmetric.

An interesting special case is that of two independent particles, as considered in section 3.2.1 in the last lecture. Remember the total Hamiltonian here is $\hat{H} = \hat{h}_1 + \hat{h}_2$ and the individual hamiltonians have eigenfunctions such that:

$$\hat{h}_i \phi_\lambda(i) = E_\lambda \phi(i) \tag{26}$$

where i is the particle label (1 or 2), and the subscript λ represents a set of quantum numbers that characterise the individual states. For this case there will be two such states: ϕ_a and ϕ_b.

For now we'll just consider fermions and construct the antisymmetric combination of the product $\phi_a\phi_b$:

$$\Psi_{-}(1,2) = \frac{1}{\sqrt{2}}\left(\phi_a(1)\phi_b(2) - \phi_b(1)\phi_a(2)\right). \tag{27}$$

To get a handle on this, imagine these are two non-interacting electrons in a Coulomb potential and the labels a and b are two sets of quantum numbers nlm_l and $n'l'm'_l$. (Remember we tried this model for the Helium atom earlier?)

Now if we try to give both electrons the same set of quantum numbers, that is $a = b$ in the above, we find that the antisymmetric combination $\psi_{-}(1, 2) = 0$: the wavefunction vanishes implying this state does not exist.

This is the Pauli Exclusion Principle at work. For the antisymmetric wavefunction of the identical fermions to be non-zero the fermions must have different sets of quantum numbers.

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

3.3.3 THE HELIUM ATOM

Now let us look more closely at the Helium atom to understand the effects of the Pauli Exclusion Principle. To begin with we'll consider the limit of no interactions between the electrons.

Helium has two electrons (indentical fermions!) so the wavefunctions must be **antisymmetric overall** with respect to exchange of the electrons. We can write the total wavefunction as a product of a space part and a spin part

$$\begin{aligned} \Psi(1,2) &= \underbrace{\Phi(\underline{r}_1, \underline{r}_2)}_{space} \; \underbrace{\chi(s_{1z}, s_{2z})}_{spin} && (28) \\ &= -\Phi(\underline{r}_2, \underline{r}_1) \; \chi(s_{2z}, s_{1z}) \; . && (29) \end{aligned}$$

The χ are eigenfunctions of $\underline{\hat{S}}^2$ where the total spin $\underline{\hat{S}} = \underline{\hat{S}}_1 + \underline{\hat{S}}_2$ is the vector sum of the individual spins, and also of $\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z}$ its z component.

Spin part

For individual electrons we know the behaviour: the spin quantum number is always 1/2. The eigenfunctions can be **spin up** α ($\uparrow, m_s = +1/2$) or **spin-down**, β ($\downarrow, m_s = -1/2$) i.e.,

$$\hat{S}_z\alpha = +1/2\alpha \tag{30}$$

or

$$\hat{S}_z\beta = -1/2\beta \ . \tag{31}$$

For a two particle system the **total** spin quantum number can be $S = 0, 1$, depending on whether the two spins are *parallel* or *anti-parallel* and:

$$\hat{S}^2\chi(s_{1z}, s_{2z}) = S(S+1)\hbar^2\chi(s_{1z}, s_{2z}) \ . \tag{32}$$

(Note for spin and angular quantum numbers of multi electrons systems we use capital letters, L, M_L, S and M_S.)

We can construct the eigenfunctions of total spin from the α and β.

(To do so rigorously we need to cover so-called Clebsch-Gordan coefficients and ladder operators, see the next advanced QM course. We will give the relevant functions without proof.)

S = 1 CASE

The z component can have three possible values: $M_s = -1, 0, 1$, so $S = 1$ is referred to as a **triplet**.

$$\begin{array}{lcc}
M_s = +1 & \chi^T = \alpha(1)\alpha(2) & \uparrow\uparrow \\
M_s = 0 & \chi^T = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \alpha(2)\beta(1)] & \uparrow\downarrow + \downarrow\uparrow \\
M_s = -1 & \chi^T = \beta(1)\beta(2) & \downarrow\downarrow
\end{array}$$

All three triplet states are **symmetric** with respect to exchange of the electrons.

S = 0 CASE

The z component can have one possible value: $M_s = 0$, so $S = 0$ is referred to as a **singlet**.

$$M_s = 0 \quad \chi^S(0) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \alpha(2)\beta(1)] \quad \uparrow\downarrow - \downarrow\uparrow$$

which is **anti-symmetric** with respect to exchange of electrons.

Space part

The **spatial wavefunction** can also be symmetric or antisymmetric:

$$\Phi_{\pm}(1,2) = \frac{1}{\sqrt{2}}[\phi_a(1)\phi_b(2) \pm \phi_a(2)\phi_b(1)]. \qquad (33)$$

Total wavefunction

When we consider the total wavefunctions of He, we must ensure that the **whole spatial-spin combination is anti-symmetric**. In order to satisfy equation 29 we have either

$$\underbrace{\phi(\underline{r}_1, \underline{r}_2) = -\Phi(\underline{r}_2, \underline{r}_1)}_{\text{spatial antisymmetric}} \quad \text{and} \quad \underbrace{\chi(s_{1z}, s_{2z}) = \chi(s_{2z}, s_{1z})}_{\text{spin symmetric}} \qquad (34)$$

or vice versa, symmetric spatial and antisymmetric spin.

For the **TRIPLET** state:

$$\Psi^T(1,2) = \phi_-(1,2)\chi^T \qquad \text{three possibilities}$$

For the **SINGLET** state:

$$\Psi^S(1,2) = \phi_+(1,2)\chi^S \qquad \text{one possibility}$$

The electronic configuration is $1s^2$, i.e. both electrons have the same values for quantum numbers n, l, m_l. In this case we want to have $\phi_a = \phi_b$ without the wavefunction vanishing and therefore the spatial part is symmetric and the spin part must be anti-symmetric.

So the ground state of He is a **SINGLET STATE**

The excited states where both electrons are in different states, e.g. $1s2s$, can be either singlets, called **para** or triplet called **ortho**. We can have anti-symmetric spatial wavefunctions which will not vanish. The symmetric spin state can be allowed because the quantum numbers n for each electron are different.

Multipicity

The value of $2S + 1$ is termed the **spin multiplicity**:

For 0 we get $2S + 1 = 1 \rightarrow$ singlet — only one value of M_s possible (zero)

For 1/2 we get $2S + 1 = 2 \rightarrow$ doublet — two values, $M_s = \pm 1/2$

For 1 we get $2S + 1 = 3 \rightarrow$ triplet — three values, $M_s = +1, 0, -1$

Remember this as it will be used in the spectroscopic term notation.

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

3.4 EXCHANGE

The spin-dependent properties of the wavefunction give rise to interactions for which there is no classical analogue, called **exchange**.

By 'no classical analogue' we mean that it is a purely *quantum mechanical* phenomenon. Concepts like these are sometimes the hardest to grasp as they are difficult to relate to our everyday experience. However as an illustration consider the following argument applied to a two electron atom, like the helium atom discussed in previous lectures.

The total wavefunction is the product of a space part $\Phi(\underline{r}_1, \underline{r}_2)$ and a spin part $\chi(s_{1z}, s_{2z})$ which is **antisymmetric** overall (remember Pauli). For a **spin triplet** (i.e. χ symmetric) the space part must be *antisymmetric*:

$$\Phi(\underline{r}_1, \underline{r}_2) = \Phi_- = \frac{1}{\sqrt{2}} \left(\phi_a(\underline{r}_1)\phi_b(\underline{r}_2) - \phi_b(\underline{r}_1)\phi_a(\underline{r}_2)\right) \tag{35}$$

which is identically zero if $\underline{r}_1 = \underline{r}_2$. So in the spin triplet state the electrons tend to 'keep away' from each other and the Coulomb repulsion will be smaller.

By contrast in the **spin singlet** (i.e. χ antisymmetric) state the space part is *symmetric* and hence non-zero when $\underline{r}_1 = \underline{r}_2$. From this we deduce that there will be times when the electrons will be closer together and experience a stronger repulsion, which means the singlet state will lie **higher** in energy than the corresponding triplet state with the same (n, l, m).

In the spin triplet case the electrons are kept apart - **spatial** separation as a result of **spin** orientation. The furthest apart they can be is on the opposite side of the nucleus where their screening effect for each other is minimal. The electrons will therefore experience a bigger attractive force from the nucleus and be more tightly bound (lower in energy).

Remember that this is a consequence of the Pauli Exclusion Principle, which has introduced a **coupling** between the spin states and the space states (that is, one depends on the other), which now act *as if there was a force* whose sign depended on the relative orientation of their spins. This is called the **exchange force**.

Looking in a little more detail at the N electron Hamiltonian we introduced as equation 3.1 in lecture 7, and considering the case of $N = 2$ electrons, the contribution to the energy from the e^-– e^- repulsion is:

$$I = \langle \frac{1}{r_{12}} \rangle = \int \Psi^*(1,2)\frac{1}{r_{12}}\Psi(1,2) d\tau d\sigma \ , \qquad (36)$$

where the integration is taken over both spin (σ) and spatial coordinates (τ).

Remember this is the *non-central* part of the Hamiltonian that caused us so much trouble before – first we tried neglecting it completely, then we tried averaging the effect over a sphere.

Let's consider the two cases of spin singlets and spin triplets separately.

Singlet case:

$$\begin{aligned}
I &= \int\int \underbrace{\Phi_+^* \chi^{S*}}_{\Psi^*} \left[\frac{1}{r_{12}}\right] \underbrace{\Phi_+ \chi^S}_{\Psi} d\sigma d\tau \\
&= \int\int \underbrace{\frac{1}{\sqrt{2}} \left\{\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)\right\}^*}_{\Phi_+^*} \\
&\quad \times \underbrace{\frac{1}{\sqrt{2}} \left\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\right\}^*}_{\chi^{S*}} \\
&\quad \times \frac{1}{r_{12}} \\
&\quad \times \underbrace{\frac{1}{\sqrt{2}} \left\{\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)\right\}}_{\Phi_+} \\
&\quad \times \frac{1}{\sqrt{2}} \underbrace{\left\{\alpha(1)\beta(2) - \alpha(2)\beta(1)\right\}}_{\chi^S} d\sigma d\tau \ . \qquad (37)
\end{aligned}$$

Which looks horrendous. However life can be made easier by realising that since $1/r_{12}$ does not act on spin, we can separate the integrals into a **space** integral that has functions of position only and a **spin** integral.

$$
\begin{aligned}
I &= \underbrace{\frac{1}{2}\int \{\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)\}^* \times \frac{1}{r_{12}} \{\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)\}\, d\tau}_{\text{Space}} \\
&\times \underbrace{\frac{1}{2}\int \{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}^* \times \{\alpha(1)\beta(2) - \alpha(2)\beta(1)\}\, d\sigma}_{\text{Spin}} \\
&= \underbrace{\int \frac{|\phi_a(1)|^2|\phi_b(2)|^2}{r_{12}} d\tau}_{\text{Coulomb}} + \underbrace{\int \frac{\phi_a^*(1)\phi_b^*(2)\phi_a(2)\phi_b(1)}{r_{12}} d\tau}_{\text{Exchange}} \\
&= \quad C \quad + \quad E \qquad (38)
\end{aligned}
$$

Where we have made use of the fact that the spin wavefunctions are normalised so the spin integral is equal to unity, and that in the space integral on expanding the integrand we obtain terms like $\frac{|\phi_a(1)|^2|\phi_b(2)|^2+|\phi_a(2)|^2|\phi_b(1)|^2}{r_{12}}$ (and similarly for the cross terms) where the two parts of the sum differ only by the (arbitrary) label we have given the electrons (1 or 2).

They must, therefore, integrate to the same value, i.e. have the same energy, introducing a factor of 2 on the top of the fraction which cancels with the factor of 2 on the bottom.

C is the **Coulomb integral** - the repulsion between the two charges.
E is the **exchange integral** - it arises from the Pauli Exclusion Principle and has no classical analogue.

We are not going to evaluate these integrals explicitly, but rather examine the form of the solution to see what we can learn about the effect they have on the energy of the state.

Both C and E are repulsive for the spin singlet, and the overall effect will be to increase the energy and make the state less tightly bound than when the $\frac{1}{r_{12}}$ term is not included.

Remember that our crude non-interacting particle estimate for the ground state (spin singlet) energy of helium was too negative? That estimate neglected $\frac{1}{r_{12}}$ term which as we see here raises the energy.

Triplet case:

We won't examine all three symmetric combinations here (I'll leave that to you for practise to make sure you really understand what's going on). Just look at the $\alpha(1)\alpha(2)$ component, i.e. $\uparrow\uparrow$.

$$\begin{aligned} I &= \int \frac{1}{\sqrt{2}} \left\{\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)\right\}^* \left\{\alpha(1)\alpha(2)\right\}^* \\ &\times \frac{1}{r_{12}} \\ &\times \frac{1}{\sqrt{2}} \left\{\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)\right\} \left\{\alpha(1)\alpha(2)\right\} d\sigma d\tau \end{aligned} \tag{39}$$

As before, we can separate that spatial and spin parts and use the normalisation of the wavefunction:

$$\int \left\{\alpha(1)\alpha(2)\right\}^* \alpha(1)\alpha(2) d\sigma = 1 \ ,$$

This means the integral is of the form:

$$\begin{aligned} I &= \int \frac{|\phi_a(1)|^2 |\phi_b(2)|^2}{r_{12}} d\tau \ - \ \int \frac{\phi_a^*(1)\phi_b^*(2)\phi_a(2)\phi_b(1)}{r_{12}} d\tau \\ &= \qquad C \qquad\qquad - \qquad\qquad E \end{aligned} \tag{40}$$

The integrals C and E are exactly as defined before.

The exchange term now acts to **reduce** the repulsive effect of the Coulomb term. The exchange force is **attractive** for the spin triplet and so it is more tightly bound than the spin singlet.

Remember: The electrons are forced apart by having parallel spins as a consequence of the Pauli Exclusion Principle, thus exposing then to a greater attractive force from the nucleus. It is the symmetry of the wavefunction – a purely quantum mechanical phenomenon – that is the origin of this.

So we have different energy levels for spin singlet and spin triplet states (see energy levels).

Helium in a spin singlet state is called **parahelium**.
Helium in a spin triplet state is called **orthohelium**.

Mnemonic: **para**helium is like **para**llel…and the spins **AREN'T**! (well it works for me)

SUMMARY OF HELIUM ATOM

We have **spin triplet**:

$$\chi(1,2) = \begin{cases} \alpha(1)\alpha(2) & \chi^T(M_s = 1) \\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) + \alpha(2)\beta(1)\right] & \chi^T(M_s = 0) \\ \beta(1)\beta(2) & \chi^T(M_s = -1) \end{cases} \tag{41}$$

or **spin singlet**

$$\chi(1,2) = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2) - \alpha(2)\beta(1)\right] \qquad \chi^S(M_s = 0)\ . \tag{42}$$

Then for the triplet state:

$$\hat{S}^2\chi^T_{M_s} = 2\hbar^2\chi^T_{M_s} \Rightarrow S = 1 \tag{43}$$

$$\hat{S}_z\chi^T_{M_s} = \hbar M_s\chi^T_{M_s} \Rightarrow M_s = -1, 0, 1\ , \tag{44}$$

and for the singlet state

$$\hat{S}^2\chi^S_{M_s} = 0\ \chi^S_{M_s} \Rightarrow S = 0 \tag{45}$$

$$\hat{S}_z\chi^S_{M_s} = 0\ \chi^S_{M_s} \Rightarrow M_s = 0\ . \tag{46}$$

So for two electrons we have four possible spin eigenstates with

$$(S, M_s) = (1,1), \quad (1,0), \quad (1,-1) \qquad \textbf{symmetric}$$

or

$$(S, M_s) = (0,0) \qquad \textbf{anti-symmetric}$$

The total wavefunction of He (product of space and spin) which is **anti-symmetric** overall:

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \left[\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)\right] \chi^T_{M_s=0,\pm1}$$

$$\Psi(1,2) = \frac{1}{\sqrt{2}} \left[\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)\right] \chi^S_{M_s=0}$$

Lowest state of He is 1s 1s $\equiv$ 1s^2 so $\phi_a = \phi_b$
$\Rightarrow$ this cannot be a triplet since then $\Psi(1,2) = 0$.

Excited He, e.g., 1s 2s, can be a triplet ($S = 1$)
and can aslo be a singlet ($S = 0$).

These states however **have different energies** due to the quantum mechanical exchange interaction:

$$E_\pm = \sum_{i=1}^{N} E_i + (C \pm E) \tag{47}$$

where $+E$ is the singlet state (parahelium) and $-E$ is the triplet state (orthohelium).

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

3.5 CONFIGURATIONS AND TERMS

3.5.1 CONFIGURATIONS

Now we consider how to we write down the configuration of a state using the spectroscopic notation introduced in chapter 2.

- The value of n is given as a number.
- The value of l as a letter, s, p, d . . .
- There are $2l + 1$ values of m_l, 2 values of m_s.
- To indicate the number of electrons which occupy a given orbital we put right-hand superscript.
- By the Pauli principle, each orbital nl can hold $2 \times (2l + 1)$ electrons.

The ground state configuration of atoms is given by filling orbitals in energy order with Z (atomic number) electrons (for a neutral atom).

Z	Symbol	configuration
1	H	1s
2	He	$1s^2$
3	Li	$1s^2$ 2s
4	Be	$1s^2$ $2s^2$
5	B	$1s^2$ $2s^2$ 2p
6	C	$1s^2$ $2s^2$ $2p^2$

Terminology

- Electrons having the same n are said to be in the same **shell**.
- Electrons having the same n and l are said to be in the same **sub-shell**. We indicate the number of electrons in the subshell as a superscript on l, i.e. p^2.
- Each shell can hold $2n^2$ electrons $= 2\sum_{l<n} 2l + 1$.
- If a shell contains $2n^2$ electrons it is said to be **closed** (filled,complete).
- If a shell contains $< 2n^2$ electrons it is said to be **open** (unfilled,incomplete).
- Electrons in open shells are **optically active**.
- The chemical properties of elements are determined by the outer electrons, also referred to as **valence electrons**.
- Electrons with the same nl are said to be **equivalent**.

  So for $l = 0$ we can have 2 electrons as l=0, m=0 and m_s=$\pm 1/2$.

  For $l = 2$ we can have 10 electrons, as l=2, m= $\pm 2, \pm 1, 0$ and m_s=$\pm 1/2$.

Mendeleev in 1869 organized elements into the periodic Table where they are grouped according to their valence structure (see table).

ALKALI ATOMS—ONE VALENCE ELECTRON

Symbol	Z	configuration
H	1	1s
Li	3	$1s^2\ 2s$
Na	11	$1s^2\ 2s^2\ 2p^6\ 3s$
K	19	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s$

Alkali atoms have on electron in the outer sub-shell. It is easily lost to form a positive ion

HALOGENS—NEARLY CLOSED SHELLS

Symbol	Z	configuration
F	9	$1s^2\ 2s^2\ 2p^5$
Cl	17	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$
Br	35	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^5$

Halogens have one electron missing in outer sub-shell, so they are very chemically reactive.

NOBLE GASES—CLOSED SHELLS

Symbol	Z	configuration
He	2	$1s^2$
Ne	10	$1s^2\ 2s^2\ 2p^6$
Ar	18	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
Kr	36	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$

Noble gases have closed shells, and so are chemically inert.

Ionization Energy versus Atomic Number Z

The Ionization energy is the energy required to remove one valence electron, it is **maximum for the noble gases** and **minimum for the alkalis**. The range is $\approx$ 4eV up to 24.6 eV.

Qualitative explanation: Electrons in same sub-shell have equivalent spatial distribution, so the screening of one another is ‘small’. Z_{eff} increases as the sub-shell fills up.

The screening will be very effective for a single electron outside a closed sub-shells, as is the case for the alkalis.

Note to remove a second electron, after having removed one, will require more energy than to remove the first one. For example the second electron in He is bound by 54.4 eV and the second one in Li is bound by 75.6 eV.

3.5.2 TERMS

We showed previously that the configurations of He split into singlet ($S=0$) or triplet ($S=1$) terms, depending on the **total** spin quantum number. In general the configurations are also split into terms according to the value of the TOTAL ORBITAL ANGULAR MOMENTUM quantum number L, with

$$\underline{\hat{L}} = \sum_i \underline{\hat{L}}_i \tag{48}$$

where $\underline{\hat{L}}_i$ is the orbital angular momentum of the i th electron.

If we go beyond the central field model, the Hamiltonian no longer commutes with the *individual* orbital angular momenta, $[\hat{H}, \underline{\hat{L}}_i] \neq 0$, and the l_i are not good quantum numbers.

However, it can be shown that the *total* orbital angular momentum quantum number, L, is a good quantum number, i.e.$[\hat{H}, \underline{\hat{L}}^2] = 0$ and similarly for the total spin angular momentum quantum number, S.

The electronic states are simultaneous eigenfunctions of $\hat{H}, \underline{\hat{L}}^2, \underline{\hat{S}}^2$.

For a given configuration, the possible values of L and S are determined by adding the individual angular momenta of each electron, rejecting values of L and S which corresponding to states forbidden by Pauli Exclusion Principle (PEP).

The terms are given as ${}^{2S+1}L$.

For $L = 0, 1, 2, 3, \ldots$ we use the notation S, P, D, F,. . . to classify the quantum levels rather than nl orbitals which arise from the central field approximation.

An important simplification results from the fact that for a **closed** shell,

$$\underline{\hat{S}} = \sum_i \underline{\hat{S}}_i = 0 \; ; \qquad \underline{\hat{L}} = \sum_i \underline{\hat{L}}_i = 0 \; , \tag{49}$$

where these sums are over the electrons in the closed shells ONLY.

So when we work out S or L we need only consider electrons *outside* closed shells, i.e., the valence or optically active electrons.

Example: An Fe^+ ion has term ^{6}D. What are L and S ?

Solution: $2S + 1 = 6$, so $S = 5/2$. $D \Rightarrow L = 2$.

Now consider how to find the **terms for a two electron atom**.

First we consider **non-equivalent electrons**, e.g. (nl and $n'l$) or (nl and nl'), etc. Note that the PEP is automatically satisfied.

Consider two electrons with $\hat{\underline{L}}_1, \hat{\underline{S}}_1$ and $\hat{\underline{L}}_2, \hat{\underline{S}}_2$ such that

$$\begin{array}{ccc} \hat{\underline{L}}_1^2\Psi_1 = l_1(l_1+1)\hbar^2\Psi_1 & \text{and} & \hat{\underline{S}}_1^2\Psi_1 = s_1(s_1+1)\hbar^2\Psi_1 \\ \hat{\underline{L}}_2^2\Psi_2 = l_2(l_2+1)\hbar^2\Psi_2 & \text{and} & \hat{\underline{S}}_2^2\Psi_2 = s_2(s_2+1)\hbar^2\Psi_2 \end{array} \tag{50}$$

The **total orbital angular momentum** is

$$\hat{\underline{L}} = \sum_{i=1,2} \hat{\underline{L}}_i, \tag{51}$$

and the total orbital angular momentum quantum number can take the values

$$\begin{aligned} L &= |\sum_i l_i|_{min} \rightarrow |\sum_i l_i|_{max} \quad \text{(in steps of 1)} \\ &= |l_1 - l_2|, \ldots, l_1 + l_2 - 1, l_1 + l_2. \end{aligned} \tag{52}$$

such that $\hat{\underline{L}}^2\Psi^T = L(L+1)\hbar^2\Psi^T$

The **total spin angular momentum** is

$$\hat{\underline{S}} = \sum_{i=1,2} \hat{\underline{S}}_i \tag{53}$$

and the total spin angular momentum quantum number can take the values

$$\begin{aligned} S &= |\sum_i s_i|_{min} \rightarrow |\sum_i s_i|_{max} \quad \text{(in steps of 1)} \\ &= |s_1 - s_2|, \ldots, s_1 + s_2 - 1, s_1 + s_2. \end{aligned} \tag{54}$$

such that $\hat{\underline{S}}^2\Psi^T = S(S+1)\hbar^2\Psi^T$.

EXAMPLE: 2p3p

PEP is automatically obeyed because n and n' are different.

$l_1 = l_2$ =1 $\rightarrow |l_1 - l_2|, |l_1 - l_2| + 1, \ldots, l_1 + l_2 - 1, l_1 + l_2$ gives $L = 0, 1, 2$, so we have S, P and D.

Also $s_1 = s_2$ =1/2 $\rightarrow$ = 0,1 $\rightarrow 2S + 1 =$ 1,3

PEP does not exclude any, so the possible terms are ^{1}S, ^{1}P, ^{1}D and ^{3}S, ^{3}P, ^{3}D.

Now we consider **equivalent electrons**

Some electrons have the same nl values, therefore by the PEP we must ensure that they have **different** m_l or m_s values.

(A) Consider the ns^2 cases.

These have the same n, l and m_l, therefore they must have opposite spin ($m_s = \pm 1/2$) and $S = 0$. So the only possible term is ^1S

(B) Consider a np^2 case, e.g., 2p^2

We have $l_1 = l_2 = 1.$ and $s_1 = s_2 = 1/2$ and for each e$^-$ we have $m_l = 0, \pm 1$ and $m_s = \pm 1/2$.

Make all the possible combinations of these quantum numbers in a table:

m_{l_1}	m_{s_1}	m_{l_2}	m_{s_2}	Pauli?	label?
1	+	1	+	X	
1	+	1	−		♣
1	+	0	+		
1	+	0	−		
1	+	-1	+		
1	+	-1	−		
1	−	1	+		X ♣
1	−	1	−	X	
1	−	0	+		♠
1	−	0	−		
1	−	-1	+		
1	−	-1	−		
0	+	1	+		X
0	+	1	−		X ♠
0	+	0	+	X	
0	+	0	−		
0	+	-1	+		
0	+	-1	−		
0	−	1	+		X
0	−	1	−		X
0	−	0	+		X
0	−	0	−	X	
0	−	-1	+		
0	−	-1	−		
-1	+	1	+		X
-1	+	1	−		X
-1	+	0	+		X
-1	+	0	−		X
-1	+	-1	+	X	
-1	+	-1	−		
-1	−	1	+		X
-1	−	1	−	X	
-1	−	0	+		X
-1	−	0	−		X
-1	−	-1	+		X
-1	−	-1	−	X	

i) States for which $m_{l1} = m_{l2}$ and $m_{s1} = m_{s2}$ are excluded by the PEP. We cross them off the list.

ii) Pairs of values (m_{l1}, m_{s1}) and (m_{l2}, m_{s2}) which differ only by the e$^-$ label (1,2) only give one state, like the states denoted with ♣ and ♠ in the table, so we cross one of them off the list.

As shown in the next table there are only **15 possible states** left. The important point here is *how to order them* so as to find the terms.

- Find the largest value of M_L, 2 in this this example, and regroup all the states which can be associated with it. How?
- We know that if we have M_L=2, this corresponds to L=2 and therefore $M_L = -2, -1, 0, 1$ and 2.
- We notice that for M_L=2 we have $M_S = 0$.
- So we regroup all the states which must belong together and have $M_L = -2, -1, 0, 1, 2$ and $M_S = 0$.
- Next, we do the same with the states that are left but now the largest M_L = 1 and so we regroup M_L = −1,0,1. However, we note that in this case we have 3 groups of M_L = −1,0,1 each with M_S equal to either −1, 0 or 1.
- Putting all these together, we are left with one term with M_L= 0 and $M_S = 0$.

m_{l_1}	m_{s_1}	m_{l_2}	m_{s_2}	$M_L = m_{l_1} + m_{l_2}$	$M_S = m_{s_1} + m_{s_2}$
1	$+1/2$	1	$-1/2$	2	0
1	$-1/2$	0	$+1/2$	1	0
0	$+1/2$	0	$-1/2$	0	0
0	$-1/2$	-1	$+1/2$	-1	0
-1	$+1/2$	-1	$-1/2$	-2	0
1	$+1/2$	0	$+1/2$	1	1
1	$+1/2$	-1	$+1/2$	0	1
0	$+1/2$	-1	$+1/2$	-1	1
1	$+1/2$	0	$-1/2$	1	0
1	$-1/2$	-1	$+1/2$	0	0
0	$+1/2$	-1	$-1/2$	-1	0
1	$-1/2$	0	$-1/2$	1	-1
1	$-1/2$	-1	$-1/2$	0	-1
0	$-1/2$	-1	$-1/2$	-1	-1
1	$+1/2$	-1	$-1/2$	0	0

There is a term with $L = 2, M_L = -2, -1, 0, 1, 2$ and $S = 0, M_S = 0$.

The term is ^{1}D.

There is a term with $L = 1$ and $S = 1$, $M_L = -1, 0, +1$ for each of $M_S = -1, 0, +1$

The term is ^{3}P

There is a term with $M_L = 0 = M_S \Rightarrow L = 0, S = 0$

The term is ^{1}S

And we have for 2p^2: ^{1}S, ^{3}P, ^{1}D

Alternative Method (for equivalent electrons)

Less tedious, but requiring a little more insight.

Use the symmetry of the wavefunction to solve the problem. Remember $\Psi = \Phi\chi$ (*space* × *spin*) and is overall antisymmetric.

The symmetry of the spin part, χ, is given by the symmetric or antisymmetric combinations of the eigenstates α and β, leading to spin triplets.

The symmetry of the space part is determined by the symmetry of the **spherical harmonics**, Y_{lm}, that are the solutions to the angular part of the Schrödinger equation for a central potential.

Fortunately this is straightforward, as upon exchange of two electrons:

$$Y_{lm}(1,2) \rightarrow (-1)^l Y_{lm}(2,1) \tag{55}$$

The **parity** of $Y_{lm} = (-1)^l$. The same is true for the total angular momentum, L. Parity is the inversion of the position vector $\underline{r}$ through the origin, such that $\underline{r} \rightarrow -\underline{r}$. This requires that $\theta \rightarrow \pi - \theta$ and $\phi \rightarrow \pi + \phi$. (An exchange of labels of the electrons is equivalent to this inversion is we take place electron at the origin and measure the position of the other relative to this.)

So for our previous example of equivalent electrons $2p^2$ where we can have $L = 2, 1, 0$ (D, P, S), the spatial wavefuncions will be symmetric, antisymmetric, symmetric in that order.

The spin wavefunctions must therefore be antisymmetric (singlet), symmetric (triplet) antismmetric (singlet) respectively.

So the allowed terms are ${}^1D,{}^3P$ and ${}^1S$. Just as we found before.

EXAMPLE 2

(1997 exam) An excited Be atom has configuration 1s^2 2p^1 3p^1. Obtain the L, S quantum numbers for the allowed terms arising from this configuration and designate them using spectroscopic notation.

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

3.5.3 HUND'S RULES FOR ORDERING TERMS

We saw that for helium the triplet lies below the singlet in energy because of the exchange interaction. Hund's rules, which were established empirically and apply rigorously only to the ground state configuration, provide guidelines for ordering terms.

HUND'S RULES

For a given electron configuration:

1. The term with the largest value of S has the lowest energy. The energy of other terms increases with decreasing S.
2. For a given value of S, the term having the maximum value of L has the lowest energy.

For example, in the case of the 2 non-equivalent electrons considered previously we have the following ordering:

$$E(^3\mathrm{D}) < E(^3\mathrm{P}) < E(^3\mathrm{S}) < E(^1\mathrm{D}) < E(^1\mathrm{P}) < E(^1\mathrm{S}) \ .$$

N.B. Hund's Rules implicitly assume L-S coupling which we will deal with next, and find a third rule for the ordering with $J = L + S$.

Justification (sort of):

1. The *spin-spin* interaction. States with symmetric spins (triplets) that have larger S are forced to be spatially separated hence feeling a greater attraction from the nucleus.
2. The *orbit-orbit* interaction. If L is large this implies the individual angular momentum vectors l_i are parallel, and the electrons are orbiting in the same direction. They will therefore encounter each other less frequently than if they were orbiting in opposite directions - they could conceivably always be on opposite sides of the nucleus in some cases - and so on average experience less of a shielding effect.

3.6 THE SPIN-ORBIT INTERACTION

3.6.1 LEVELS SPLITTING

We have seen that *configurations* split into *terms*. In turn *terms* split into energy *levels*. **Why?**

Because of **spin-orbit** interaction.

The atomic Hamiltonian may be written:

$$\hat{H}_T = \hat{H} + \hat{H}_{\mathrm{LS}} \tag{56}$$

where

$$\hat{H} = \sum_i \left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right) + \sum_{\substack{i,j\\ i>j}} \frac{1}{r_{ij}} \tag{57}$$

is the multi-electron Hamiltonian we have used earlier.

We shall show below that

$$\hat{H}_{\mathrm{LS}} = A(L,S)\underline{\hat{L}} \cdot \underline{\hat{S}} \tag{58}$$

is the Spin-Orbit term. $A(L,S)$ is a constant, containing the $\langle 1/r^3 \rangle$ expectation value. It represents a small energetic perturbation relative to $\hat{H}$.

Advance Warning! Remember our previous discussions about making changes to the form of the potential lifting degeneracies? Going from a Coulomb to a non-Coulomb but still central potential lifted the degeneracy with respect to l. Again we have added a small term to the Hamiltonian which we can expect to lift a degeneracy and split terms into energy levels.

The spin-orbit term appears most naturally from the relativistic version of the Schrödinger equation, the *Dirac equation*. We will use a simple classical model, along the lines of the Bohr picture of electrons in circular orbits, to gain a physical insight.

A current loop/rotating charge yields a **magnetic moment**. An electron moving in a circular Bohr orbit (of radius r around a fixed nucleus), so having **orbital** angular momentum, acts like a current loop and so is associated with a magnetic moment. And although the electron spinning is a more abstract quantum relativistic property—rather than a little sphere spinning on its axis it has **intrinsic** angular momentum—it can still be associated with a magnetic moment.

Remember: angular momentum ⇒ magnetic moment.

In order to describe this interaction using a semi-classical approach we use the so-called 'vector-model' description of the atom, i.e. we use $\underline{L}$ and $\underline{S}$ as vectors. But remember that in quantum mechanics they are operators and that the vector approach is just there to help us visualize things.

3.6.2 MAGNETIC MOMENTS

So we first make a small diversion into electromagnetism (Thank you Dr Renzoni)!

The magnetic moment $\underline{\mu}_X$ and the angular momentum, $\underline{X}$, (where I am using $\underline{X}$ to represent either orbital, $\underline{L}$, or intrinsic, $\underline{S}$, angular momentum) of an arbitrary rotating body with mass M, and charge Q, always satisfy a relation of the form:

$$\underline{\mu}_X = g_X \frac{Q}{2M} \underline{X} \ , \tag{59}$$

where g_X is the so-called **Landé g-factor** and depends on the details of the rotating charge distribution.

Now classically if a magnetic moment $\underline{\mu}_X$ is placed in a uniform $\underline{B}$-field, a **torque** $\underline{\tau}$ arises:

$$\underline{\tau} = \frac{d\underline{X}}{dt} = \underline{\mu}_X \times \underline{B} = g_X \frac{Q}{2M} \underline{X} \times \underline{B} \tag{60}$$

using eq. 59 and remember $\underline{X}$ is a *general* angular momentum vector.

So $\underline{\tau}$ is perpendicular to $\underline{X}$ and $\underline{B}$ and results in a *precession* of $\underline{X}$ around $\underline{B}$.

We define the **Larmor precession frequency**

$$\omega = g_X \frac{Q}{2M} B \tag{61}$$

and write the torque as

$$\underline{\tau} = -\underline{\omega} \times \underline{X} \tag{62}$$

Also, the system with a magnetic moment $\underline{\mu}_X$ placed in a magnetic field, $\underline{B}$, has an **interaction potential energy**

$$V = -\underline{\mu}_X \cdot \underline{B} \tag{63}$$

Example: Let's see the case of an electron in a circular Bohr orbit. The electron circling in a loop gives rise to a current of magnitude

$$i = e\nu \ .$$

From elementary electromagnetism theory, we know that such a current loop produces a magnetic field equivalent to that produced by a magnetic dipole.

For a current, i, in a loop of area πr^2, the magnetic moment is

$$\mu_L = (\text{current} \times \text{area}) = i\pi r^2 = e\nu\pi r^2 \ . \qquad (64)$$

Now the orbital angular momentum of the electron is:

$$L = mvr = m\omega r^2 = m2\pi\nu r^2 \ . \qquad (65)$$

From Eqs (64) and (65), we see that the ratio,

$$\frac{\mu_L}{L} = \left(\frac{e\nu\pi r^2}{m2\pi\nu r^2}\right) = \frac{e}{2m} \ , \qquad (66)$$

depends only on **fundamental constants**. For a current loop produced by a *negative* charge, $\underline{\mu}_L$ is *opposite* to $\underline{L}$, i.e.,

$$\underline{\mu}_L = -\frac{e}{2m}\underline{L} \ . \qquad (67)$$

From Eqs (67) and (59) we identify the **orbital g-factor**:

$$g_L = 1 \ . \qquad (68)$$

Expressing $\underline{\mathrm{L}}$ in units of $\hbar$, we obtain,

$$\underline{\mu}_L = -g_L\mu_B\frac{\underline{L}}{\hbar} \qquad (\text{with } g_L = 1) \ , \qquad (69)$$

where μ_B is the **Bohr magneton**:

$$\mu_B = \frac{e\hbar}{2m} = \begin{cases} 1/2 \ \text{ atomic units} \\ 9.274 \times 10^{-24}\,\text{Am}^2 \\ 5.788 \times 10^{-9}\,\text{eV/Gauss} \end{cases} .$$

N.B. $1\text{Am}^2 = 1\text{JT}^{-1}$, so also $\mu_B = 9.274 \times 10^{-24}\text{JT}^{-1}$.

Now for the **spin**: analogous to Eq. (59), we can introduce a *spin magnetic moment* associated with the intrinsic angular momentum of the electron:

$$\underline{\mu}_S = -g_S \mu_B \frac{\underline{S}}{\hbar} \,, \tag{70}$$

where g_S is the **spin g-factor** and, from Dirac's relativistic quantum theory (where spin properly belongs) of the electron interacting with a magnetic field, we have $g_S = 2$ in good agreement with experiment (to 1 part in 10^4—one of the achievements of QED was to derive the small correction giving the accurate value of $g_S = 2.002319$).

Together with spin and antiparticles, this is another key result of Dirac's theory as it confirms the electron as a structureless (or fundamental) particle.

Contrast this result with another spin-$\frac{1}{2}$ Fermion, the proton, which, according to Dirac's theory, should have $g_S = 2$ if structureless, instead is found to have

$$\underline{\mu}_P = 2.79 \frac{e}{2M_P} \underline{S} \,.$$

Even more drastic is the result for the magnetic moment of the neutron (if structureless then $\mu_N = 0$ since $Q = 0$); instead we find

$$\underline{\mu}_N = -1.91 \frac{e}{2M_N} \underline{S} \,.$$

These results show that the proton and neutron are, in fact, composites and NOT fundamental particles. You will learn more about this in the Nuclear and Particle Physics course (3rd year with Dr Saakyan).

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

THE SPIN-ORBIT TERM

We now want to find the effect on the energy of the system that the spin magnetic moment will have. Consider an electron (charge -e) moving in a Bohr orbit around a nucleus with (charge +Ze). Let the velocity of the electron be $\underline{v}$ and its position w.r.t. the nucleus be $\underline{r}$.

In the **electron** reference frame, the nucleus is moving around with a velocity $-\underline{v}$, constituting a *current* in the electron's frame:

$$\underline{i} = -\frac{Ze\underline{v}}{2\pi r} \tag{71}$$

which will produce a *magnetic field* at the instantaneous location of the electron.

We can estimate the resulting magnetic field from the **Biot-Savart Law**:

$$d\underline{B} = \frac{\mu_0 i}{4\pi r^3}\left(d\underline{l} \times \underline{r}\right) \rightarrow \underline{B} = \frac{\mu_0}{2r^2}\left(\underline{i} \times \underline{r}\right) \tag{72}$$

So the internal magnetic field $\underline{B}_{int}$ arising from the apparent motion of the nuclear charge is:

$$\underline{B}_{int} = \frac{\mu_0}{4\pi}\frac{Ze(-\underline{v}) \times \underline{r}}{r^3} \tag{73}$$

If we express the electric (Coulomb) field of the nucleus as

$$\underline{E} = \frac{1}{4\pi\epsilon_0}\frac{Ze\underline{r}}{r^3} \tag{74}$$

and using $\mu_0\epsilon_0 = \frac{1}{c^2}$ we get

$$\underline{B}_{int} = \frac{-\underline{v} \times \underline{E}}{c^2} \tag{75}$$

Note that this result is of general validity: any charged particle moving with a velocity $\underline{v}$ through an arbitrary $\underline{E}$ will experience a motional magnetic field. (Apply Lorentz transformation to Maxwell's eqs.)

Now we can also write B_{int} in terms of the angular momentum, using $\underline{L} = m\underline{r} \times \underline{v}$ and substituting into equation 73 we get

$$\underline{B}_{int} = \frac{\mu_o Ze}{4\pi}\frac{\underline{r} \times \underline{v}}{r^3} = \frac{Ze}{4\pi\epsilon_0}\frac{\underline{L}}{mr^3c^2} \tag{76}$$

Note: The change of sign comes from the change of order of the corss product, and we have used $\mu_0\epsilon_0 = \frac{1}{c^2}$. This relates $\underline{B}_{int}$ to $\underline{L}$.

An alternative way of expressing $\underline{B}_{int}$ includes the electrostatic potential energy of the electron, $V = \frac{-Ze^2}{4\pi\epsilon_0 r}$:

$$\underline{B}_{int} = \frac{1}{emc^2}\frac{1}{r}\frac{dV}{dr}\underline{L} \tag{77}$$

So in the case of the electron which has *spin* angular momentum and hence a magnetic moment interacting with the magnetic field due to its *orbital* motion we have the **spin-orbit interaction**, the energy of which is:

$$\begin{aligned} V_{\mathrm{LS}} &= -\underline{\mu}_S \cdot \underline{B}_{int} = \left(g_s \frac{\mu_B}{\hbar} \underline{S}\right) \boldsymbol{\cdot} \left(\frac{Ze}{4\pi\epsilon_0} \frac{\underline{L}}{mr^3c^2}\right) \\ &= \frac{Ze^2}{4\pi\epsilon_0} \left(\frac{\underline{L} \boldsymbol{.} \underline{S}}{m^2r^3c^2}\right) \\ &= \frac{1}{m^2c^2} \frac{1}{r} \frac{dV}{dr} \underline{L} \cdot \underline{S} \end{aligned} \tag{78}$$

using the definition of the Bohr magneton, $\mu_B = \frac{e\hbar}{2m}$.

Note: This calculation is not quite complete because it has been done in the rest frame of the moving electron, not the nucleus. There is a relativistic ("*Thomas*") precession of axes of the frame in which the electron in instantaneously at rest relative to the nuclear set. A full treatment of this effect is beyond the scope of this course, but may be found in Appendix J of Eisberg & Resnick.

Suffice to say that it introduces a factor of one half into the expression above such that the **final form of the spin-orbit interaction** is

$$V_{\mathrm{LS}} = \frac{Ze^2}{4\pi\epsilon_0} \left(\frac{\underline{L} \boldsymbol{.} \underline{S}}{2m^2r^3c^2}\right) = \frac{1}{2} \frac{1}{m^2c^2r} \frac{dV}{dr} \underline{L} \cdot \underline{S} \tag{79}$$

This interaction energy can be written in terms of the dimensionless quantity called the **fine structure constant** that we have encountered in earlier lectures:

$$\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} = \frac{1}{137.0} \tag{80}$$

which if we include in the above gives:

$$V_{\mathrm{LS}} = Z\alpha \frac{\hbar}{2m^2c}\left(\frac{\underline{\hat{L}}.\underline{\hat{S}}}{r^3}\right) \tag{81}$$

Note that the energy depends on the scalar product of $\underline{\hat{S}}$ and $\underline{\hat{L}}$ and therefore on their *relative orientation.*

How big is this effect? To estimate we can say that $r \simeq a_0$ and $\langle \underline{L} \cdot \underline{S} \rangle \simeq \hbar^2$, which for $Z = 1$ gives:

$$\begin{aligned} V_{\mathrm{LS}} &\simeq \frac{1}{2}\frac{e^2}{4\pi\epsilon_0}\frac{1}{a_0}\frac{\hbar^2}{m^2c^2a_0^2} \\ &\simeq \underbrace{\left(\frac{e^2}{4\pi\epsilon_0\hbar}\right)^2}_{\alpha^2}\underbrace{\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2}_{R_\infty} \\ &\simeq \alpha^2 R_\infty \end{aligned} \tag{82}$$

Remember that $\alpha \simeq \frac{1}{137}$, so this effect is small – hence *fine structure!* – but it **is** measurable!!

We have reintroduced the operator notation in the above and can now see that the two vector-operators are *coupled together*, i.e. we have **spin-orbit coupling**.

As such they no longer have fixed z components and we cannot use m_s and m_l as good quantum numbers, however, the **total** angular momentum $\underline{\hat{J}} = \underline{\hat{L}} + \underline{\hat{S}}$, **does** have a fixed z component.

3.6.3 LANDÉ INTERVAL RULE

Rather than being eigenstates of L^2, L_z, S^2, S_z like the terms and configurations, the effect of the spin-orbit term is to split the energies into **levels** which are eigenstates of J^2, J_z, L^2 and S^2.

For the **one-electron case**

$$\Delta E_{\mathrm{LS}} = \int \Psi_{n,l,j,m_j} V_{LS} \Psi_{n,l,j,m_j} d\tau \ . \tag{83}$$

where $V_{LS} \propto \underline{\hat{L}} \cdot \underline{\hat{S}}$. Now using

$$\underline{\hat{J}}^2 = (\underline{\hat{L}} + \underline{\hat{S}})^2 = \underline{\hat{L}}^2 + \underline{\hat{S}}^2 + 2\underline{\hat{L}} \cdot \underline{\hat{S}} \tag{84}$$

and therefore operating with $\frac{1}{2}\left[\underline{\hat{J}}^2 - \underline{\hat{L}}^2 - \underline{\hat{S}}^2\right]$ instead of $\underline{\hat{L}} \cdot \underline{\hat{S}}$ and integrating eq. 83 we get

$$\Delta E_{\mathrm{LS}} = \frac{1}{2} A(l,s)\left[j(j+1) - l(l+1) - s(s+1)\right] \tag{85}$$

and $A(l,s)$ is a constant containing $\langle 1/r^3 \rangle$ and is $\propto Z^4$ (factor of Z from the Coulomb potential V, and Z^3 from $\langle 1/r^3 \rangle$).

For the **multi-electron case** a similar derivation gives

$$\Delta E_{\mathrm{LS}} = \frac{1}{2} A(L,S)\left[J(J+1) - L(L+1) - S(S+1)\right] \tag{86}$$

If we now consider the difference between the spin-orbit energy between two adjacent levels we obtain

$$\Delta E_{\mathrm{LS}}(J) - \Delta E_{\mathrm{LS}}(J-1) = A(L,S)J \tag{87}$$

THE LANDÉ INTERVAL RULE

The separation between adjacent energy levels is proportional to the larger of the two J values.

3.6.4 TOTAL ANGULAR MOMENTUM $\underline{\hat{J}}$

A) The one-electron case

$$\underline{\hat{J}} = \underline{\hat{L}} + \underline{\hat{S}} \tag{88}$$

AND z-component:

$$\hat{J}_z = \hat{L}_z \ + \ \hat{S}_z \ . \tag{89}$$

The eigenvalue equations (just like previously for angular momentum) are now

$$\underline{\hat{J}}^2\Psi = j(j+1)\hbar^2\Psi \qquad \text{and} \qquad \hat{J}_z\Psi = m_j\hbar\Psi \tag{90}$$

$j = |l-s|, \ldots, |l+s|$ in step of one, is called the **total angular momentum quantum number**.

$m_j = -j, \ldots, j$ in step of one, is called the **total angular momentum magnetic quantum number**.

The *good quantum numbers* for a one-electron atom are therefore n, l, j and m_j, i.e. $\Psi_{n,l,m_l,m_s} \longrightarrow \Psi_{n,l,j,m_j}$

Notation: We know that the spin-orbit interaction will change the energy depending on $\underline{\hat{S}}$ and $\underline{\hat{L}}$, so we have different levels for different $\underline{\hat{J}}$

We now label each **energy level** with spectroscopic notation $n^{2s+1}l_j$.

Note similarity with term notation and that as $s = 1/2$ we have $2s+1$=2. (However, some books, e.g. Brehm and Mullin, use $n^{2s+1}L_j$,where L stands for l written as capital letter, not the total orbital angular momentum.)

Example 1: How many lines should we expect for the 3p→ 3s transition of Na ?

We can now see that the $3p$ state will be split depending on the relative orientations of l and s. The total angular momentum j can have values in this case $l + s = 3/2$ and $l - s = 1/2$, so the allowed energy levels are ${}^2p_{3/2}$ and ${}^2p_{1/2}$.

The $3s$ state will not be split as there is only one possible value for $j = 1/2$, and the energy level is denoted ${}^2s_{1/2}$.

We therefore expect there to be two lines for this transition, but as the difference in energy arises from the spin-orbit interaction we expect the difference in wavelength to be small. This is indeed the case – this is the famous sodium Fraunhofer D-line doublet.

Example 2: How many lines would the 3d→3p transition give ?

The $3d$ state is also split into two by the spin-orbit interaction, in this case the energy levels are ${}^2d_{5/2}$ and ${}^2d_{3/2}$. We might expect that there would be four lines as there are two upper states and two lower states. In fact there is a **selection rule** governing the transition:

$$\Delta j = 0, \pm 1 \tag{91}$$

with the exception that $j = 0$ to $j' = 0$ is forbidden. This rules out one of the possible transitions, meaning that the 'diffuse' series ${}^2d_{5/2,3/2} \rightarrow {}^2p_{3/2,1/2}$ is actually a *triplet* (don't confuse this with the spin triplet discussed earlier, here we mean three very closely spaced spectral lines).

B) The multi-electron case

In these cases the problem is more complex.

We have the eigenvalue eqs.

$$\underline{\hat{J}}^2\Psi = J(J+1)\hbar^2\Psi \qquad \text{and} \qquad \hat{J}_z\Psi = M_J\hbar\Psi \quad (92)$$

but J can now be obtained in **two different manners** depending on the 'strength' of the spin-orbit interaction.

(i) The LS or Russell-Saunders coupling

Used for low-Z atoms for which the spin-orbit interaction is much less than the interaction between electrons.

- Combine all individual spins, $\sum_i \underline{\hat{S}}_i = \underline{\hat{S}}$, to give total spin quantum number S.
- Combine all individual orbital angular momenta, $\sum_i \underline{\hat{L}}_i = \underline{\hat{L}}$, to give total orbital angular momentum quantum number L.
- Then combine the quantum numbers L and S to give J as

$$J = |L-S|, |L-S+1|, \ldots, |L+S-1|, |L+S|. \quad (93)$$

A third **Hund's rule** exist regarding the J-values:

3(a) **Normal case** - outershell is less than half-full. The lowest energy in the lowest energy term corresponds to the *smallest J-value*

3(b)**Inverted case** - outershell is more than half-full. The lowest energy in the lowest energy term corresponds to the *largest J-value*

3(c) When the subshell is half full there is no multiplet splitting.

The degeneracy with respect to j is lifted by the spin-orbit coupling, but the degeneracy with respect to m_j remains, although it can be lifted by, for example, an external magnetic field (as we shall see later).

(ii) jj-coupling

In high-Z atoms, the spin-orbit coupling between $\underline{\hat{S}}_i$ and $\underline{\hat{L}}_i$ for each individual electron is strong and combines them to give each electron an individual $\underline{\hat{J}}_i$ with quantum number j_i. These are then combined together to give a total $\underline{\hat{J}}$,

$$\underline{\hat{J}} = \sum_i \underline{\hat{J}}_i. \tag{94}$$

The total angular quantum number is then

$$J = |\sum_i j_i|_{min} \rightarrow |\sum_i j_i|_{max} \qquad \text{in steps of one} \tag{95}$$

where

$$j_i = l_i + s_i. \tag{96}$$

Neither LS or jj coupling describe perfectly the total angular momentum especially for medium Z atoms (see figure).

3.6.5 PARITY

Parity describes the behaviour of ψ under reflection at the origin (nucleus), i.e., $\underline{r} \to -\underline{r}$.

$$\Psi(\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N) = \pm\Psi(-\underline{r}_1, -\underline{r}_2, \ldots, -\underline{r}_N) \ . \qquad (97)$$

Whether the wavefunction is even or odd depends on l.

For a one electron atom, the parity is $(-1)^l$, i.e., the parity of a spherical harmonic.

For N electrons it is:

$$(-1)^{l_1}(-1)^{l_2}(-1)^{l_3}...(-1)^{l_N} = (-1)^{\sum l_i} \ . \qquad (98)$$

EXAMPLE 1

For Lithium in a 1s 2p 3p configuration, what is the parity? What about 1s 2p 3d ?

EXAMPLE 2

For Na in a $1s^2\ 2s^2\ 2p^6\ 3s$ configuration what is the parity?

If a term is ODD, we write e.g., $^2\mathrm{P}^{(o)}$.
If a term is EVEN, we omit superscript, e.g., $^2\mathrm{D}$.

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 $(-1)^{\Sigma l_i}$