ATOMIC PHYSICS REVISION NOTES:

1 Electron Spin

An electron has spin $s = \frac{1}{2}$, wehich means that in units of $\hbar$ the electron can have a component of spin $\pm\frac{1}{2}$ in any given direction (or more generally the electron can be in a quantum superposition of the two states).

An atom with two electrons (helium) can have a total electron spin $S = 1$ or $S = 0$. For the $S = 1$ state the possible values of the component of spin in any one direction (the z-direction) are 1, 0 or -1 (in units of $\hbar$).

The states with $S_z = 1$ and $S_z = -1$ are the states in wich the two spin $\frac{1}{2}$ electrons *both* have $s_z = \frac{1}{2}$ or both have $s_z = -\frac{1}{2}$, respectively. However, the states with $S_z = 0$ are superpositions of states in which one electron has $s_z = \frac{1}{2}$ and the other has $s_z = -\frac{1}{2}$, and vice versa, i.e.

$$\frac{1}{\sqrt{2}}\left(\uparrow\downarrow + \downarrow\uparrow\right) \quad S = 1,\ S_z = 0$$

$$\frac{1}{\sqrt{2}}\left(\uparrow\downarrow - \downarrow\uparrow\right) \quad S = 0,\ S_z = 0$$

For an atom with n electrons the total spin can take values from $S = \frac{1}{2}$ (if n is odd) or $S = 0$ (if n is even) up to $\frac{n}{2}$, in integer steps. For a given value of total spin, S, the component of total spin in any given direction will be from $-S$ to S in integer steps.

2 Pauli Exclusion Principle

No two identical fermions (half odd-integer spin particles) can occupy the same state (including the spin state). A maximum of two fermions can have the same spatial wavefunction provided their combined spin is zero (i.e. the spin part of the wavefunction is antisymmetric under interchange).

The complete wavefunction of a system of identical fermions is antisymmetric under the interchange of any two of the fermions.

3   Spin-Orbit Interaction (j-j Coupling Scheme)

The spin-orbit coupling between the magnetic moment due to the spin angular momentum and the magnetic field due to the orbital angular momentum, splits the energy levels of the electron with a given orbital angular momentum quantum number, l, into states depending on the total angular momentum quantum number, j.

$$j \;=\; l \pm \frac{1}{2}.$$

The splitting is proportional to $\mathbf{l} \cdot \mathbf{s}$ and using $\mathbf{j} = \mathbf{l} + \mathbf{s}$, we have

$$\mathbf{l} \cdot \mathbf{s} \;=\; \frac{1}{2}\left(j^2 - l^2 - s^2\right)$$

The eigenvalues of j^2, l^2 and s^2 are $j(j+1)\hbar^2$, $l(l+1)\hbar^2$ and $s(s+1)\hbar^2$, $(s = 1/2)$, respectively so that the splitting is proportional to

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

The states of the electrons are denoted as

$$n\{l\}_j,$$

where n is the principle quantum number, $\{l\}$ is a code which indicates the orbital angular momentum as follows

$$
\begin{array}{ll}
s & l = 0 \\
p & l = 1 \\
d & l = 2 \\
f & l = 3 \\
g & l = 4, \quad (etc.)
\end{array}
$$

For example, the outer shell of Bi has three electrons with $n = 6$ and $l = 1$ - the first two have $j = 1/2$ and since this is then full, the third must have $j = 3/2$, This outer sub-shell is denoted by

$$(6p)^2_{\frac{1}{2}}(6p)_{\frac{3}{2}}$$

Below this sub-shell Bi has a closed sub-shell with $n = 4$, 3, which has a total of 14 electrons (j can take the values 7/2 and 5/2 permitting 8 and 6 electrons respectively), a closed sub-shell with $n = 5$, $l = 2$ with a total of 10 electrons, and a closed subshell with $n = 6, l = 0$ containing two electrons, . Since these are closed sub-shells we do not usually indicate the values of j and we would write the configuration for the entire outer shell as

$$(4f)^{14}(5d)^{10}(6s)^2(6p)^2_{\frac{1}{2}}(6p)_{\frac{3}{2}}$$

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4 Parity

The parity of a system of n electrons, defined by

$$\Psi(-\mathbf{r_1}, -\mathbf{r_2}, \cdots -\mathbf{r_n}) = \eta\Psi(\mathbf{r_1}, \mathbf{r_2}, \cdots \mathbf{r_n})$$

is given by

$$\eta = \prod_{i=1}^{n}(-1)^{l_i},$$

where l_1 is the orbital angular momentum of electron i.

5 Transition rates

The amplitude for an electric dipole transition is proportional to

$$\int \Psi_f(\mathbf{r})kr\Psi_i(\mathbf{r})d^3\mathbf{r},$$

where $\Psi_i(\mathbf{r})$ and $\Psi_f(\mathbf{r})$ are the initial and final wavefunctions of the electron that makes the transition. k is the wavenumber of the emitted photon.

This is obtained from the expansion of e^{ikr} in the dependence on r of the electric field of the perturbing potential. Because $kr \ll 1$ for r of the order of an atomic radius, this expansion ois truncated at first order. However, weak transitions arising from higher terms in the expansion are possible (multipole transitions). For these multipole transitions we lose a factor of kr in the transition amplitude (an hence a factor of $(kr)^2$ in the transition rate) for each higher order in the expansion.

For the above matrix element to be non-zero we require that the orbital angular momentum of the electron in the initial and final state must differ by one unit. This means that the initial and final states must be of opposite parity.

The selection rule on orbital angular momentum can be broken by higher multipole transitions. It is also possible to violate the selection rule on the parity change via magnetic dipole or magnetic multipole transitions. For a magnetic dipole transition the parity of the initial an final states must be the same. Magnetic dipole transition rates are suppressed relative to electric dipole transition rates so that these spectral,lines are weaker.

6 Selection Rules

For an individual electron making a transition via the electric-dipole interactions, the changes in orbital angular momentum quantum number l and total angular momentum quantum number j, between the initial and final states, must be

$$\Delta j = 0, \pm 1,$$

$$\Delta l = \pm 1.$$

7 Weak Field Zeeman Effect

Apply an external magnetic field in the z-direction.

The effective magnetic moment in the z-direction is

$$\mu^z = (g_s s^z + l^z)\mu_B,$$

where

$$\mu_B = \frac{e}{2m_e},$$

is the Bohr magneton and g_s is the electron gyro-magnetic ratio (almost equal to 2 in the case of the electron).

The expectation value of μ^z in a state which is an eigenstate of s^2, l^2, j^2 and j^z may be written

$$\langle\mu^z\rangle = \mu_B \frac{\langle(g_s \mathbf{s}\cdot\mathbf{j} + \mathbf{l}\cdot\mathbf{j})\rangle}{\langle j^2\rangle}j^z.$$

Using $\mathbf{j} = \mathbf{l} + \mathbf{s}$ (or rather $\mathbf{l} = \mathbf{j} - \mathbf{s}$ and squaring both sides) leads to

$$\mathbf{s}\cdot\mathbf{j} = \frac{1}{2}\left(j^2 + l^2 - s^2\right),$$

so that the expectation value becomes

$$\langle\mathbf{s}\cdot\mathbf{j}\rangle = \frac{\hbar^2}{2}\left(j(j+1) + l(l+1) - s(s+1)\right),$$

and likewise using $\mathbf{s} = \mathbf{j} - \mathbf{l}$ and squaring we get

$$\langle\mathbf{l}\cdot\mathbf{j}\rangle = \frac{\hbar^2}{2}\left(j(j+1) + s(s+1) - l(l+1)\right),$$

and we also have

$$\langle j^2\rangle = j(j+1)\hbar^2$$

so that the effective magnetic moment is

$$\langle\underline{\mu}\rangle = \mu_B \frac{(g_s\left(j(j+1) + l(l+1) - s(s+1)\right) + j(j+1) + s(s+1) - l(l-1))}{j(j+1)}\mathbf{j}$$

8 Natural Linewidths

The natural linewidth, Γ, of a spectral line is related to the lifetime τ of the excited state by

$$\Gamma = \frac{\hbar}{\tau}$$