3 MANY-ELECTRON ATOMS

3.1 MANY-ELECTRON HAMILTONIAN

For a one-electron atom, the Hamiltonian, in atomic units is:

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

For an N-electron atom, the Hamiltonian, in atomic units is:

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

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

and $\hat{h}_i(\underline{r}_i) = -\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}$.

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

NOTE: We have to write the $1/r_{ij}$ term carefully to avoid ‘double-counting’.

3.2 APPROXIMATE SOLUTIONS

3.2.1 INDEPENDENT PARTICLE MODEL

As a first approximation, we neglect $1/r_{ij}$ entirely. Then,

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

$\hat{H}$ separates into N one-electron Hamiltonians $\hat{h}_i$,

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

which in turn are separable. We have N hydrogen-like solutions.

For example, for $N = 2$, the helium ground state, with $Z = 2$

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

The true energy is $E = -2.9\,\text{a.u}$. The neglect of the inter-electron repulsion yields a value which is too negative. One can roughly estimate the magnitude the inter-electron repulsion as the average separation of the helium $n = 1$ electrons is $1\,\text{a.u.}$; hence the average repulsive energy is

$$E_r = \int \Psi^* \frac{1}{r_{12}} \Psi d\tau \approx \frac{1}{< r_{12} >} \approx 1\text{a.u.} \tag{6}$$

$$E + \frac{1}{< r_{12} >} \sim -3\,\text{a.u.}\ .$$

Still need to consider Pauli principle.

3.2.2 CENTRAL FIELD APPROXIMATION

We take a central potential $V_c(r_i)$ which represent the average interaction of the ith e$^-$ with the nucleus screened by the other electrons.

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

where

$$V_c(r_i) = < \sum_j \frac{1}{r_{ij}} > \ . \tag{9}$$

The brackets indicate that we have averaged out the effect of the *other* electrons over a sphere. V_c has no angular (ϕ,θ) dependence: it is spherically symmetric, ISOTROPIC.

We can then solve the N one-particle equations:

$$\hat{h'}_i \Phi(\underline{r}_i) = \epsilon_i \Phi(\underline{r}_i) = \epsilon_i F_{nl}(r_i) Y_{lm}(\theta, \phi) \tag{10}$$

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:

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

The s, p, d, f terminology is still useful. The form of the radial part, F_{nl}, though, can be quite complicated and is not like hydrogen.

Now the energies $\epsilon_i \rightarrow \epsilon_{nl}$ depend on both n as well as l, unlike hydrogen. We label the orbitals 1s, 2s, 2p, 3s, 3p... etc. To indicate the number of electrons which occupy a given orbital we put right-hand superscript, e.g $3p^2$.

The central field model makes most sense mostly for alkali-atoms Li, Na, K,... or similar ones. For these 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.

$$-\frac{N}{r_i} + V_c(r_i) \rightarrow -\frac{N}{r_i} \qquad \text{as} \ \ r_i \rightarrow 0 \tag{13}$$

AND

$$-\frac{N}{r_i} + V_c(r_i) \rightarrow -\frac{1}{r_i} \qquad \text{as} \ \ r_i \rightarrow \infty \tag{14}$$

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.

The 3d orbitals overlap weakly with the inner region. BUT...

The 3s orbitals 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) (SEE FIGURE 2.7).

- 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.
- 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 w.r.t l,

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

for a multi-electron atom it is lifted,

$$E(\mathrm{1s}) < E(\mathrm{2s}) < E(\mathrm{2p}) < E(\mathrm{3s}) < E(\mathrm{3p}) < E(\mathrm{3d}) \sim E(\mathrm{4s}) \ .$$

3.2.3 QUANTUM DEFECTS AND SCREENING CONSTANTS

For multi-electron atoms with a core plus a single optically active outer electron, such as the alkalis or some ions. We can give an analytical expression for the energy, in a.u., of the outer electron:

$$E_{nl} = -\frac{Z_{\mathrm{eff}}^2}{2(n - \Delta_{nl})^2} \ , \tag{15}$$

1. Z_{eff} = effective charge (Nuclear charge + charge of inner core electrons)
2. Δ_{nl} = the QUANTUM DEFECTS

Properties of quantum defects

In general the Δ_{nl} are positive. To a good approximation they depend only on l

$$\Delta_{nl} \to \Delta_l \tag{16}$$

For high l the quantum defects tend rapidly to zero.

EXAMPLE. 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

Quantum defects can be found by fitting the formula to well established spectroscopic data. These results can then be used to calculate quantum defects for energy levels where no experimental data is available and also to obtain other atomic parameters, such as scattering data.

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'. Instead of Eq. (15) we have:

$$E_{nl} = -\frac{(Z - \sigma_{nl})^2}{2n^2} = -\frac{(Z^*)^2}{2n^2} \tag{17}$$

where σ_{nl} is the SCREENING CONSTANT. N.B. In Eq. (15), 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 INDISTINGUISHABLE PARTICLES

Consider a system of 2 identical particles. If the particles are indistinguishable, then, since the probability densities must be the same

$$|\Psi(1,2,t)|^2 = |\Psi(2,1,t)|^2 \ , \tag{18}$$

where 1 stands for $\underline{r}_1, s_{1z}$ and 2 for $\underline{r}_2, s_{2z}$, and $\underline{r}$ is the spatial coordinate and s_{1z}, s_{2z} are the spin components along the z-axis.

So either the **wavefunction is symmetric** with respect to exchange of particles:

$$\Psi(1,2,t) = \Psi(2,1,t) \ , \tag{19}$$

OR it is **antisymmetric** with respect to exchange of particles:

$$\Psi(1,2,t) = -\Psi(2,1,t) \ . \tag{20}$$

3.3.2 THE PAULI EXCLUSION PRINCIPLE (PEP)

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 fulfil the condition that no two electrons can be in the same quantum state, specified by n, l, m_l, and m_s.

A two-electron **spatial wavefunction** which is **anti-symmetric** is:

$$\phi_-(1,2) = \frac{1}{\sqrt{2}}[\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)] = -\Psi(2,1) \ . \tag{21}$$

where a and b stand for a given set of n, l, m_l, and m_s. However, if $\phi_b = \phi_a$ then $\Psi(1,2) = 0$ and PEP respected. $\phi_a(i)$ and $\phi_b(i)$ are normalized eigenfunctions of the system. A two-electron **spatial wavefunction** which is **symmetric** is:

$$\phi_+(1,2) = \frac{1}{\sqrt{2}}[\phi_a(1)\phi_b(2) + \phi_a(2)\phi_b(1)] = \Psi(2,1) \ . \tag{22}$$

THE HELIUM ATOM

He has two electrons so the wavefunctions must be **antisymmetric overall** with respect to exchange of the electrons:

$$\Psi(1,2) = \Phi(\underline{r}_1, \underline{r}_2)\ \chi(s_{1z}, s_{2z}) = -\Phi(\underline{r}_2, \underline{r}_1)\ \chi(s_{2z}, s_{1z}) \ . \tag{23}$$

The χ are normalized 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 $\hat{S}_z = \hat{S}_{1z} + \hat{S}_{2z}$ its z component.

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

$$\hat{S}_z\alpha = +1/2\alpha \tag{24}$$

OR

$$\hat{S}_z\beta = -1/2\beta \ . \tag{25}$$

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 it is the eigenvalue of:

$$\hat{S}^2\chi(s_{1z}, s_{2z}) = S(S+1)\hbar^2\chi(s_{1z}, s_{2z}) \ . \tag{26}$$

The value of $2S+1$ is termed the **SPIN MULTIPLICITY**,

For 0 we get $2S+1 = 1 \rightarrow$ singlet,

For 1/2 we get $2S+1 = 2 \rightarrow$ doublet

For 1 we get $2S+1 = 3 \rightarrow$ triplet

SPIN WAVEFUNCTIONS IN HELIUM ATOM

We have TRIPLET:

$$\chi(1,2) = \begin{cases} \alpha(1)\alpha(2) & \chi^T(M_s=1)\ \uparrow\uparrow \\ \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)+\alpha(2)\beta(1)\right] & \chi^T(M_s=0)\ \uparrow\downarrow + \downarrow\uparrow \\ \beta(1)\beta(2) & \chi^T(M_s=-1)\ \downarrow\downarrow \end{cases} \tag{27}$$

or SINGLET

$$\chi(1,2) = \frac{1}{\sqrt{2}}\left[\alpha(1)\beta(2)-\alpha(2)\beta(1)\right] \qquad \chi^S(M_s=0)\ \uparrow\downarrow - \downarrow\uparrow\ . \tag{28}$$

Then:

$$\begin{aligned} \hat{S}^2\chi^T_{M_s} &= 2\hbar^2\chi^T_{M_s} \Rightarrow S=1 && (29) \\ \hat{S}_z\chi^T_{M_s} &= \hbar M_s\chi^T_{M_s} \Rightarrow M_s=-1,0,1\ , && (30) \end{aligned}$$

AND

$$\begin{aligned} \hat{S}^2\chi^S_{M_s} &= 0\ \chi^S_{M_s} \Rightarrow S=0 && (31) \\ \hat{S}_z\chi^S_{M_s} &= 0\ \chi^S_{M_s} \Rightarrow M_s=0\ . && (32) \end{aligned}$$

So, for two electrons, we have four possible spin eigenstates with

$$(S,M_s) = (1,1), \quad (1,0), \quad (1,-1) \qquad \text{SYMMETRIC}$$

or

$$(S,M_s) = (0,0) \qquad \text{ANTI-SYMMETRIC}$$

TOTAL WAVEFUNCTION OF HE

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

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

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 ALSO be a singlet ($S=0$).

3.4 EXCHANGE

The spin-dependent properties of the wavefunction give rise to interactions for which there is no classical analogue, called EXCHANGE. Consider case of the singlet and triplet from the same configuration of electrons, e.g., 1s 2s in helium. The contribution from the e^-– e^- repulsion is:

$$I = < \frac{1}{r_{12}} > = \int \Psi^*(1,2)\frac{1}{r_{12}}\Psi(1,2)d\tau d\sigma \ , \tag{33}$$

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

(a) **Singlet case:**

$$I \ = \ \int\int \phi_+^* \chi^{S*}\left[\frac{1}{r_{12}}\right]\phi_+\chi^S d\tau d\sigma. \tag{34}$$

Since $1/r_{12}$ does not act on spin, we can separate the integrals:

$$\begin{aligned} I &= \frac{1}{2}\int \{\phi_a(1)\phi_b(2)+\phi_a(2)\phi_b(1)\}^* \\ &\times \underbrace{\frac{1}{r_{12}}\{\phi_a(1)\phi_b(2)+\phi_a(2)\phi_b(1)\}\,d\tau}_{\text{Spatial}} \\ &\times \frac{1}{2}\ \underbrace{\int \{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}^*\{\alpha(1)\beta(2)-\alpha(2)\beta(1)\}\,d\sigma}_{\text{Spin integral = 1 since spin function is normalized}} \\ &= \underbrace{\int\frac{|\phi_a(1)|^2|\phi_b(2)|^2}{r_{12}}d\tau}_{\text{Coulomb integral gives repulsion between two charge clouds}} + \underbrace{\int\frac{\phi_a^*(1)\phi_b^*(2)\phi_a(2)\phi_b(1)}{r_{12}}d\tau}_{\text{Exchange integral has no classical analogue—arises from Pauli Principle}} \\ &= \quad C \quad + \quad E \end{aligned} \tag{35}$$

Note: we have two times two terms in integrand differing only by the labels. These will integrate to same result, so cancel 1/2. Both C and E are repulsive, **exchange interaction is repulsive** and the overall effect will be to make the state less tightly bound, than when the $\frac{1}{r_{12}}$ term is not included.

(b) **Triplet case:**

Consider the $\alpha(1)\alpha(2)$ component, i.e. $\uparrow\uparrow$.

$$\begin{aligned} I &= \int \frac{1}{\sqrt{2}} \left\{\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)\right\}^* \left\{\alpha(1)\alpha(2)\right\}^* \frac{1}{r_{12}} \\ &\times \frac{1}{\sqrt{2}} \left\{\phi_a(1)\phi_b(2) - \phi_a(2)\phi_b(1)\right\} \left\{\alpha(1)\alpha(2)\right\} d\sigma d\tau \ . \end{aligned} \tag{36}$$

As before, we can separate that spatial and spin parts and use,

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

so

$$\begin{aligned} I &= \int \frac{|\phi_a(1)|^2|\phi_b(2)|^2}{r_{12}} d\tau \ - \ \int \frac{\phi_a^*(1)\phi_b^*(2)\phi_a(2)\phi_b(1)}{r_{12}} d\tau \\ &= \qquad C \qquad\qquad - \qquad\qquad E \end{aligned} \tag{37}$$

The exchange part is now negative, **exchange is attractive**, it decreases the overall repulsion between the electrons and the state is more tightly bound than the singlet state. Can be qualitatively understood by considering the antisymmetric spatial wavefunction which vanishes when $\underline{r_1} = \underline{r_2}$ so that on average the electrons are further apart and each one 'screens' the nucleus less for the other one, resulting in a more tightly bound state.

So we have different energy level for singlet (Parahelium) and triplet (Orthohelium) states (see energy levels in figure 3.1).

3.5 CONFIGURATIONS AND TERMS

3.5.1 CONFIGURATIONS

configurations and spectroscopic notation

- 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).

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*.

See figure 3.2 for Periodic Table. See Brehm and Mullin or other books for the configurations of the atoms and discussion on their behaviour.

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. Note to remove a second electron, after having removed one, will require more energy than to remove the first one. See figure 3.3 for Ionization Energy versus Z.

3.5.2 TERMS

Configurations of He split into singlet ($S = 0$) or triplet ($S = 1$) terms, depending on the TOTAL spin quantum number. Also split into terms according to the value of the TOTAL ORBITAL ANGULAR MOMENTUM quantum number L, with

$$\underline{\hat{L}} = \sum_i \underline{\hat{L}}_i \tag{38}$$

where $\underline{\hat{L}}_i$ is the orbital angular momentum of the i th electron. The total orbital angular momentum quantum number, L, and and the total spin angular momentum quantum number, S. are good quantum numbers

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 (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,

$$\underline{\hat{S}} = \sum_i \underline{\hat{S}}_i = 0 \; ; \qquad \underline{\hat{L}} = \sum_i \underline{\hat{L}}_i = 0 \; , \tag{39}$$

where these sums are over the electrons in the sub-closed shells ONLY (consider the vector addition of the operators). So when we work out S or L we need only consider electrons outside sub-closed shells, i.e., the valence or optically active electrons.

- **2 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 $\underline{\hat{L}}_1, \underline{\hat{S}}_1$ and $\underline{\hat{L}}_2, \underline{\hat{S}}_2$ and the **total orbital angular momentum** is

$$\underline{\hat{L}} = \sum_{i=1,2} \underline{\hat{L}}_i, \tag{40}$$

with

$$\begin{aligned} L &= |\sum_i l_i|_{min} \rightarrow |\sum_i l_i|_{max} \qquad \text{(in steps of 1)} \\ & \quad |l_1 - l_2|, |l_1 - l_2| + 1, \ldots, l_1 + l_2 - 1, l_1 + l_2. \end{aligned} \tag{41}$$

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

The **total spin angular momentum** is

$$\underline{\hat{S}} = \sum_{i=1,2} \underline{\hat{S}}_i \tag{42}$$

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

$$\begin{aligned} S &= |\sum_i s_i|_{min} \rightarrow |\sum_i s_i|_{max} \qquad \text{(in steps of 1)} \\ & \quad |s_1 - s_2|, |s_1 - s_2| + 1, \ldots, s_1 + s_2 - 1, s_1 + s_2. \end{aligned} \tag{43}$$

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

- **2 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 $m_s = \pm 1/2$.

There are 24 possible combination of these quantum numbers (see figure 3.4a) but:

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

ii) Two 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.

As shown in figure 3.4b there are only **15 possible states** left. The important point here is the way you order them so as to find the terms which turn out to be ^{1}S, ^{3}P , ^{1}D (see figure 3.4b).

3.5.3 HUND'S RULES FOR ORDERING TERMS

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:

- The term with the largest value of S has the lowest energy. The energy of other terms increases with decreasing S.
- 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 in above we have the following ordering:

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

3.6 THE SPIN-ORBIT INTERACTION

3.6.1 LEVELS SPLITTING

Terms split into levels because of SPIN-ORBIT Interaction. The atomic Hamiltonian may be written:

$$\hat{H}_{tot} = \hat{H} + \hat{H}_{\text{SO}} \tag{44}$$

where

$$\hat{H} = \sum_i \left(-\frac{1}{2}\nabla_i^2 - \frac{Z}{r_i}\right) + \sum_{\substack{i,j \\ i>j}} \frac{1}{r_{ij}} \tag{45}$$

is the multi-electron Hamiltonian. We shall show below that

$$\hat{H}_{\text{SO}} = A(L,S)\underline{\hat{L}} \cdot \underline{\hat{S}} \tag{46}$$

is the Spin-Orbit term and represents a small energetic perturbation relative to $\hat{H}$ and $A(L,S)$ is a constant.

An electron moving in a circular Bohr orbit (of radius r around a fixed nucleus) acts like a current loop and so is associated with a 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 QM they are operators and that the vector approach is just there to help us visualize things.

3.6.2 MAGNETIC MOMENTS

The magnetic moment $\underline{\mu}_X$ and the general angular momentum, $\underline{X}$, of an arbitrary rotating body with mass M, and charge Q, always satisfy a relation of the form:

$$\underline{\mu}_X = g_X \frac{Q}{2M} \underline{X}\ , \tag{47}$$

where g_X is the so-called **GYROMAGNETIC or 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:

$$\underline{\tau} = \frac{d\underline{X}}{dt} = \underline{\mu}_X \times \underline{B} = g_X \frac{Q}{2M} \underline{X} \times \underline{B}. \tag{48}$$

So $\underline{\tau}$ is perpendicular to $\underline{X}$ and $\underline{B}$ and results in a precession of $\underline{X}$ around $\underline{B}$ (see figure 3.7).

We define the **Larmor precession frequency**

$$\omega = g_X \frac{Q}{2M} B \qquad \rightarrow \qquad \underline{\tau} = -\underline{\omega} \times \underline{X} \tag{49}$$

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

$$V = -\underline{\mu}_X . \underline{B}_{int} \tag{50}$$

note there was an error in the lectures in this eq.

For a current loop produced by a *negative* charge, $\underline{\mu}_L$ is <u>OPPOSITE</u> to $\underline{L}$, i.e.,

$$\underline{\mu}_L = -\frac{e}{2m} \underline{L} \ . \tag{51}$$

See figure 3.5 and standard text book for derivation. From Eqs (51) and (47) we identify the <u>ORBITAL</u> g-factor:

$$g_L = 1 \ . \tag{52}$$

Expressing <u>L</u> in units of $\hbar$, we obtain,

$$\underline{\mu}_L = -g_L \mu_B \frac{\underline{L}}{\hbar} \qquad \text{(with } g_L = 1) \ , \tag{53}$$

where μ_B is the <u>BOHR MAGNETON</u>:

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

Now, for the <u>**spin**</u>: analogous to Eq. (47), we can introduce a spin magnetic moment associated with the intrinsic angular momentum of the electron:

$$\underline{\mu}_S = -g_S \mu_B \frac{\underline{S}}{\hbar} \ , \tag{54}$$

where g_S is the <u>SPIN</u> g-factor and, from Dirac's relativistic quantum theory (where spin properly belongs) of the electron interacting with a magnetic field, we have $g_S = 2$.

3.6.3 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 e$^-$ 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 which will produce a magnetic field at the instantaneous location of the e$^-$ (see figure 3.6).

From the Biot-Savart Law:

$$\underline{B}_{int} = \frac{\mu_0}{4\pi}\frac{Ze(-\underline{v}) \times \underline{r}}{r^3}. \tag{55}$$

The Coulomb field of the nucleus is

$$\underline{E} = \frac{1}{4\pi\epsilon_0}\frac{Ze\underline{r}}{r^3} \tag{56}$$

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

$$\underline{B}_{int} = \frac{-\underline{v} \times \underline{E}}{c^2} \tag{57}$$

We can also relate $\underline{B}_{int}$ to $\underline{L}$, using $\underline{L} = m\underline{r} \times \underline{v}$,

$$\underline{B}_{int} = \frac{\mu_o Ze}{4\pi}\frac{\underline{r} \times \underline{v}}{r^3} = \frac{Ze}{4\pi\epsilon_0}\frac{\underline{L}}{mr^3c^2}. \tag{58}$$

Note: Change of sign from change of order, used $\mu_0\epsilon_0 = \frac{1}{c^2}$.

So in the case of the 'spinning' electron interacting with the magnetic field due to its orbital motion we have the **spin-orbit interaction**

$$V_{\mathrm{SL}} = -\underline{\mu}_S.\underline{B}_{int} \tag{59}$$

$$= \frac{Ze^2}{4\pi\epsilon_0}\left(\frac{\underline{S}.\underline{L}}{m^2r^3c^2}\right) \tag{60}$$

using the definition of the Bohr magneton and 58.

In the reference frame where the nucleus is at rest an additional factor, called the Thomas Factor =1/2, arises due to the fact that the e$^-$ is in an accelerated orbital motion. The nucleus sees the set of axis in which the e^- is instantaneously at rest as precessing relative to its own set - Thomas frequency (see figure 3.8).

So the **final form of the spin-orbit interaction** is

$$V_{\mathrm{SL}} = \frac{Ze^2}{4\pi\epsilon_0}\left(\frac{\underline{S}.\underline{L}}{2m^2r^3c^2}\right) \tag{61}$$

which can be written in terms of the dimensionless quantity called the **fine structure constant:** α (see part 1), as

$$V_{\mathrm{SL}} = Z\alpha\frac{\hbar}{2m^2c}\left(\frac{\hat{\underline{S}}.\hat{\underline{L}}}{r^3}\right) \tag{62}$$

Note that the energy depends on the scalar product of $\hat{\underline{S}}$ and $\hat{\underline{L}}$ and therefore on their relative orientation. We have reintroduced the operator notation and see the two vector-operators are now coupled together and no longer have fixed z components! However, the total angular momentum $\hat{\underline{J}} = \hat{\underline{L}}+\hat{\underline{S}}$, has a fixed z component.

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

A) The one-electron case.

$$\hat{\underline{J}} = \hat{\underline{L}} + \hat{\underline{S}} \qquad \text{and} \qquad \hat{J}_z = \hat{L}_z + \hat{S}_z\ . \tag{63}$$

The eigenvalue eqs. are now

$$\hat{\underline{J}}^2\Psi = j(j+1)\hbar^2\Psi \qquad \text{and} \qquad \hat{J}_z\Psi = m_j\hbar\Psi \tag{64}$$

$j = |l-s|, \ldots, |l+s|$ 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.

$$\Psi_{n,l,m_l,m_s} \rightarrow \Psi_{n,l,j,m_j}$$

See figure 3.9.

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

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.

The **2p state of H is split** because of the spin-orbit interaction into two levels, $2^2\mathrm{p}_{1/2}$ and $2^2\mathrm{p}_{3/2}$, depending on the value of j. Such a splitting of a state due to the spin-orbit interaction is called the **fine structure**.

B) The multi-electron case.

We have the eigenvalue eqs.

$$\hat{\underline{J}}^2\Psi = J(J+1)\hbar^2\Psi \qquad \text{and} \qquad \hat{J}_z\Psi = M_J\hbar\Psi. \tag{65}$$

We now label each **energy level** with spectroscopic notation $n^{2S+1}L_J$ but J can now be obtained in two different manners.

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, $\sum_i \hat{\underline{S}}_i = \hat{\underline{S}}$, to give total spin quantum number S.

- Combine all individual orbital angular momenta, $\sum_i \hat{\underline{L}}_i = \hat{\underline{L}}$, to give total orbital angular momentum quantum number L.

- Then combine the quantum numbers L and S to give J as

$$J = |L-S|, |L-S+1|, \ldots, |L+S-1|, |L+S|. \tag{66}$$

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

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

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

- When the subshell is half full there is no multiplet splitting.

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 $\underline{\hat{J}}$,

$$\underline{\hat{J}} = \sum_i \underline{\hat{J}}_i. \tag{67}$$

The total angular quantum number is then

$$J = |\sum_i j_i|_{min} \to |\sum_i j_i|_{max} \qquad \text{in steps of one} \tag{68}$$

where

$$j_i = l_i + s_i. \tag{69}$$

Note: Neither LS or jj coupling describe perfectly the total angular momentum especially for medium Z atoms (see figure 3.10).

3.6.5 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**

$$\Delta E_{\rm SL} = \int \Psi_{n,l,j,m_j} V_{SL} \Psi_{n,l,j,m_j} d\tau \ . \tag{70}$$

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

$$\underline{\hat{J}}^2 = (\underline{\hat{L}} + \underline{\hat{S}})^2 = \underline{\hat{L}}^2 + \underline{\hat{S}}^2 + 2\underline{\hat{L}} \cdot \underline{\hat{S}} \tag{71}$$

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. 70 we get for the **one-electron case**

$$\Delta E_{\mathrm{SL}} = \frac{1}{2} A(l,s)\left[j(j+1) - l(l+1) - s(s+1)\right] \tag{72}$$

and $\underline{A(l,s) \text{ is a constant containing } < 1/r^3 > \text{ and is } \propto Z^4.}$

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

$$\Delta E_{\mathrm{SL}} = \frac{1}{2} A(L,S)\left[J(J+1) - L(L+1) - S(S+1)\right] \tag{73}$$

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

$$\Delta E_{\mathrm{SL}}(J) - \Delta E_{\mathrm{SL}}(J-1) = A(L,S)J \tag{74}$$

THE LANDÉ INTERVAL RULE

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

3.6.6 PARITY

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

$$\Psi(\underline{r}_1, \underline{r}_2, \ldots, \underline{r}_N) = \pm\Psi(-\underline{r}_1, -\underline{r}_2, \ldots, -\underline{r}_N)\ . \tag{75}$$

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:

$$(-1)^{l_1}(-1)^{l_2}(-1)^{l_3}...(-1)^{l_N} = (-1)^{\sum l_i}\ . \tag{76}$$