ATOMIC SPECTROSCOPY NOTES

Expected: knowledge of Quantum + Perturbation Theory: calculating eigenfunctions that are difficult by using:

$$\hat{H} = H_o + H'$$

where H' is a perturbation on H_o (zeroth order wavefunction). 1st Order:

$$E = E_o + \langle H' \rangle$$

Angular Momentum –

Measure of torque required to stop a body rotating.
Single particle: l = r^p, where l is vector perpendicular to plane of rotation.

$$| l^2 | = l_x^2 + l_y^2 + l_z^2$$

$$l_z = -i\hbar\frac{\partial}{\partial\phi} = \frac{\hbar}{i}[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial z}]$$

$$l^2 = -\hbar^2 \Lambda^2 \qquad \Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}$$

Commutation –

$$[\, l^2, l_z \,] = [\, l^2, l_x \,] = [\, l^2, l_y \,] = 0$$

$$[\, l_x, l_y \,] = i\hbar l_z \qquad [\, l_y, l_z \,] = i\hbar l_x \qquad [\, l_z, l_x \,] = i\hbar l_y$$

Electrons in atoms:

$$[\, l^2, H \,] = 0 \text{ and } [\, l_z, H \,] = 0$$

Thus, energy, square of orbital angular momentum and one of its components can all be simultaneously specified (eigenvalues).

Hydrogenic (1e) Atoms –

$$[\frac{-h^2}{2\mu}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_o r}]\psi = E\psi$$

Spherical Symmetry ➔ polar coordinates preferred.

Boundary Conditions,

ψ finite for all r (including origin).
$\psi \to 0$ as $r \to \infty$.
$\psi(r,\theta,\phi) = \psi(r, [\theta+2n\pi], [\phi+2m\pi])$ n, m integers.

Separate,

$\psi = R(r)\, Y(\theta,\phi)$ Radial and Angular components

Solutions as,

$$\psi_{n,l,ml} = R_{n,l}(r)\, Y_{l,\,ml}(\theta, \phi)$$

Quantisation,

$$E = \frac{-\mu e^4 z^2}{32\pi^2 {\varepsilon_o}^2 \hbar^2 n^2} = \frac{-RhcZ^2}{n^2}$$

$$where\ R = \frac{\mu e^4}{8{\varepsilon_o}^2 h^3 c},\ n = 1,2,3...$$

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Solving,

$$\frac{-\hbar^2}{2\mu}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}r\right]R(r)Y(\theta,\phi) - \frac{\hbar^2}{2\mu}\left[\frac{R(r)}{r^2}\Lambda^2 Y(\theta,\phi)\right]$$
$$+ V(r)R(r)Y(\theta,\phi) = ER(r)Y(\theta,\phi)$$
$$\left(\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right)$$

Only Λ^2 can change $Y(\theta,\phi)$ variables, therefore for a valid solution it is implied that this does not happen, i.e.

$$\Lambda^2 Y(\theta,\phi) = C\,Y(\theta,\phi) \qquad [\,C = \text{constant}\,]$$

Make substitution to remove angular parts:

$$\frac{-\hbar^2}{2\mu}\left[\frac{1}{r}\frac{\partial^2}{\partial r^2}rR(r) + \frac{C}{r^2}R(r)\right] + V(r)R(r) = ER(r) \qquad \textcircled{A}$$

Angular ψ identical to particle on a sphere, i.e.

$$\psi(\theta,\phi) = \Theta(\theta)\,\Phi(\phi) \qquad \textcircled{0}$$

Treat θ as constant,

$$\frac{d^2}{d\phi^2}\Phi(\phi) = (\text{const})\,\Phi(\phi) \qquad \textcircled{1}$$

This is a particle on a ring,

$$\Phi(\phi) = A e^{iM\phi} + B e^{-iM\phi} \qquad \textcircled{2}$$

Subbing 2 into 1,

$$\frac{d^2}{d\phi^2}\Phi(\phi) = -M^2\Phi(\phi)$$
(eigenfunction)

Choose A = $^1/_{\sqrt{2\pi}}$ and B = 0 (Normalised).

Subbing in (1) & (2) into (0):

$$\left[-\frac{M^2}{\sin^2\theta} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta}\right]\Theta(\theta) = C\,\Theta(\theta)$$

Solve to give Associated Legendre Functions. Boundary Condition gives rise to l quantum numbers.

$$Y_{l,m}(\theta,\phi) \qquad (\text{spherical harmonic})$$
$$\Lambda^2 Y_{l,m} = -l(l+1)Y_{l,m}$$
$$C = -l(l+1).$$

Sub this into A and let P(r) = r[R(r)]:

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + V_{eff}\right]P(r) = EP(r) \qquad \textcircled{3}$$
Radial Equation

$$V_{eff} = \frac{-Ze^2}{4\pi\varepsilon_0 r} + l(l+1)\frac{\hbar^2}{2\mu r^2}$$

V_{eff} – effective potential energy ➔ true V + correction for centrifugal E(l).
Solve (3) as R(r) → 0, r → ∞ and R(r) finite.

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Quantum Numbers –

1) Principle Quantum Number, n.

Determines energy. Determines mean radius of electron orbital. For l = 0,

$$\langle r \rangle = \frac{3}{2} a_0 \frac{n^2}{Z}$$

$$a_0 = \text{Bohr Radius}, \quad \frac{4\pi\varepsilon_0\hbar^2}{m_e e^2}$$

2) Orbital Angular Momentum, l

Determines "shapes" – angular distribution. Angular momentum.

$$\langle \underline{L}^2 \rangle^{1/2} = [l(l+1)]^{1/2}\hbar$$

L is a vector of length $[\, l(l+1) \,]^{1/2} \hbar$, where l has integral values o → n-1.
Electrons with different l have different radial wavefunctions, because of centrifugal effect.

3) Magnetic Quantum Number, m_l

Projection of orbital angular momentum on a given axis ➔ Direction of orbital.

$$\langle l_z \rangle = m_l\hbar$$

m_l takes values –l, -l+1, …, +l
i.e. (2l+1) values in total.

Eigenvalues and Eigenfunctions

For H atom, E is independent of l and m_l. Note: for p orbitals, l = 1. p_x, p_y, $p_z \neq m_l = 0, \pm 1$.

$$\psi_{p_x} = \frac{1}{\sqrt{2}}\left[\,|n, l=1, m_l=-1\rangle - |n, l=1, m_l=+1\rangle\,\right]$$

$$\psi_{p_y} = \frac{i}{\sqrt{2}}\left[\,|n, l=1, m_l=+1\rangle + |n, l=1, m_l=-1\rangle\,\right]$$

Real linear combinations:

$$\psi_{pz} = |\, n, l=1, m_l=0 \,\rangle$$

For degenerate orbitals, any linear combination is a solution of the Schrodinger Equation.

Solutions to the Schrodinger Equation (1 electron)

$$E = \frac{hcRZ^2}{n^2}, \quad \psi_{n,l,m_l} = R_{nl}(r)\, Y_{l m_l}(\theta,\phi)$$

R almost constant (depending on atomic number).
$Y_{l,\, ml}(\theta,\phi)$ – complex, but independent of n.
$R_{nl}(r)$ – near nucleus varies as r^l, but large distances varies as exp [- Zr/na_o]

Spectrum of a Hydrogen Atom

Experimental – low pressure electric discharge in H_2

- accelerated electrons / ions cause dissociation, ionisation and excitation.
- Electron / proton recombination also important.

Light emitted by excited H atoms analysed by spectrometer. Observe distinct series:

	Lyman (UV)	Balmer (vis)	Paschen (IR)
Emit down to:	n=1	n=2	n=3

(in absorption observe Lyman only).

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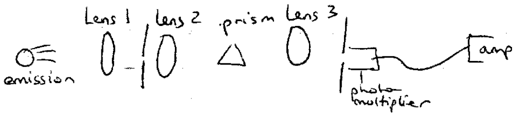
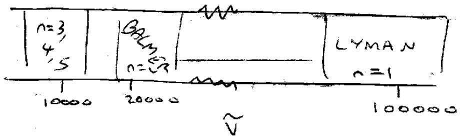




Transition Energies:

$$\Delta E = +hcRZ^2\left(\frac{1}{n^2_{lower}} - \frac{1}{n^2_{upper}}\right)$$

Wavenumber, v = ΔE/hc. $v = RZ^2\left(\frac{1}{n''^2} - \frac{1}{n'^2}\right)$

Note the dependence on R, and also the slight isotope dependence of R.

He$^+$ -

$$\tilde{\nu} = 4R\left(\frac{1}{n^2} - \frac{1}{m^2}\right)$$

If n, m even

$$\tilde{\nu} = 4R\left(\frac{1}{(\frac{n}{2})^2} - \frac{1}{(\frac{m}{2})^2}\right) \Rightarrow$$ appears like H lines.

Selection Rules – which transitions are allowed.

Δ**n** = anything integral. Δ**l** = ±1. Δ**m$_l$** = 0, ±1.

This comes from:

$$\int \underset{upper}{\psi'^*}\,\hat{\mu}\,\underset{lower}{\psi''}\,d\tau \neq 0$$ (i.e. totally symmetric)

$\hat{\mu}$ – dipole moment operator [E of radiation interaction $\hat{H} = \hat{H}_0 + \mu E$ $(\mu = -e.r)$]

Consider symmetry wrt inversion:

x,y,z → -x,-y,-z

$\hat{\mu}$ is $\textcircled{a}$

ψ is $\textcircled{s}$ for $l = 0, 2, 4 \ldots$

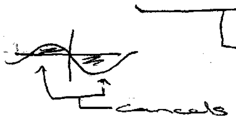
ψ is $\textcircled{a}$ for $l = 1, 3, 5 \ldots$

Integral:

$l_{even} \longleftrightarrow l_{even}$ $\quad \textcircled{s} \times \textcircled{a} \times \textcircled{s} = \textcircled{a}$ $\quad$ ZERO

$l_{odd} \longleftrightarrow l_{even}$ $\quad \underbrace{\textcircled{a} \times \textcircled{a} \times \textcircled{s}}_{} = \textcircled{s}$ $\quad$ NON-ZERO

$\textcircled{s} \Rightarrow$



Integrand must be $\textcircled{s}$ ∴

$\psi' \times \psi'' \Rightarrow \textcircled{a}$

∴ Δl = odd.

$\Delta l = \pm 1$ (not ±3: photon angular momentum only ±ħ)

Electron Spin –

Inferred empirically from very high resolution spectra.

- splittings due to extra degree of freedom.
- Intrinsic angular moment of electron "spin".
- Quantum number s = ½ only.

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<u>Spin Angular Momentum =</u>

$$\sqrt{s(s+1)}\hbar = \frac{\sqrt{3}}{2}\hbar$$

$$\text{OR} \quad \hat{s}^2 \psi_{spin} = s(s+1)\hbar^2 \psi_{spin}$$

$$\text{Spin projection, } m_s = \hat{s}_z \psi_{spin} = m_s \hbar \, \psi_{spin}$$

<u>Degeneracy –</u>

For each n → n values of l, l = 0, 1, … (n-1)
For each l → (2l+1) values of m_l, m_l = -l, -l+1, … +l.
Implies total degeneracy of n^2 for each. Including spin ➔ $2n^2$ degenerate.

Spin-Orbit Coupling

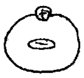
Spin possesses a magnetic moment.

$$\underline{m}_{spin} = g_e \gamma_e \underline{s} = -g_e \frac{\mu_B}{\hbar} \cdot \underline{s}$$

$$\hookrightarrow \text{gyromagnetic ratio, } = \frac{-e}{2m_e}$$

$$\mu_B = \text{Bohr Magneton, } = \frac{e\hbar}{2m_e}$$

$$g_e = 2.002\ldots \text{ (twice expected)}$$



$m_l = \gamma_e l$
$m_s = 2\gamma_e s$
$E = -m_s B$

Orbiting electron creates a magnetic field “seen” by the electron spin. Field due to relative motion of charges – nucleus orbits electron!
Causes coupling of l and s to give total electronic angular momentum, j = l + s.
j^2, j_x^2, j_y^2, j_z^2 – same commutation properties as *l* equivalent.

$$j^2\psi = j(j+1)\hbar^2\psi$$
$$j_z\psi = m_j\hbar\psi$$

For one-electron case, j is half-integral = l ± ½. m_j takes values j, j-1, … -j, i.e. (2j+1) degenerate.

$$\frac{E_{so}}{hc} = \frac{1}{hc}\langle H_{so}\rangle = \frac{\zeta_{nl}}{\hbar^2}\langle l.s\rangle \qquad \zeta_{nl} = \frac{\alpha^2 R Z^4}{n^3 l(l+\frac{1}{2})(l+1)}$$

R = Rydberg,
α = fine structure, $\alpha = \frac{e^2}{4\pi\varepsilon_0\hbar c}$

< l.s > is evaluated using j = l + s, $j^2 = l^2 + s^2 + l.s$

$$\therefore \frac{E_{so}}{hc} = \frac{1}{2\hbar^2}\langle \zeta(j^2 - l^2 - s^2)\rangle$$
$$= \frac{1}{2\hbar^2}\zeta\left[\langle j^2\rangle - \langle l^2\rangle - \langle s^2\rangle\right]$$
$$= \frac{1}{2}\zeta\left[j(j+1) - l(l+1) - s(s+1)\right]$$

<u>Term Symbols</u>

$^{2S+1}L_j$, e.g. 3d ➔ $^2D_{5/2}$, $^2D_{3/2}$

Spectrum Including S-O Coupling

New selection rules –

ΔJ = 0, ±1 $\qquad$ Δm_j = 0, ±1 $\qquad$ Δn = anything $\qquad$ Δl = ±1

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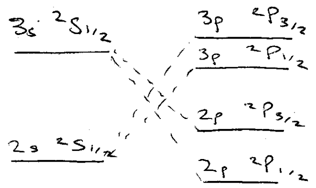
e.g.



Lamb Shift – quantum field effect. Also relativistic increase in mass with velocity.

Alkali Metals – many electron atoms

1e: $\Psi = \psi(x,y,z)\,\psi_{spin}$
$= \psi(x,y,z,m_s)$

2e: $\psi = \psi(x_1,y_1,z_1,(m_s)_1\;;\;x_2,y_2,z_2,(m_s)_2)$
6 spatial, 2 spin coordinates
(generally 3N spatial + N spin)

Schrodinger –

$$\Big[\underset{\substack{\uparrow\\\text{electron}\\\text{KEs}}}{\sum_i \frac{-\hbar^2}{2m_e}\nabla_i^2} + \underset{\substack{\uparrow\\\text{electron-}\\\text{nuclear}\\\text{attractions}}}{\sum_i V_{i,N}} + \underset{\substack{\uparrow\\\text{electron-}\\\text{electron}\\\text{repulsions}}}{\sum_{i\neq j} V_{i,j}}\Big]\psi = E\psi$$

Energies, E, include the energies of all electrons and all interactions:

$$V_{i,N} = \frac{-Ze^2}{4\pi\varepsilon_0 r_i} \quad ; \quad \underbrace{V_{i,j} = \frac{e^2}{4\pi\varepsilon_0 |\underline{r}_i - \underline{r}_j|}}_{\text{can no longer exactly solve S.E}}$$

Orbital Approximation –
Assume,

$$\Psi_{space}(r_1, r_2 .. r_n) = \underset{\substack{\uparrow\\\text{3D 1e wavefunction}}}{\phi_a(r_1)}\,\phi_b(r_2) \cdots \phi_z(r_n)$$

$$\Big[\frac{-\hbar^2}{2m_e}\nabla_i^2 + V_{iN} + \overset{\text{average repulsion over positions of all other electrons}}{\overline{\sum_{i\neq j} V_{ij}}}\Big]\phi(r_i) = \varepsilon_i\,\phi(r_i)$$

1e equation solved by numerical method using self-consistent field approach:

- each electron moves in an orbital in the average field of the other electrons.
- Energies = "orbital energies".

Not quite true, should obey Pauli Exclusion and be linear combination, e.g.

$$\phi_a(r_1)\,\phi_b(r_2) \pm \phi_a(r_2)\,\phi_b(r_1)$$

Total wavefunction has to be antisymmetric with respect to interchange of electron coordinates.

Self-Consistent Field Approach
Total Energy is not just sum of orbital energies, i.e. $\Sigma\varepsilon_i$ because e-e repulsion is counted twice.

$$E_{tot} = \sum_i \varepsilon_i - \Big\langle \sum_{i\neq j} V_{ij} \Big\rangle$$

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NB: as for H atom:

$$\Phi_a(r_i) = \underbrace{R_{nl}(r_i)}_{\text{non-Hydrogenic}} \underbrace{Y_{lm_l}(\theta_i,\phi_i)}_{\text{same, spherical harmonic}}$$

<u>Electron Configuration</u> – which orbitals occupied and how many electrons (Pauli).
Use orbital approximation.
Determine Ground State by Aufbau and Pauli Exclusion Principles

Li: $1s^2 2s^1$ Na: $1s^2 2s^2 2p^6 3s^1$

etc.

Spectra of Many Electron Atoms

Within Orbital Approximation, can only change orbital of 1 electron during transition, e.g.

$$1s^2 2s^2 2p^6 3s^1 \longrightarrow 1s^2 2s^2 2p^6 np^1$$
$$\not\longrightarrow 1s^2 2s^2 2p^5 nd^2$$

$$\underline{\mu} = \sum_i e\underline{r}_i \quad \text{(electric dipole operator)}$$

Main concern is valence electron excitation. Core electrons can be excited, but much higher energy (ionisation may occur).

<u>Selection Rules for Alkali Metals</u>

Closed shell core – no resultant spin or orbital angular momentum.
Alkali Metals ➔ pseudo-1s atom, so same selection rules as for Hydrogenics.

<u>Comparison with H-atom –</u>

1) different l-states of same n are non-degenerate, due to effects of e-e repulsion (penetration and shielding).
2) Bigger spin-orbit coupling (low resolution spectra ➔ observable).

<u>Penetration and Shielding –</u>

Effects of valence electron ↔ core electron repulsion.

Consider Li,
In $1s^2 3d$ excited configuration, 3d orbital is almost completely outside the core.

- experiences attraction to +3 nucleus
- but repulsion due to core electrons
- act like a -2 point charge “shielding”.

Net Effective Nuclear Charge ≈ +1.
In $1s^2 2s^1$ configuration, substantial penetration of 2s electron inside $1s^2$ core ➔ incomplete shielding, $Z_{eff} \approx +1.28$.
$1s^2 2p$ – 2p electron less penetrating. $Z_{eff} \approx +1.02$.
Therefore 2s electron is more tightly bound than 2p, therefore lower in energy.

NB: also 2s orbital in Li lower in energy than in H-atom. Same true for 2p, but not as different.
In general, ns < np < nd < nf, etc.

<u>Sodium Atom Spectrum</u>

1) 3s → 3p – lowest energy transition in absorption.

cf. H atom 3s and 3p approximately degenerate.

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2) Several series:
ns → 3p SHARP
np → 3s PRINCIPAL – also present in absorption
nd → 3p DIFFUSE
nf → 3d FUNDAMENTAL – almost same E as H-atom transitions

3) Spin-Orbit Splitting –
Same j states obtained as in H-atom but hydrogenic theory does not work.
Splittings larger. Increase with Z (not as rapidly as Z^4).
cf. spin-orbit coupling constants:

Li(2p)	$0.3\ \mathrm{cm}^{-1}$	H (2p)	$0.243\ \mathrm{cm}^{-1}$
Na (3p)	$17.2\ \mathrm{cm}^{-1}$	H (3p)	$0.072\ \mathrm{cm}^{-1}$
K (4p)	$57.7\ \mathrm{cm}^{-1}$	H (4p)	$0.031\ \mathrm{cm}^{-1}$

Quantum Defect –
For H-atom, $E = IE - hcR/n^2$
For alkali metals, effects of e-e repulsion means energies lower than predicted by Rydberg formula (above).

$$E_{nl} = IE - \frac{hcR}{\nu_{nl}{}^2}$$

Where ν_{nl} is effective principal quantum number.
Define the quantum defect,

$$\delta_{nl} = n - \nu_{nl}$$

$$E_{nl} = IE - \frac{hcR}{(n-\delta_{nl})^2}$$

For a given l, it turns out that δ_{nl} is almost independent of n → δ_l.

Electrons spend such short time close to the nucleus that its behaviour is almost independent of n. Therefore transition energies:

$$(nl \leftarrow n'l') = hcR\left[\frac{1}{(n'-\delta_{l'})^2} - \frac{1}{(n-\delta_l)^2}\right]$$

For a given series (common n' l'):

$$\Delta E = const - \frac{hcR}{(n-\delta_l)^2}$$

A plot of ΔE against $1/(n-\delta_l)^2$ gives straight line (adjust δ_l for best fit).

NB: Ionisation Energy = $\dfrac{hcR}{(n-\delta_l)}$ where nl is the lowest state.

Helium Atom

New Features – 2e in unfilled shells (except Ground State) → 2 sources of orbital and spin angular moment. New important effects on energy levels and degeneracies.

Orbital Angular Momentum –
Primarily concerned with configurations 1snl. Doubly excited states are unstable wrt ionisation.

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1s electron has $l = 0$, therefore total orbital angular momentum is the angular momentum of the excited electron, l. Total orbital angular momentum $L = l$.

Spin Angular Momentum –

Both electrons have $s = ½$, $m_s = ½$ or $-½$ (α or β).
Ground State ($1s^2$)
Pauli ➔ $m_{s1} = \pm ½$ and $m_{s2} = \mp ½$
Spin paired (antiparallel) ➔ "singlet" state.
Resultant $s = 0$, $m_s = 0$.

Excited Configurations, 1snl

- no restrictions on m_{s1}, m_{s2} from Pauli.
Spin Parallel ➔ resultant magnetic moment.
Spin Paired (opposed) ➔ no resultant magnetic moment.
Define total spin angular momentum, $S = s$.

$$|S| = \sqrt{(s(s+1))}\,\hbar.$$

- shows same commutation relationships as other angular momentum operators.
➔ quantisation.

$$\hat{S}^2 \psi_{spin} = s(s+1)\hbar^2 \psi_{spin}$$

S takes values $s_1+s_2, \ldots |s_1-s_2|$
$= 0$ or 1

S_z is quantised with eigenvalues M_s
$M_s = +S, \ldots, -S$
For $S = 1$; $M_s = 1, 0, -1$ triplet
$S = 0$; $M_s = 0$ only singlet

In general triplet state has lower energy than singlet state from same configuration.

Selection Rules –

New rule, $\Delta S = 0$.
Therefore singlet ↔ triplet is forbidden.

In Absorption:
Observe $1s^2$ ($^1S_0$) → 1snp (^1P)

In Emission:
Use discharge lamp – ionisation followed by recombination

$$He^+ + e^- \rightarrow He^* \rightarrow \text{emission}$$

Excited atoms formed in configurations.
1snl (^1L) or 1snl (^3L)
As $\Delta S = 0$, two sets of transitions observed.
Singlet ↔ singlet or triplet ↔ triplet.

1s electron shields outer electron from nucleus.
Penetration effects ➔ different l states have different energy.

$$ns < np < nd < nf \text{ etc.}$$

Spin-Orbit Coupling in many electron atoms –
$J = L + S$ ➔ J^2 and J_z quantised.

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Quantum Numbers:

$$J = L + S, \ldots, |L-S|$$
$$M_J = J, J-1, \ldots, -J.$$

NB: can only occur for triplet states in Helium.

e.g. $S = 1, L = 1 \rightarrow {}^3P$ “Term”

$J = 2,1,0 \rightarrow {}^3P_2, {}^3P_1, {}^3P_o$ “Level”

Additional Selection Rules:

$$\Delta J = 0, \pm 1 \qquad\qquad \Delta M_J = 0, \pm 1$$

NB: in He, spin-orbit interaction is very strong → very small splittings.

Spin Wavefunctions and Pauli Principle

For a 2e system:

$$\psi_{tot} = \underset{\substack{\downarrow \\ \text{6 coords}}}{\psi_{space}}\,\underset{\substack{\downarrow \\ \text{2 spin coords}}}{\psi_{spin}}$$

For Helium excited states, each electron can have $m_s = \pm \frac{1}{2}$ (represent ψ by α and β).
This suggests 4 possibilities:

$$\psi_1 = \alpha(1)\alpha(2) \quad \uparrow\uparrow \qquad \psi_2 = \beta(1)\beta(2) \quad \downarrow\downarrow$$
$$\psi_3 = \alpha(1)\beta(2) \quad \uparrow\downarrow \qquad \psi_4 = \beta(1)\alpha(2) \quad \downarrow\uparrow$$

ψ_3 and ψ_4 have $M_s = 0$.

Neither singlet nor triplet – electrons are indistinguishable.
Wavefunction must contain both possibilities with equal weighting. Two ways:

$$\psi^+ = \frac{1}{\sqrt{2}}(\psi_3 + \psi_4) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

$$\psi^- = \frac{1}{\sqrt{2}}(\psi_3 - \psi_4) = \frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

Equal probability of electron 1 or 2 being in spin state α or β.

Pauli Principle –

Total ψ must be antisymmetric wrt exchange of any 2 electrons (applies generally to all identical half-integral particles).
Therefore $\psi_{tot} = \psi_{space}\psi_{spin}$ = antisymmetric wrt interchange.

Consider spin, $\psi_1\psi_2\psi_\pm$

$$\underset{\substack{\uparrow \\ \text{exchange operator}}}{P_{12}}\psi_1 = P_{12}\alpha(1)\alpha(2) = \alpha(2)\alpha(1) = \psi_1$$

Similarly,

$$P_{12}\psi_2 = \psi_2$$
$$P_{12}\psi_\pm = P_{12}[\alpha(1)\beta(2) \pm \beta(1)\alpha(2)]/\sqrt{2}$$
$$= [\alpha(2)\beta(1) \pm \beta(2)\alpha(1)]/\sqrt{2}$$
$$= \psi_\pm$$
$$\therefore \psi_1, \psi_2, \psi^\pm \text{ are } \textcircled{s}$$

Hence, ψ_{space} must be antisymmetric.

e.g. 1s2s configuration with ψ_{spin} symmetric.

$$\psi_{space} = \frac{1}{\sqrt{2}}[\phi_{1s}(r_1)\phi_{2s}(r_2) - \phi_{2s}(r_1)\phi_{1s}(r_2)]$$

TRIPLET

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Conversely,

$$\psi^- \text{ is } ⓐ \Rightarrow \psi_{space}\ Ⓢ$$

$$\psi_{space} = \frac{1}{\sqrt{2}}\left[\phi_{1s}(r_1)\phi_{2s}(r_2) + \phi_{2s}(r_1)\phi_{1s}(r_2)\right]$$

SINGLET

NB: ψ_1, ψ_2, ψ^+ make up <u>triplet</u>
ψ^- is the <u>singlet</u>

Why is Triplet Lower in Energy than Singlet?

<u>"Fermi Hole"</u>
Probability of finding both electrons at same point in space.

$$\underline{r}_1 = \underline{r}_2 = \underline{r}$$

spatial

$$P(r_1, r_2) = P(r, r) = |\psi(r, r)|^2$$

For Triplet –

$$\psi(r_1, r_2) = -\psi(r_2, r_1)$$
$$\therefore \psi(r, r) = -\psi(r, r)$$

Zero probability – 2 electrons keep apart,
⇒ Fermi Hole at $r_1 = r_2$

For Singlet –

$$\psi(r_1, r_2) = \psi(r_2, r_1)$$
$\therefore P(r, r)$ can be non-zero.

Therefore for triplet state electrons must stay further apart ➔ less repulsion.

Not whole truth though, as in triplet state, 1s electron is less shielded, therefore nl orbital is slightly more compact than corresponding orbital in singlet state.

Angular Momentum Coupling in many electron atoms

General atom – more than 1e with both orbital and spin angular momentum.
e.g. C – $1s^2 2s^2 2p^2$. Excited states: $1s^2 2s^2 2p3d$, etc.

Configuration split into energy levels by 3 types of interaction –
a) spin correlation (couples spins, electrostatic).
b) Orbital electrostatic interaction.
c) Spin-Orbit Coupling (magnetic).
Pattern of energies, quantum numbers, etc – depend on which effect is largest.

Russell-Saunders Coupling (L-S Coupling)

(a) >~ (b) >> (c) – common for light elements.

a) Define $S = \Sigma s_i$ –sum of spin angular momenta.
e.g. $S = s_1 + s_2, \ldots |s_1 - s_2|$ for 2 electrons.

b) $L = \Sigma l_i$ – resultant orbital angular momentum.
e.g. $L = l_1 + l_2, l_1 + l_2 - 1, \ldots |l_1 - l_2|$

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Good quantum numbers L & S ➔ ψ_{tot} is eigenfunction of L^2 and S.
e.g. for a 2p 3d configuration:
$l_1 = 1$, $l_2 = 2$, ➔ L = 3,2,1 (F, D, P)
$s_1 = ½$, $s_2 = ½$ ➔ S = 1, 0.
➔ Terms are ^3F, ^1F, ^3D, ^1D, ^3P, ^1P.

Singlet-Triplet Splitting – due to spin correlation.
Splitting of different L values – due to different electrostatic repulsions (different orbitals).
For max L – electrons "orbit" in same direction.
For min L – electrons "orbit" in opposite directions (➔ more repulsions).

If spin-orbit interaction small – spin and orbital angular momenta couple → Total Angular Momentum J = L + S.
Hence Quantum Number J = L + S, L + S -1 …

e.g. ^3F: S=1, L=3 → J = 4,3,2.

Degeneracies –
Each state J is (2J+1) degenerate.
M_J = J, J-1, .. –J.
For 2p 3d configuration there are 60 states.

Lande Interval Rule –
Spin-orbit Hamiltonian, $H_{SO} = \sum_i J_i l_i s_i$

Approximate by hcA L.S

$$E/hc = \frac{1}{2} A\left[J(J+1) - L(L+1) - S(S+1)\right]$$

$$E(J+1) - E(J) = \frac{hcA}{2}\left[(J+1)(J+2) - J(J+1)\right] = hcA(J+1)$$
(same L & S values)

Terms from Configurations with Equivalent Open-Shell Electrons

e.g. for $2p^2$ configuration two equivalent 2p electrons.
Pauli Principle → restrictions
Would expect $l_1 = 1$, $l_2 = 1$, $s_1 = ½$, $s_2 = ½$.
➔ ^3D, ^1D, ^3P, ^1P, ^3S, ^1S.
In fact only get ^1D, ^3P, ^1S – why?

Microstates in decoupled representation

Consider 2p3d configuration again.
In limit when all couplings → 0, the defined quantum numbers would be:
l_1, m_{l1}, s_1, m_{s1}, l_2, m_{l2}, s_2, m_{s2}.
The 2p3d configuration would then be:
$(2l_1+1)(2s_1+1)(2l_2+1)(2s_2+1) = 3 \times 2 \times 5 \times 2$ = 60-fold degenerate.

NOTE: Couplings do not create any new states – they only lift degeneracies.

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Furthermore, number of states with given value of $m_{l1} + m_{s1} + m_{l2} + m_{s2}$ = # of states (in L-S coupling) with same value of m_J.

Returning to $2p^2$ configuration, consider possible microstates, can have situation with both electrons have same n, l, m_l – NOT ALLOWED

$m_{l_1}=1, m_{s_1}=\frac{1}{2}, m_{l_2}=1, m_{s_2}=-\frac{1}{2}$ – $\Sigma m = m_J = 2$

(since $M_L = \Sigma m_l = 2$ – part of ^1D)

$$\left.\begin{array}{l} m_{l_1}=1, m_{s_1}=\frac{1}{2}, m_{l_2}=0, m_{s_2}=-\frac{1}{2} \\ m_{l_1}=0, m_{s_2}=-\frac{1}{2}, m_{l_2}=1, m_{s_2}=\frac{1}{2} \end{array}\right\} \text{interchange quantum numbers}$$

Electrons indistinguishable → 1 microstate.

Consider all possibilities:
Total number of microstates only 15 (not 60).
NB: Degeneracies in L-S representation.

$^3D_{3,2,1}$	$^1D_2$	$^3P_{2,1,0}$	$^1P_1$	$^3S_1$	$^1S_0$
7+5+3	5	5+3+1	3	3	1

Group Microstates according to Σm (obeying Pauli Principle)

$m_J = +2$	$+1$	0	-1	-2
$(1, \frac{1}{2}, 1, -\frac{1}{2})$	$(1, \frac{1}{2}, 0, -\frac{1}{2})$	$(1, \frac{1}{2}, -1, -\frac{1}{2})$		
$(1, \frac{1}{2}, 0, \frac{1}{2})$	$(1, -\frac{1}{2}, 0, \frac{1}{2})$	$(1, -\frac{1}{2}, -1, \frac{1}{2})$		
	$(1, \frac{1}{2}, -1, \frac{1}{2})$	$(0, \frac{1}{2}, 0, -\frac{1}{2})$	3 states	2 states
		$(1, \frac{1}{2}, 0, -\frac{1}{2})$		
		$(-1, \frac{1}{2}, 0, \frac{1}{2})$		

No Σm = ±3 states ➔ no $^3D_3$ ➔ no ^3D.
2 Σm = ±3 states ➔ both $^1D_2$ and $^3P_2$.

^1D requires $1m_J=2$, $1m_J=1$, $1m_J=0$, $1m_J=-1$ …
^3P requires $1m_J=2$, $2m_J=1$, $3m_J=0$, $2m_J=1$ …
After counting all these states, leaves one other ➔ ^1S_o.

(SEE TUTORIAL QUESTION)

Order of Quantum States – Hund's Rules

For a given configuration with LS coupling – order of states normally given by:

1) Terms with largest S, i.e. lie lowest in energy.
2) For given S, terms with largest L are lowest, e.g.

from $d^2 \rightarrow {}^1G, {}^3F, {}^1D, {}^3P, {}^1S$

(1) Gives $^3F, {}^3P < {}^1G, {}^1D, {}^1S$

(2) Gives $^3F < {}^3P; {}^1G < {}^1D < {}^1S$

3) For less than half full shells lowest J-value has lowest energy.

For more than half full shells highest J-value has lowest energy.
(S.O constant. A is negative).
Note – p^4 has same terms as p^2, therefore O similar to C, but J order reversed:
For d^2, obtain $^3F_2 < {}^3F_3 < {}^3F_4$.
For d^8, obtain $^3F_4 < {}^3F_3 < {}^3F_2$.

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Spectra of L-S Coupled Atoms

Selection Rules:

Δn = anything	$\Delta l = \pm 1$	$\Delta S = 0$
$\Delta J = 0, \pm 1$ (but not $J=0 \leftrightarrow J=0$)	$\Delta L = 0, \pm 1$	$\Delta M_J = 0, \pm 1$

NB: heavier elements show "intercombination" lines e.g. $^5S \rightarrow {}^3P$ ($\Delta S = 1$)
Spin-Orbit coupling can weakly mix states of different S = breakdown of L-S Coupling scheme.

j-j Coupling

Occurs when spin orbit coupling is large compared to spin correlation or orbital/orbital interaction.
NB: spin-orbit coupling is a magnetic interaction and magnetic fields are relativistic electric fields, therefore coupling large for heavier atoms.
If spin-orbit coupling sufficiently large, the spin and orbital angular momentum of each electron coupled → j.
e.g.

$l_1 + s_1 = j_1$	MAGNETIC
$l_2 + s_2 = j_2$	MAGNETIC
$j_1 + j_2 = J$	ELECTROSTATIC

Quantum Numbers,

$$j_1 = l_1 + \tfrac{1}{2},\ l_1 - \tfrac{1}{2} \ \text{etc.}$$

$$2p3d \begin{cases} l_1 = 1 \Rightarrow j_1 = 3/2 \text{ or } 1/2 \\ l_2 = 2 \Rightarrow j_2 = 5/2 \text{ or } 3/2 \end{cases}$$

Now couple j_1 and j_2 to give J states, written as:

$$[3/2, 5/2]_{4,3,2,1} \qquad [3/2, 3/2]_{3,2,1,0}$$

$$[1/2, 5/2]_{3,2} \qquad [1/2, 3/2]_{2,1}$$

Note: L & S no longer defined – no ^1P, ^3P, etc.

Spectra in j-j Coupling

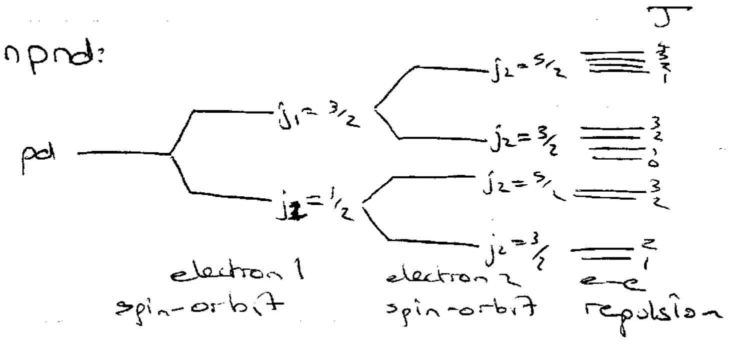
Selection Rules:

$\Delta l = \pm 1$, $\Delta \mathbf{j} = 0, \pm 1$ for 1 electron and $\Delta l = \Delta j = 0$ for other electrons.

$\Delta J = 0, \pm 1$ $\qquad$ $\Delta M_J = 0, \pm 1$

Energy Levels (j-j) –

Determined by j_1 and j_2:



No L or S, therefore no S/L selection rules.
j-j coupled states are a mixture of singlet and triplet components.
Some atoms show intermediate behaviour, therefore neither L-S or j-j selection rules are obeyed.

Group IV Atoms –

C = L-S Coupled

$$\left.\begin{array}{l}\text{Si}\\ \text{Ge}\\ \text{Sn}\end{array}\right\}\text{ intermediate}$$

Pb = j-j Coupled

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