Electronic Selection Rules (I)

Introduction

- electronic transitions can occur in the visible range leading to colour, for some examples see the web-links
- how do transition metal complexes produce colour? We already know it has to do with excitations in the dAO based MOs of a complex, and that these are sensitive to the coordinating ligands (spectrochemical series).
- you made $NiCl_2(PPh_3)_2$ in the 1st year lab and studied the tetrahedral vs square planar isomers which are green and red respectively
- the visible spectrum runs from 400-700nm and UV-vis spectroscopy is the typical way to study soluble coloured complexes
- at longer wavelengths are infra-red (heat cameras) and at shorter wavelengths is ultra-violet light (bee/butterfly vision)
- in chemistry we typically meet coloured transition metal complexes, but the presence and use of colour is much broader. Chemistry meets art in the Roger Hiorns installation in Peckham, London, which uses bright blue $CuSO_4$
- pigments are typically coloured solids, where crystal field theory gives us a very basic model such as Cr surrounded by 6 oxygen atoms in $Cr_2O_3{\bullet}H_2O$ also known as the dark-green colour called viridian. Rubies are red and emeralds are green for similar reasons.
- however, there are also other more complex solid state process that can give rise to colour, such as transitions from the valence to conduction band in insulators.
- dyes typically involve an organic molecule and a $n\text{->}\pi^*$ or $\pi\text{->}\ \pi^*$ transition, dyes include cloth dyes, indicators, as well as colourants for plastics, food, cosmetics, glass, paints, soaps, and for use in ink-jet printers!
- in small nanoparticles, those about the size of the wavelength of visible light, the electric field of the light can (induce) an oscillating dipole within the nanoparticle (collective movement of the free electrons in the metal=surface plasmons) leading to the emission of secondary radiation, and absorption in the visible range and excitation of the surface plasmons.
    - historical applications include stained glass
    - applications include modern biological and chemical sensing, developments in photovoltaics and quantum optics, and surface enhanced Raman spectroscopy
- novel materials are being synthesised within ionic liquids, which allow the formation of clusters and nanoparticles

The Visible region

- the visible region is 350-750nm
- approximate ranges are:
    - 380-450 nm violet, 450-485 nm blue, 485-500 nm cyan, 500-565 nm green, 565-590 nm yellow, 590-625 nm orange, 625-740 nm red.
    - you should know this ordering! (the exact range for each colour is not required)
- just higher is ultra-violet, and just lower is the infra-red spectrum

UV-Vis Spectroscopy

- UV-vis spectroscopy is used extensively to study coloured transition metal complexes
- think back to carrying out a UV-vis experiment. We know from the Beer Lambert rule that the **absorbance**(A) depends on the molar absorption coefficient (ε) the concentration (*c*) and the dimension of the cuvette (*l*)

$$A = -\log_{10}\left(\frac{I_0}{I}\right) = \varepsilon c l = \kappa l \qquad \text{Equation 1}$$

- the **extinction coefficient** ε or **absorption coefficient** κ contains the molecule specific information that we need to understand, it is related to the ability of the molecule to interact with the incident light. The absorption coefficient will be dependent on:
  - the energy of the incident light wave which must exactly match the difference in energy between initial and final rotational/vibrational/electronic energy levels $\Delta E = \hbar \nu_{fi}$
  - not all such transitions are "allowed" the Einstein coefficient, B_{fi} gives the probability that a transition will occur
  - the molecule must also have a population inversion (N_i-N_f) between the ground and excited state

$$\kappa' = \frac{h\nu_{fi}}{c} B_{fi}(N_f - N_i) \qquad \text{Equation 2}$$

  - we have assumed a perfectly sharp absorption, in reality there will be a small range of frequencies, and an absorption peak of finite width, in which case we would integrate κ' over the range of frequencies, ν
- the probability that a molecule absorbs light is given by the **Einstein coefficient**, B_{fi} which depends on the transition dipole moment

$$B_{if} = B_{fi} = \frac{|\mu_{if}|^2}{6\varepsilon_0 \hbar^2} \quad \mu_{fie} = \int \psi_f (\mu_e) \psi_i d\tau_e = \langle \psi_f | \mu_e | \psi_i \rangle \qquad \text{Equation 3}$$

  - we can determine when the transition dipole moment is non-zero through symmetry, thus we need to know the symmetry of the initial and final electronic wavefunctions

Pure Electronic Selection Rules

- for an electronic transition between **different electronic states**

$$\mu_{fi} = \int \chi_f \langle \mu_e \rangle \chi_i d\tau_n = \int \chi_f \left[\int \psi_f (\mu_e) \psi_i d\tau_e \right] \chi_i d\tau_n \qquad \text{Equation 4}$$

  - while there can also be a vibrational and rotational transition at the same time, we will first restrict our description to a pure electronic transition

$$\begin{aligned} \mu_{fi} &= \int \psi_f (\mu_e) \psi_i d\tau_e \\ &= \langle \psi_f | \mu_e | \psi_i \rangle \end{aligned} \qquad \text{Equation 5}$$

  - where ψ_f is the final electronic state, ψ_i is the initial electronic state and μ_e is the electronic dipole moment

- to determine weather a transition occurs we do not need to actually evaluate the electronic integrals, we only need to know if they are zero or non-zero
    - we only need to determine if the direct product of the symmetry of the functions forming the integrand are totally symmetric
    - to do this we need to know the symmetry of the ψ_f and ψ_i electronic states and to combine this with our knowledge of the symmetry of the electronic dipole moment
- for a molecule we determine the symmetry of an electronic state by taking the direct product of the IRs for **all the electrons in each electronic molecular orbital**
    - for a spin paired system this is easy because with two electrons in an orbital the direct product is always the totally symmetric IR
    - thus we only need to consider the symmetry of any unpaired electrons, or electrons in HOMOs of degenerate symmetry
- for example water has a configuration $(1a_1)^2(2a_1)^2(1b_1)^2(3a_1)^2(1b_2)^2$, **Figure 1**

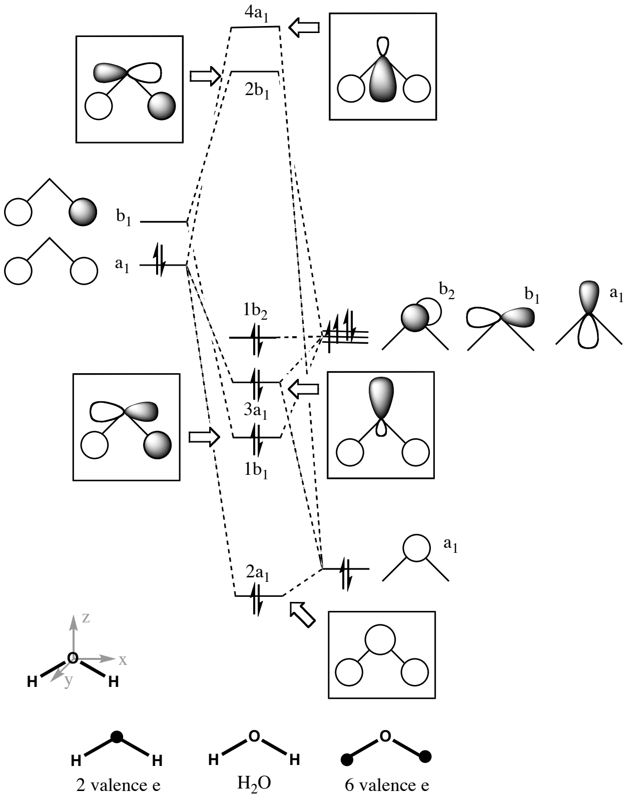


Figure 1 MO diagram of water

- the ground state of water is A_1 because all of the electrons are paired:

$$A_1 \otimes A_1 = A_1 \quad B_1 \otimes B_1 = A_1 \quad B_2 \otimes B_2 = A_1$$

$$(1a_1)^2(2a_1)^2(1b_1)^2(3a_1)^2(1b_2)^2$$
$$= A_1 \otimes A_1 \otimes A_1 \otimes A_1 \otimes A_1 = A_1$$

- an excitation of 1e from the $1b_2$ HOMO to the $2b_1$ MO gives a final state of A_2 symmetry

$$(1a_1)^2(2a_1)^2(1b_1)^2(3a_1)^2(1b_2)^1(2b_1)^1$$
$$= \left[A_1 \otimes A_1 \otimes A_1 \otimes A_1\right] \otimes B_2 \otimes B_1$$
$$= A_1 \otimes B_2 \otimes B_1 = A_2$$

- an excitation of 2e from the $1b_2$ HOMO to the $2b_1$ MO gives a final state that has A_1 symmetry

$$(1a_1)^2(2a_1)^2(1b_1)^2(3a_1)^2(1b_2)^0(2b_1)^2$$
$$= A_1 \otimes A_1 \otimes A_1 \otimes A_1 \otimes A_1 = A_1$$

- we then evaluate if the transition dipole moment integral is zero or not:

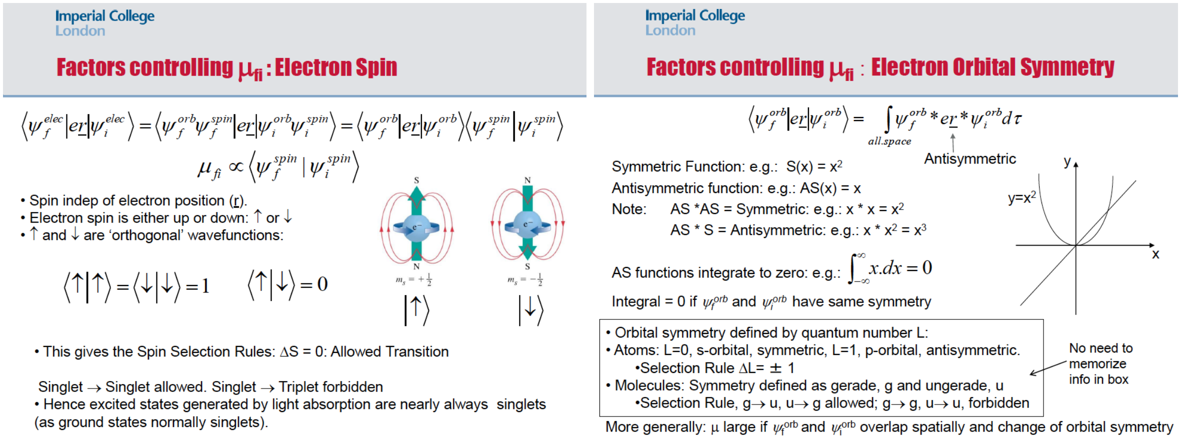
$$\{A_1 \otimes A_2\} \otimes \Gamma^{\mu} = A_2 \otimes \begin{bmatrix} B_1 \\ B_2 \\ A_1 \end{bmatrix} = \{B_2, B_1, A_2\} \quad \{A_1 \otimes A_1\} \otimes \Gamma^{\mu} = A_1 \otimes \begin{bmatrix} B_1 \\ B_2 \\ A_1 \end{bmatrix} = \{B_1, B_2, \boxed{A_1}\}$$

- thus a single excitation from the $1b_2$ to $2b_1$ MO is not allowed but the double excitation is allowed (assuming the multiplicity remains constant)
- water is a trivial example, and more commonly the selection rules are applied to organic chromophores and transition metal complexes

The Spin Selection Rule

- so far we have not mentioned that the electronic wavefunction includes a spin component
  - you have met the "**spin selection rule**" before, this states that transitions between states of different spin are forbidden, **Figure 2**
  - actually for transition metal complexes it is normally phrased as the *spin multiplicity cannot change* (we will discuss multiplicity shortly).
  - we can factor the electronic wavefunction into a spatial and spin components, the electronic dipole moment does not depend on spin and is evaluated as shown above
  - the spin component reduces to a simple "orthogonality" relationship represented by $\delta_{\alpha\beta}$ and the whole integral will be zero if the initial and final states have different spin

$$\mu_{fi} = \int \psi_f (\mu_e) \psi_i d\tau \neq 0$$
$$\psi_i = \psi_i s(\sigma_i) \quad s(\sigma_i) = \alpha, \beta$$
$$\mu_{fi} = \int \psi_f (\mu_e) \psi_i d\tau \bullet \int s_f(\sigma) s_i(\sigma) ds \neq 0 \qquad \text{Equation 6}$$
$$\langle \alpha | \beta \rangle = 0 \quad \langle \alpha | \alpha \rangle = \langle \beta | \beta \rangle = 1$$
$$\mu_{fi} = \int \psi_f (\mu_e) \psi_i d\tau \bullet \delta_{\alpha\beta} \neq 0$$



Imperial College London

Factors controlling μ_{fi} : Electron Spin

$$\langle \psi_f^{elec} | e\underline{r} | \psi_i^{elec} \rangle = \langle \psi_f^{orb} \psi_f^{spin} | e\underline{r} | \psi_i^{orb} \psi_i^{spin} \rangle = \langle \psi_f^{orb} | e\underline{r} | \psi_i^{orb} \rangle \langle \psi_f^{spin} | \psi_i^{spin} \rangle$$
$$\mu_{fi} \propto \langle \psi_f^{spin} | \psi_i^{spin} \rangle$$

- Spin indep of electron position (r).
- Electron spin is either up or down: ↑ or ↓
- ↑ and ↓ are 'orthogonal' wavefunctions:

$$\langle \uparrow | \uparrow \rangle = \langle \downarrow | \downarrow \rangle = 1 \qquad \langle \uparrow | \downarrow \rangle = 0$$

- This gives the Spin Selection Rules: ΔS = 0: Allowed Transition

Singlet → Singlet allowed. Singlet → Triplet forbidden
- Hence excited states generated by light absorption are nearly always singlets (as ground states normally singlets).

Imperial College London

Factors controlling μ_{fi} : Electron Orbital Symmetry

$$\langle \psi_f^{orb} | e\underline{r} | \psi_i^{orb} \rangle = \int_{all.space} \psi_f^{orb} * e\underline{r} * \psi_i^{orb} d\tau$$

Antisymmetric

Symmetric Function: e.g.: $S(x) = x^2$
Antisymmetric function: e.g.: $AS(x) = x$
Note: AS *AS = Symmetric: e.g.: $x * x = x^2$
AS * S = Antisymmetric: e.g.: $x * x^2 = x^3$

AS functions integrate to zero: e.g.: $\int_{-\infty}^{\infty} x.dx = 0$

Integral = 0 if ψ_f^{orb} and ψ_i^{orb} have same symmetry

- Orbital symmetry defined by quantum number L:
- Atoms: L=0, s-orbital, symmetric, L=1, p-orbital, antisymmetric.
  - Selection Rule ΔL= ± 1
- Molecules: Symmetry defined as gerade, g and ungerade, u
  - Selection Rule, g→ u, u→ g allowed; g→ g, u→ u, forbidden

No need to memorize info in box

More generally: μ large if ψ_f^{orb} and ψ_i^{orb} overlap spatially and change of orbital symmetry

Figure 2 Slides from your photochemistry course with Saif Haque

The Parity Selection Rule

- parity is also very important
  - the **parity selection rule**: *transitions must occur between states of the different parity*. Thus, only transitions that involve a g->u or u->g transition are allowed. Or alternatively we say that the parity must change, **Figure 2**.
  - orbitals with even parity are labelled "g" gerade which is German for "even". This means that under inversion there is no sign change, gerade orbitals are symmetric for i, **Figure 3**
  - orbitals with odd parity are labelled "u" ungerade which is German for "odd. This means that under inversion there is a sign change, ungerade orbitals are antisymmetric for i.

C_i	E	i
A_g	1	1
A_u	1	−1

Figure 3 C_i character table

  - the electronic dipole moment has ungerade parity (as it depends on x,y and z which are ungerade), sometimes we just say the dipole moment is an odd function
  - this means that for the transition dipole integrand to contain the totally symmetric IR, the direct product $\left\{\Gamma^{\langle\chi_f|} \otimes \Gamma^{|\chi_i\rangle}\right\}$ must be ungerade (u). For this to be true one of the initial or final states must be u and the other must be g. That is there must be a change in parity during the excitation.
- the parity selection rule is often conflated with the "**Laporte selection rule**", which is an **angular momentum selection rule**: *a transition must involve angular momentum change of plus/minus 1*, $\Delta l = \pm 1$,
  - sAOs have g parity and pAOs have u parity, thus and s->s or a p->p transition is forbidden by parity. Putting this together you can see that a transition is only allowed if we have a change in angular momentum because that allows a change in parity
  - notice that the parity selection rule still allows a d->s transition, but the Laporte selection rule forbids this as this is a change of $\Delta l=2$
  - these rules lead to d-d transitions in TM complexes being "forbidden" because they involve a d-d transition (no angular momentum change) and because they involve a t_{2g} to e_g transition and thus involve a g->g transition (parity selection rule)
  - clearly transition metals still have d-d transitions, so how are these rules "broken"? We will discuss this later!

Atomic Electronic States

- pure electronic transitions within TM complexes or in the solid state depend, to a first approximation, on the nature of the dAOs in the isolated cation ie where the TM is a **"free ion"**.
  - this is particularly true for weakly interacting ligands where the metal dAOs are not substantially perturbed
  - and also in the solid state, where ionic bonds rather than covalent bonds dominate

- when the ligands are **strong field ligands** we need to take another approach, treated shortly
- thus to study TM isolated cations or "free ions" in more detail we need to go back and consider the orbital characteristics of atoms in more detail, we need to know the exact symmetry of initial and final electronic states so that we can determine if a transition should occur

IMPORTANT

this is going to involve some tough quantum mechanics!
don't try to understand it all the first time you read it …
on the first reading soak up the concepts and then come
back again focusing more on the details

- you are already aware of the different components of the electronic wavefunction:

$$\psi_{el} = R_n(r)Y_{l,m_l}(\theta,\phi)s_{s,m_s}(\sigma) \qquad \text{Equation 7}$$

  - we have the principle quantum number which relates to the radial equation
  - the angular quantum numbers which relate to the angular solutions
  - and the spin quantum number which relates to the spin component
- for example in labelling the atomic configuration of an atom such as carbon we would write: C $1s^2 2s^2 2p^2$ -> this looks easy. Actually it is not so easy!!
- we have quietly ignored the fact that there are three 2p AOs
  - p really means l=1 where l is the angular momentum of the orbital (l=0 called s and l=2 called d and so on)
  - each l has m_l=-l, (-l+1) …0… (l-1), l associated with it
  - so pAO has m_l=-1, 0, 1 and there are the three different pAOs, each of these orbitals has a different symmetry.
  - which of these pAOs do the electrons occupy?
- we have also ignored the fact that the electrons have spin
  - we know from experiment that s takes on only one value s=1/2
  - the m_s values for s are defined similarly to m_l; m_s=-s, (-s+1) …0… (s-1), s
  - if s=1/2 the possible m_s values are (-s)=-1/2 and (-s+1)= (-1/2+1)=s=1/2
  - thus one electron can have spin m_s=+1/2 or m_s=-1/2, you might be more familiar with the α and β terminology!
  - are our two pAO electrons spin paired or do they have parallel spins?
- it is evident we need a more detailed and accurate description of the states of atoms and molecules.
  - for example a single electron p^1 electron has 6 possible **microstates**, it can have a value of m_l=-1, 0, 1 and each of these can have m_s=+1/2, -1/2
  - determining the number of microstates for more than one electron is made more difficult because electrons are indistinguishable and some of the microstates are identical and we only count the unique states
  - however there is a useful formula when n=2*number of orbitals and n_e= the number of electrons and n_h=number of holes:

IMPORTANT

$$N = \frac{n!}{n_e!n_h!} \qquad \text{Equation 8}$$

- thus for p^2 there are $n=6$, $n_e=2$ and $n_h=4$, giving 15 microstates

$$N = \frac{6!}{2!4!} = \frac{6\bullet5\bullet4\bullet3\bullet2\bullet1}{(2\bullet1)(4\bullet3\bullet2\bullet1)} = \frac{6\bullet5}{2} = 15$$

- these microstates do not all have the same energy, this is because the e-e interactions are different, e-e repulsion changes, e-e exchange changes, and electrons that are parallel have different energies from electrons that are spin paired

In Notes Problem

- calculate how many microstates the d^4 configuration has:

number of orbitals =
number of electrons =
number of holes =
work out the equation …

- the situation is significantly more complex for five dAOs, the larger number of electrons means a much larger number of microstates, **Table 1**

d^n	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
microstates	10	45	120	210	252	210	120	45	10	1

Table 1 microstates for different dAO configurations

Quantum Mechanics of Angular Momentum

- it is clear we need a better description of the atomic states, and that this will involve energy levels or states with a large number of degeneracies
- in this section I will only give a rough outline, as you don't yet have sufficient quantum mechanics to treat this topic properly.
- you are directed to relevant textbooks for a full explanation, for example see Chapter 4: Angular Momentum in Atkin's "Molecular Quantum Mechanics"
- you have meet angular momentum in the context solving the Schrödinger equation for the Hydrogen atom
  - different people use different notations I am going to use $\boldsymbol{l}$ for the **orbital angular momentum vector**, just the way a position vector can be defined **r**= x**i**+ y**j**+z**k** where i, j and k are the orthogonal Cartesian unit vectors, linear momentum can also be defined **p**= p_x**i**+ p_y**j**+p_z**k**, and also angular momentum $\boldsymbol{l}= l_x\mathbf{i}+ l_y\mathbf{j}+l_z\mathbf{k}$
  - the length of a vector can be described as $r^2=x^2+y^2+z^2$, and the length of the angular momentum vector can be defined $l^2=l_x^2+l_y^2+l_z^2$
  - when using angular momentum we focus on the following eigenvalue equations for l^2 and l_z, the eigenfunctions are the spherical harmonics $Y(\theta,\varphi)$ and the eigenvalues are the quantum numbers l and m_l:

$$\begin{aligned} l^2Y(\theta,\phi) &= l(l+1)\hbar^2Y(\theta,\phi) \quad l=0,1,2\ldots \\ l_zY(\theta,\phi) &= m_l\hbar Y(\theta,\phi) \quad m_l=-l,(-l+1)\ldots(l-1),l \end{aligned}$$

Equation 9

  - notice that for each l value we will have $2l+1$ m_l states

- the length and z-component of the angular momenta commute $[l^2, l_z]$, however the length and the x- or y- components do not commute.
  - we focus on l^2 and l_z because they both commute with the Hamiltonian
  - any operators that commute have the same eigenfunctions and so this is an easy way to determine the eigenfunctions for H
  - operators that commute with H are the only observable operators, and thus these are the operators that are important in spectroscopy
- instead of writing the eigenfunctions in the spherical harmonic notation it is common to represent the eigenfunctions in a Dirac notation, emphasising the quantum numbers for each wavefunction:

$$\begin{aligned} l^2\left|l,m_l\right\rangle &= l(l+1)\hbar^2\left|l,m_l\right\rangle \quad l=0,1,2\ldots \\ l_z\left|l,m_l\right\rangle &= m_l\hbar\left|l,m_l\right\rangle \quad m_l=-l,(-l+1)\ldots(l-1),l \end{aligned} \qquad \text{Equation 10}$$

In Notes Problem

- if l=2 how many states are there and what are the m_l values?

IMPORTANT

- the orbital angular momentum functions l^2 and l_z are particular cases of the **general class** of angular momentum operators, this class all have similar equations, if we assume a general angular momentum vector ***k*** then:

$$\begin{aligned} k^2\left|k,m_k\right\rangle &= k(k+1)\hbar^2\left|k,m_k\right\rangle \quad k=0,1,2\ldots \\ k_z\left|k,m_k\right\rangle &= m_k\hbar\left|k,m_k\right\rangle \quad m_k=-k,(-k+1)\ldots(k-1),k \end{aligned} \qquad \text{Equation 11}$$

  - for each k value we will have $2k+1$ m_k states
- it may not have been explicitly stated before, but "spin" is a special form of an angular momentum operator, the **spin operators** are s^2 and s_z, the eigenfunctions are $|s,m_s>$ and the eigenvalues are quantum numbers s and m_s

$$\begin{aligned} s^2\left|s,m_s\right\rangle &= s(s+1)\hbar^2\left|s,m_s\right\rangle \quad s=0,\frac{1}{2},1,\frac{3}{2},2\ldots \\ s_z\left|s,m_s\right\rangle &= m_s\hbar s\left|s,m_s\right\rangle \quad m_s=-s,(-s+1)\ldots(s-1),s \end{aligned} \qquad \text{Equation 12}$$

  - the quantum number s is called the spin of the particle, mathematically there is no restriction on s! However, experiment shows that all electrons have a single value of s=1/2. Protons and neutrons also have s=1/2, pions have s=0 and photons have s=1.
  - the electron spin eigenfunctions for electrons are defined as α and β

$$s=\frac{1}{2} \quad and \quad m_s=-s\cdots s=-\frac{1}{2},\frac{1}{2}$$

$$\left|s,m_s\right\rangle=\left|\frac{1}{2},\frac{1}{2}\right\rangle=\alpha \Rightarrow \quad S_z\alpha=\frac{1}{2}\hbar\alpha \quad \left|s,m_s\right\rangle=\left|\frac{1}{2},-\frac{1}{2}\right\rangle=\beta \Rightarrow \quad S_z\beta=-\frac{1}{2}\hbar\beta \qquad \text{Equation 13}$$

- getting back to our multi-electron system, we can identify individual angular momentum vectors $\boldsymbol{l}_\mathbf{i}$ and spin $\mathbf{s}_\mathbf{i}$ *for each electron*. The individual momenta commute with each other and so for a multi-electron system we can write a single wavefunction dependent on the individual quantum numbers:

$$\left| l_1, m_{s1}, l_2, m_{s2}, \cdots \right\rangle \qquad \text{Equation 14}$$

- however in a molecule the individual angular momenta are not useful for us, we are interested in the **total angular momenta vectors**: total orbital angular momentum (**L**) and total spin (**S**)

$$\begin{aligned} \hat{L} &= \sum_i \hat{l}_i \qquad \hat{S} = \sum_i \hat{s}_i \\ L_z &= \sum_i l_{zi} \qquad S_z = \sum_i s_{zi} \end{aligned} \qquad \text{Equation 15}$$

  - these have an associated component in the z-direction L_z and S_z and an associated magnitude for the total orbital angular momentum (L^2) or total spin magnitude (S^2)
  - the total angular momentum operators are within the class of angular momentum operators and so fit the same pattern for satisfying the eigenvalue equations:

$$\begin{aligned} &L^2\Phi = L(L+1)\hbar^2\Phi \quad L = 0,1,2\ldots \\ &L_z\Phi = M_L\hbar\Phi \quad M_L = -L,(-L+1)\ldots(L-1),L \end{aligned}$$

$$\text{Equation 16}$$

$$\begin{aligned} &S^2\Phi = S(S+1)\hbar^2\Phi \quad S = 0,1,2\ldots \\ &S_z\Phi = M_S\hbar\Phi \quad M_S = -S,(-S+1)\ldots(S-1),S \end{aligned}$$

  - the eigenfunctions depend on the total quantum numbers and parametrically on the individual electron quantum numbers:

$$\left| L, M_L; l_1, l_2 \cdots \right\rangle \qquad \text{Equation 17}$$

- the associated quantum numbers can be a bit difficult to work out! The best technique is to *start by working out the* m_L and m_S *value*s and from those work out the possible L and S quantum numbers. Please see L7 and the exam preparation problems from L7 for more details.
  - for example if we had 2 electrons:

$$\begin{aligned} &\hat{L} = \hat{l}_1 + \hat{l}_2 && \hat{S} = \hat{s}_1 + \hat{s}_2 \\ &M_L = m_{l1} + m_{l2} && M_S = m_{s1} + m_{s2} \\ &L = l_1 + l_2, (l_1 + l_2 - 1), (l_1 + l_2 - 2), \cdots \left| (l_1 - l_2) \right| && S = s_1 + s_2, (s_1 + s_2 - 1), (s_1 + s_2 - 2), \cdots \left| (s_1 - s_2) \right| \\ &\text{number of states} = (2l_1 + 1)(2l_2 + 1) && \text{number of states} = (2s_1 + 1)(2s_2 + 1) \\ &\left| L, M_L; l_1, l_2 \right\rangle && \left| S, M_S; s_1, s_2 \right\rangle \end{aligned}$$

Equation 18

  - working out the coupling of more electrons is difficult and is usually carried out by coupling 2 electrons and then coupling the resulting momenta/spin with the 3rd electron and so on; coupling is worked out pairwise. Coupling of more than 2 electrons is beyond this course!

IMPORTANT

- the operators L^2 and S^2 commute with the Hamiltonian and thus are important quantities for spectroscopy and for defining the multi-electron wavefunctions or eigenvectors.
  - the allowed values of L and S form the **Clebsch-Gordan series**
  - we use the quantum numbers (L and S) to define the electronic states of multi-electron systems
  - similarly to single electron systems where l=0, 1, 2… are replaced by s, p d … we replace the total angular momentum eigenvalues L=0, 1, 2 … by S, P, D … with the capital letters indicating a total angular momentum rather than an individual orbital angular momentum
  - spin is not specified directly by S but by the **multiplicity**=2S+1
- the eigenfunctions one works with can change depending on which momenta are the focus, for example the wavefunction for two particles
  - can be defined by the individual angular momenta: $|l_1 m_{l1}\rangle|l_2 m_{l2}\rangle$
  - or they can be defined by the total angular momenta: $|L, M_L; l_1, l_2\rangle$
  - L^2 does not commute with the individual l_{zi} and so these two sets of eigenfunctions are different, however it is possible to interconvert them where the coefficients are known as the **Clebsch-Gordan coefficients**

$$|L_T, M_L; l_1, l_2\rangle = \sum C(L_T, M_L; l_1, l_2, m_{l1}, m_{l2})|l_1 m_{l1}\rangle|l_2 m_{l2}\rangle$$

Equation 19

  - think of this as expanding the total (angular momentum) wavefunction in terms of the individual (angular momentum) wavefunctions
- angular momentum is complex and we have just touched on it here, there is much more, see specialist texts on quantum mechanics if you are interested!

Spin Orbit Coupling

- spin-orbit coupling occurs when the spin and orbital angular momenta couple, this can occur via two mechanisms
  - the total angular momenta **S** and **L** couple to form **J**
  - the total coupled angular momentum has equations exactly analogous to the total angular momentum and spin momentum operators, **Figure 4**

$$\begin{aligned}
&\hat{J} = \hat{L} + \hat{S} \quad J_z = L_z + S_z \\
&M_J = M_S + M_L \\
&J = L + S, (L + S - 1)\ldots|L - S| \\
&J^2\Phi = J(J+1)\hbar^2\Phi \quad J = 0,1,2\ldots \\
&J_z\Phi = M_J\hbar\Phi \quad M_J = -J, (-J+1)\ldots(J-1), J
\end{aligned}$$

Equation 20

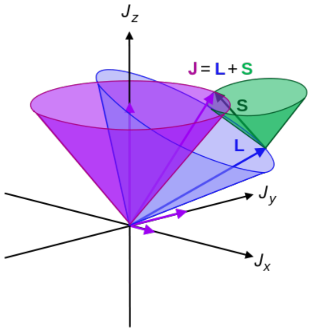


Figure 4 L and S (orbital and spin) angular momenta coupling.[1]

  - this type of coupling is called **Russell-Saunders coupling** or **L-S coupling**, and is appropriate for systems where the electron-electron repulsive interaction is larger than the spin-orbit coupling

---

[1] Image from http://en.wikipedia.org/wiki/Angular_momentum_coupling, 25 Feb 2014

- spin-orbit coupling is a relativistic effect and thus when atoms get heavy (and the inner electrons are moving near the speed of light) relativistic effects can dominate electron-electron repulsion.
- in this case spin-orbit coupling occurs at the individual electron level and this type of coupling is called **j-j coupling**

$$\begin{aligned}
&\hat{j}_i = \hat{l}_i + \hat{s}_i \\
&j_i^2\Phi = j(j+1)\hbar^2\Phi \quad j = 0,1,2\ldots \\
&j_{z,i}\Phi = m_j\hbar\Phi \quad m_j = -j,(-j+1)\ldots(j-1),j \\
&J = \sum_i \hat{j}_i
\end{aligned} \qquad \text{Equation 21}$$

- for most heavy atoms the reality sits somewhere between j-j and L-S coupling and calculations are difficult! For 3d and 4d transition metals we can work in the L-S coupling scheme
- for the heavier elements we need to consider the j-j coupling scheme, this is very relevant in your "Lanthanides and Actinides" course.

Key Points

- be able to describe some of the many instances in which colour is evident in the lab and in "real life"
- be able to make a connection between a UV-vis experiment and the mathematics that describes electronic transitions
- be able to determine the symmetry of the ground and excited electronic states for a simple molecule (like H_2O)
- be able to use the transition dipole moment to determine when a transition will occur
- be able to explain the spin and parity selections rules
- be able to determine the number of microstates for a given atomic configuration
- know the eigenvalue equations for the general class of angular momentum operators, l, s, L, S, j and J

Self-Study / Tutorial / Exam Preparation Problems

- no practice problems, spend your time going over the equations covered today