Introduction to Molecular Orbital Theory

6 lecture Course

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Tutorial Sheet 1 and 2

1. What is the relationship between the possible angular momentum quantum numbers to the principal quantum number?

2. How many atomic orbitals are there in a shell of principal quantum number n ?

3. Draw sketches to represent the following for $3s$, $3p$ and $3d$ orbitals.
a) the radial wave function
b) the radial distribution
c) the angular wave function

4. Penetration and shielding are terms used when discussing atomic orbitals
a) Explain what the terms penetration and shielding mean.
b) How do these concepts help to explain the structure of the periodic table

5. Draw the d atomic orbitals as enclosed surfaces, showing the sign of the original wavefunction on each lobe. Label these orbitals.

6. Why do the MO energy level diagrams for Li_2 and F_2 molecules differ ?

7. Explain why CO is described as a s-donor, p-acceptor ligand and is a strong field ligand.

Answers

1.   What is the relationship between the possible angular momentum quantum numbers to the principal quantum number ?

This question is revision of JF course Dr. Morton Blake. See also lecture 1 of this course
The angular momentum quantum number, l can have values of n-1, n-2 ......to 0 for any value of n.

2.   How many atomic orbitals are there in a shell of principal quantum number n ?

This question is revision of JF course Dr. Morton Blake.

There are n^2 orbitals in a shell of principal quantum number n

e.g.
when n= 1, $l = 0$, i.e. a 1s orbital
when n=2, $l = 1$ or 0 i.e one 2s orbital and three 2p orbitals , four orbitals in total
when n-3, l =2, 1 or 0 i.e. one 3s orbital, three 3p orbitals and five 3d orbitals, nine orbitals in total

3.   Draw sketches to represent the following for 2s and 2p orbitals.
a)   the radial wavefunction
b)   the radial distribution function
c)   the angular wavefunction

To answer this question look at lectures 2 and 3 of the course

a)   The radial wavefunction is a graph of the changes in R(r) with distance from the centre of the nucleus, r. We expect this graph to resemble a wave. To sketch it we need to determine at what radius the value of R(r) is a maximum and where it equals zero (a radial node).

2s: For **all** s orbitals the maximum R(r) is at the nucleus.

The no. of radial nodes $= n - l - 1$, i.e. in this case $2 - 0 - 1 = 1$. There is one radial node some distance from the nucleus.

2p: For **all** p orbitals the value of R(r) at the nucleus is zero.

The no. of radial nodes for a $2p$ orbital is $2 - 1 - 1 = 0$. There is no radial node.

b)   The radial distribution is a graph of the changes in the function $4\pi r^2 R(r)^2$ with distance from the centre of the nucleus. The squared terms, r^2 and $R(r)^2$, mean that this function can never have negative values.

This function shows that Bohr's idea, of electrons traveling in orbits, was not entirely wrong but incomplete. The distance from the nucleus at which the maximum in radial distribution occurs represents the most probable radius of a thin spherical shell (like an orbit) in which to find an electron.

In a $1s$ orbital there is one maximum and it corresponds to the radius that Bohr predicted for an electron traveling in an orbit in a H-like atom.

We know from part a) of this question how many radial nodes there are in $2s$ and $2p$ orbitals. The radial distribution will also equal zero at the same distances from the nucleus. In addition, the radial distribution must also equal zero when r equals zero.

Radial distribution functions allow us to compare the relative penetration of the nucleus of different orbitals on the same graph.

c) the angular wavefunction is dependent on the angles θ and ϕ in Cartesian coordinates. It cannot be drawn as a 2D graph. This question is asking for the shapes of the orbitals i.e. as boundary surfaces. Usually the value of the radial wavefunction is added to such sketches either by adding a + or – sign or by shading the portion of the orbital with a + value of the radial wavefunction.

4)   *Penetration and shielding are terms used when discussing atomic orbitals*
  a) *Explain what the terms penetration and shielding mean.*
  b) *How do these concepts help to explain the structure of the periodic table ?*

Penetration – the ability of an orbital to get close to the nucleus.
This can be demonstrated by drawing the RDF's. RDF's of 3*s*, 3*p* and 3*d* show that penetration goes 3s > 3p > 3d
Notice that the more nodes – the greater the penetration.
WHY ?

The nodes generate peaks close to the nucleus → greater penetration.

(ii) The effective charge that an electron feels depends on the nuclear charge and the shielding. Z (effective) = Z -S
Shielding is the ability of an electron to screen the interaction of other electrons with the nucleus.
With only one electron in a system this has no effect on the energy – since there are no other electrons to screen.
Hence the energy of 3s = 3p = 3d in one electron systems.

b) Once more than one electron is present they are screened by each other. Those close to the nucleus are more effective at screening. Hence 2s and/or 2p orbital electrons will screen electrons in n = 3 orbitals.

However the effect is not the same for all n = 3 orbitals.

WHY ?

Penetration !!!!!

The *s* orbitals penetrate close to the nucleus and hence have a stronger interaction with the nucleus. Hence *s* orbitals are not screened as effectively.

Hence $E(3s) < E(3p) < E(3d)$

In Summary

  a) A penetrating orbital is one that enters into (diffuses into) the space occupied by the nucleus. The degree of penetration can be seen by comparing the radial distribution graphs. The order of penetration for orbitals in the same shell is s>p>d.
  b) Shielding refers to the screening of nuclear charge by electron density in inner orbitals, so that the outer orbitals feel a reduced effective nuclear charge.

The two terms have an impact of the order in which orbitals are filled. Those that are most penetrating are also the most effective at shielding the nucleus and will be filled first.

5. Draw the d atomic orbitals as enclosed surfaces, showing the sign of the original wavefunction on each lobe. Label these orbitals.

See Dr. Kruger's SF notes and lecture 4 in this course.

Firstly remember that there are five d orbitals to draw. Two point along axes and three have lobes that point between axes.

Secondly remember that the 'names' tell you which axes the lobes point along or between.

Thirdly remember to correctly shade in the + wavefunction lobes first. You can tell which these are by the labels e.g. in dxy, the shaded lobes are the one in the quadrant flanked by the +ve x and +ve y axis and so is the lobe that points in the quadrant flanked by the –ve x and –ve y axis. This is because the product of xy is positive in these cases and that is what you are drawing.

6. Why do the MO energy level diagrams for Li$_2$ and F$_2$ molecules differ ?

See lecture 5 of the course.

This is a result of the difference in the relative energies of the 2s and 2p orbitals in Li and the same orbitals in F. The greater effective nuclear charge in the F atom means that the 2s orbital in a F atom is lower in energy than the same orbital in Li.

This has an impact when the 2s and 2p atomic orbitals on the two atoms combine to form molecular orbitals.

In a Li$_2$ molecule the $2\sigma_u$ and $3\sigma_g$ molecular orbitals can mix, whereas in a F$_2$ molecule they are too far apart in energy to mix.

7. Explain why CO is described as a σ-donor, π-acceptor ligand and is a strong field ligand

See lectures 5 and 6 of the course

Generally ligands are Lewis bases and donate a pair of electrons.

In CO the lone pair of electrons on the C are the ones that are available for donation to a Transition Metal atom. These electrons are accommodated in the Highest Occupied

Molecular Orbital (HOMO). This has σ symmetry i.e. is symmetrical with respect to rotation about the internuclear axis.

In addition CO can accept electron density from the metal. This electron density must be accommodated in an empty CO orbital, the Lowest Unoccupied Molecular Orbital (LUMO). This has π symmetry i.e. has one nodal plane passing through the internuclear axis.

To show the symmetry of the HOMO and LUMO you need to draw them and a really good answer will show the completed molecular orbital energy level diagram for CO, to prove these are the fully occupied and empty respectively.

Strong field ligands cause an increase in the splitting of the metal d orbitals on the formation of a complex. This is because of π interaction between the ligand and the metal centre. The high energy LUMO of CO (π^*) interact with the t_{2g} set of d orbitals so as to produce this change. You need to look at the figures on the handout provided in lecture 6 of this course.

A practice question (with hints and brief answers) from the **annual SF paper 2 exam 1997**

Account for four of the following:

a)   **the atomic orbitals on the metal atom in [PtCl$_4$]$^{2-}$ can be described as sp^{2}d hybridized.**

(hint: look up hybridization in your notes, sp^{2}d means that four atomic orbitals on the Pt have been hybridised, i.e. the complex is tetrahedral or square planar.)

(answer: It must be square planar (Pt(II), and the hybridization tell you this). The four atomic orbitals that mix are s, p_x , p_y and dx^2-y^2 (to make a flat square).

b)   XeF₄ is square planar

(hint: you need to draw the Lewis structure remembering the number of valence electrons on each element, tetrahedral is more common - so think)

(answer: there are two lone pairs of electrons on the Xe, which are held as far apart as possible, above and below the plane of the F atoms)

c)   *2s orbitals have no nodal planes but one radial node*

(hint: for nodal planes you need to consider the shape of the orbital, for radial nodes you need to remember how this relates to n and l)

(answer: the orbital is spherical, n-l-1 = 1, the answer requires two sketches)

d)   *the HOMO in N₂ has the symmetry label 3σg*

(hint: you *may* need to draw the molecular orbital energy level diagram for N_2 (mixing) and put in the correct number of electrons. You are *required* to draw the orbital to explain its σ symmetry and the label g)

(answer: σ symmetry, spherical with respect to rotation about the internuclear axis, g, even with respect to inversion)

e)   *halides can be described as σ-donor, π-donor ligands*

(hint: think of Cl⁻, it has four pairs of electrons, one in 3s, and three in 3p orbitals)

(Answer: it donates electrons from an sp hybrid and filled p orbitals. The latter low lying bonding orbitals are available for π interaction with the t_{2g} set on the metal, reducing the degree of d orbital splitting).