Name **Student Number**

03-59-250 **Final Exam** **08/12/18 (3 hours)**

Note: Exams written in pencil will NOT be re-marked.
Fill out your name on each page. Make sure all pages are handed in at the end.

Hint: There are questions of varying difficulty. Read through the exam and answer the easy ones first!

The distribution of marks for the questions is approximate, and may change. You may use the back of any page for additional space or rough work.

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1) Quick fire round!
   a) The $2s$ and $2p$ orbitals for the hydrogen atom have the same energy.

True **False**

   b) How many quantum numbers are needed to describe an electron?

   c) Left to right across a period, electron attachment enthalpy ….

Increases **Decreases**

   d) Top to bottom down a group, electron attachment enthalpy….

Increases **Decreases**

   e) After the gain of an electron, the radius of an atom…

Increases **Decreases**

   f) BRIEFLY explain why the electron attachment enthalpy of silicon is more exothermic than that of phosphorus

   g) The possible spin states of a nucleus with I = 1 are:

   h) The bonding molecular orbitals of a heteronuclear molecule typically have larger coefficients (c) for the atomic orbital functions (ϕ) of the more electronegative element

True **False**

   i) In an infrared experiment, the spectrum is constructed from the _____ of the infrared light beam.

j) In a Raman experiment, the spectrum is constructed from the _____ of the light beam.

k) Suggest an element that could be added to silicon to make an n-type semiconductor

l) In the labels of representations in a character table, an A representation (e.g. A_1) is symmetric with respect to what symmetry element?

m) In the labels of representations in a character table, a representation labelled with a double prime (e.g. A_2'') means it is _____ with respect to σ_h. (circle the correct answer)

Symmetric **Asymmetric** **Antisymmetric**

n) What symmetry element needs to be present in a molecule for an orbital to be labelled *gerade* (g) or *ungerade* (u)?

o) How many vibrational modes would the CO_2 molecule have?

p) The reducible representation for **all** the oxygen p-orbtials (capable of both σ and π bonding) in MoO_3 is:

$$\Gamma_{O\ 2p} = A_1' + A_2' + A_2'' + 2E' + E''$$

How many bonding molecular orbitals can be formed between these SALCs and the molybdenum?

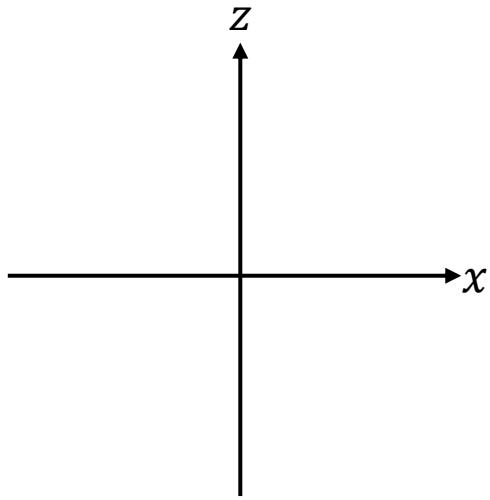
2) The picture shows an image of the supernova remnant 'E0102-72' located in a galaxy some 200,000 light years from Earth. The ring is about 30 light years across and contains more than a billion times the oxygen contained in the Earth's oceans and atmosphere, and is at a temperature of many millions of degrees Kelvin. At such temperatures, any atoms are highly ionised and electronic transitions within these ions may be detected by telescopes such as *Chandra*. Analysis of the spectra recorded enable astronomers to determine the composition of such bodies.

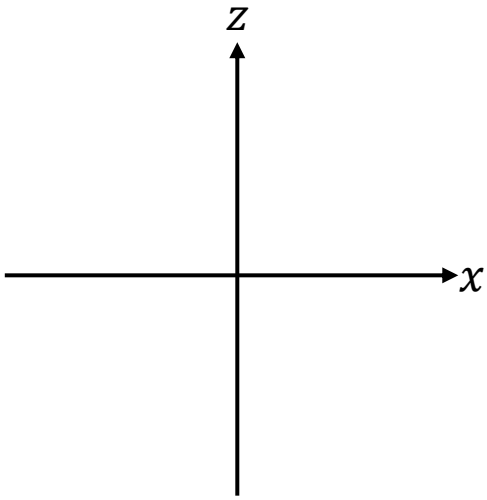
Emission lines corresponding to electronic transition from n = 5 to n = 1 have been detected for the hydrogen-like ion O^{7+}.

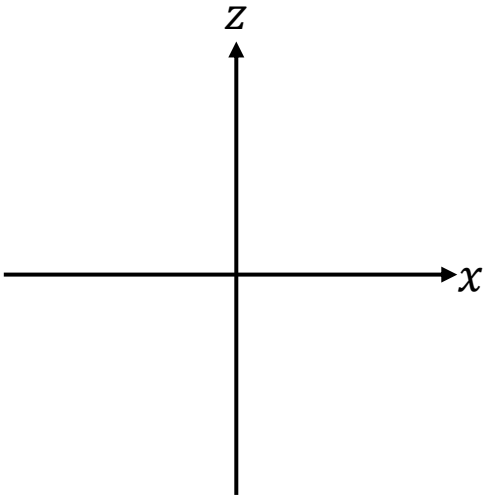
a) Calculate the energy for these transitions (in electron volts, eV). [2 marks]

b) Given that Planck's constant $h = 4.136\times10^{-15}$ eV·s, calculate the frequency and wavelength of light associated with this transition. [2 marks]

c) Sketch one of each of the $5s$, $5p$ and $5d$ orbitals (your choice):
[3 marks]







3)

a) Rationalise the following trends in the atomic radii of the group 2 elements:

Element	**Be**	**Mg**	**Ca**	**Sr**	**Ba**	**Ra**	**Element 120 (calc.)**
Radius/Å	1.12	1.60	1.97	2.15	2.22	2.15	2.00

[4 marks]

b) Ionization energy typically increases as you go to the right of the periodic table; however:

i) the 1st ionization energy of B is less than that of Be. Why? [2 marks]

ii) The 2nd ionisation of F is less than that of O. Why? [2 marks]

4)

a) Given the values below, construct a Born-Haber cycle and calculate the crystal lattice energy of $PbCl_2(s)$ in kJ/mol.

Sublimation of Pb(s)	178 kJ/mol
Ionization energy of Pb(g) to $Pb^{2+}(g)$	2160 kJ/mol
Electron attachment enthalpy of Cl(g)	–342 kJ/mol
Bond dissociation of Cl_2	236 kJ/mol
Heat of formation of $PbCl_2(s)$	–352 kJ/mol

[5 marks]

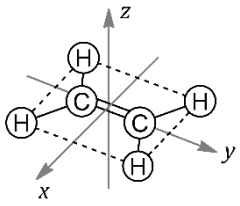
b) Predict the lattice enthalpy for strontium diiodide, $SrI_2(s)$ using the ionic radii:
1.13 Å for Sr^{2+} 2.16 Å for I^-. [3 marks]

5) Let's consider the bonding in the oxygen molecule.
   a) Draw a valence bond description of the bonding in O_2 **without** hybridising the oxygen atoms; which orbitals are interacting to make the bond(s)? [2 marks]

   b) Construct a molecular orbital diagram for O_2, label it fully. Indicate the HOMO and LUMO. Calculate the bond order. [5 marks]

   c) What is the big difference between the VBT and MO models?

6) Ethene (shown) is the simplest alkene and possesses both σ and π bonds. Note: *the circles are just to show the position of the atoms, not to represent any orbitals.*



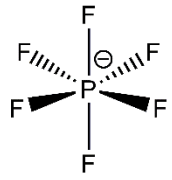
It is assigned to the D_{2h} point group and the irreducible representation for the H $1s$ orbitals (using the coordinate system shown) is:

$$\Gamma_{1s} = A_g + B_{1g} + B_{2u} + B_{3u}$$

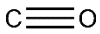
a) Draw SALCs that correspond to the individual irreducible representations. [4 × 1 mark]

b) Draw all the bonding combinations of the H SALCs and carbon orbitals for ethene. There are 6 in total, one of which is π! Hint: Think of the possible combinations of the orbitals on the two carbons, and then how those LCs match up with the H $1s$ SALCs. [6 × 1 mark]

7) Assign the point groups to the following:
[1 mark each]



Point Group =



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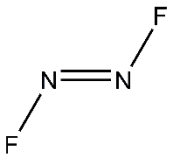
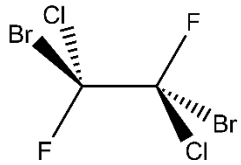


Point Group =

$SOCl_2$

Point Group =



Point Group =

BrF_5

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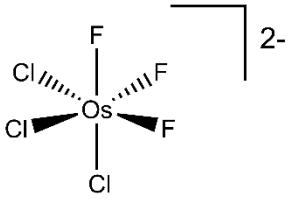

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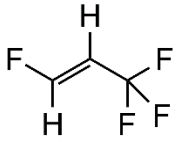
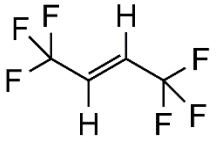
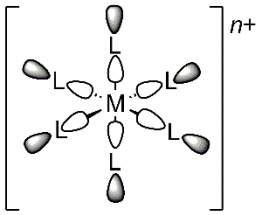
8) Hydrofluorocarbons (HFCs) are refrigerants used as more environmentally benign replacements of chlorofluorocarbons (CFCs). The latest generation of HFCs contain an alkene group and are referred to as hydrofluoroolefins (HFOs). These HFOs have 0.1% of the global warming potential as standard HFCs.
Predict the number of 1H, 13C and 19F peaks in the NMR spectra of the following HFOs: [3 × 3 × 1 marks]





9) Next semester in 59-251 with Dr Rawson you will be looking at a lot of octahedral metal complexes, where the central metal ion is surrounded by 6 ligands (L).

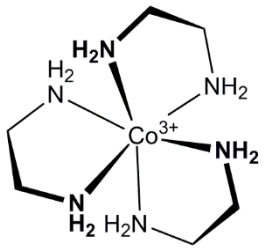


a) Considering the symmetry elements of the octahedral point group, fill out the table below to give the reducible representation for the ligand p-orbitals that are involved in σ-bonding to the central ion.
You do NOT need to reduce this (you can do that with Dr Rawson!)
[½ mark per symmetry element]

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
$\Gamma_{\mathrm{L}\,p(\sigma)}$										

b) What is the order for the O_h point group? [1 mark]

10) The *tris*(ethylenediamine)cobalt(III) complex has D_3 symmetry.



By creating an appropriate reducible representation and reducing it, predict how many peaks would appear in the photoelectron spectrum of this complex <u>that correspond to the 6 Co−N σ bonds</u>. [6 marks]

$\boldsymbol{D_3}$	**E**	**2C$_3$ (z)**	**3C′$_2$**
$\Gamma_{\mathrm{Co-N}\ \sigma}$			

11) XeF_4 is a square planar molecule with D_{4h} symmetry. The irreducible representation for total atomic motions (Γ_{tot}) is shown below:

$$\Gamma_{tot} = A_{1g} + A_{2g} + B_{1g} + B_{2g} + E_g + 2\,A_{2u} + B_{2u} + 3\,E_u$$

a) How many vibrational modes do you expect XeF_4 to have? [1 mark]

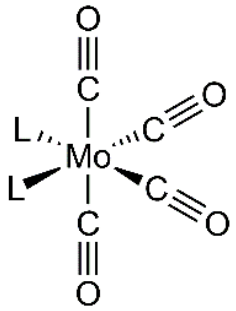
b) List all the representations that correspond to vibrations (Hint: think which of these representations you need to remove). [2 marks]

c) How many peaks would you expect to see in the **IR** spectrum? List the representation(s). [2 marks]

d) How many peaks would you expect to see in the **Raman** spectrum? List the representation(s). [2 marks]

12) In one of our tutorials, we talked about the vibrational modes of a molybdenum tetracarbonyl compound (remember in coordination chemistry a carbon monoxide residue is called a carbonyl). An isomeric compound with C_{2v} symmetry is shown here (L = triphenylphosphine):

a) Draw a set of arrows/vectors to represent all the CO bond stretches [1 mark]:



b) Fill out the following table to create a reducible representation for the carbonyl stretching, $\Gamma_{C\equiv O}$.

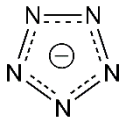
C_{2v}	E	C_2 (z)	σ_v(xz)	σ_v(yz)
$\Gamma_{C\equiv O}$				

c) Reduce $\Gamma_{C\equiv O}$ into its irreducible representations.

d) How many CO bond stretching peaks would be seen in the IR spectrum? [1 mark]

e) How many CO bond stretching peaks would be seen in the Raman spectrum? [1 mark]

13) The N_2 molecule has a very high stability, as we have discussed in class; this results in great thermodynamic instability in any larger molecules composed exclusively of nitrogen. Such molecules are of interest as rocket fuels and explosives. The first synthesis of the cyclic N_5^- anion was accomplished in 2017.

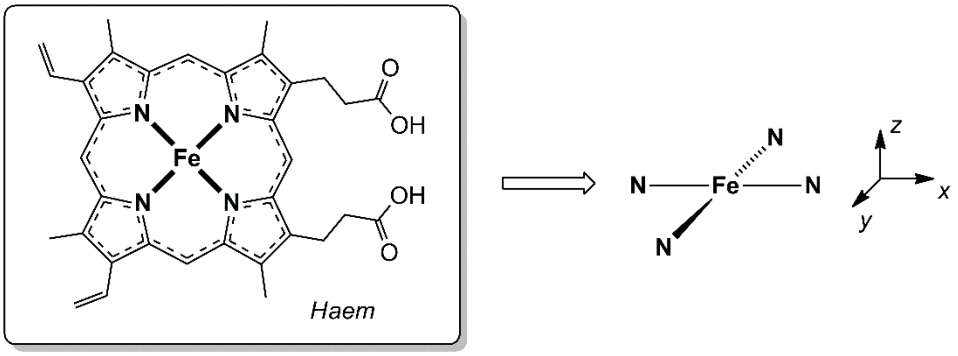


a) Cyclic N_5^- is more stable than an open chain isomer because of the additional stability imparted by having 6 electrons in its cyclic π system. What term do we give to such compounds? [1 mark]

b) N_5^- has 3 bonding π bonding orbitals, two of which are degenerate. Sketch these three bonding combinations of orbitals (hint: think about how many nodes each one might have). [3 × 1 mark]

c) Draw a molecular orbital energy diagram for this system [2 marks]

14) Haem is an iron complex made of a large conjugated ligand system called a porphyrin and an iron atom. It is a key component of many proteins, most notably haemoglobin. The four nitrogen atoms are arranged around the iron atom in a square planar arrangement; the core can thus be thought to have D_{4h} symmetry.



The iron atom forms π bonds with the ligand by interaction with the $2p_z$ orbitals of nitrogen. The irreducible representation of the four nitrogen orbitals is:

$$\Gamma_{\mathrm{N}\ 2p_z} = E_g + A_{2u} + B_{2u}$$

a) There are three SALCs that give bonding combinations with available orbitals on iron. Sketch these bonding combination (SALC+Fe orbital) [3 × 2 marks]

b) BONUS! Sketch the nonbonding SALC. [2 marks]

Wishing you all the best for the future, good luck in the rest of your exams!