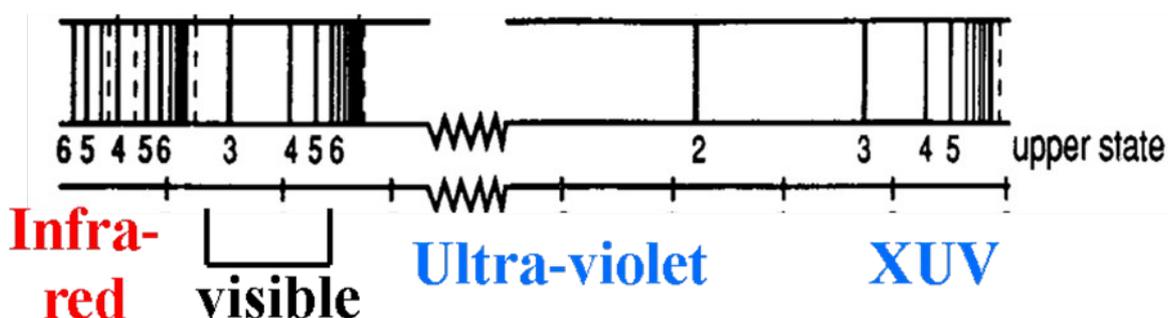


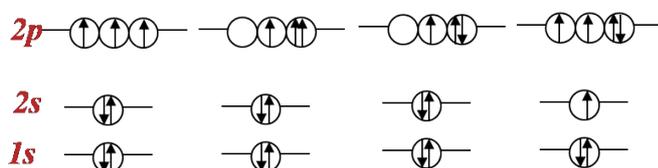
Problem Set
Atomic Structure and Periodic Trends (6 Lectures)
Prof. Peter Edwards and Dr Christiane Timmel

1. Upon what basis did Mendeleev construct his periodic table?
2. (a) Including in your answer a discussion of the concept of quantization, interpret the features of the (incomplete) H-atom emission spectrum shown below.
(b) How might such a spectrum be obtained experimentally?
(c) Which well-known equation should be used to predict the appearance of this spectrum?
(d) How would you expect the spectrum to differ if ^1H were to be replaced by ^2H ?



3. (a) What is an “atomic orbital”.
(b) Name the quantum numbers that are required to define an orbital.
(c) Give the allowed values for each quantum number.
4. “The hydrogenic wavefunctions can be expressed as the product of a radial and an angular part.” Discuss this statement (sensibly).
5. Using the expressions provided for the radial wavefunctions in the lecture course
(a) discuss which of the wavefunctions are non-zero at the nucleus.
(b) having provided a definition of the term “node”, give a general equation for the number of nodes of an orbital described by quantum numbers n and l .
(c) At large distances from the nucleus all wavefunctions, independent of the quantum numbers defining them, decay to zero. Discuss.
6. What is the Born Interpretation?
7. Define the terms *probability density* and *radial distribution function* (for a spherical orbital in the latter case is sufficient) mathematically. Why are radial distribution functions used frequently in the discussion of atomic properties and periodic trends?

8. Show how you would construct the 3s radial distribution function from the 3s wavefunction.
9. Sketch the radial wave functions and radial distribution functions for the 3s, 3p, 3d and 4s orbitals of the hydrogen atom on graphs with the same scale.
10. What do we mean by “*boundary surface*” of an orbital? Sketch the boundary surfaces of all orbitals with $l = 0, 1$ and 2 , indicating where necessary different phases of the corresponding wavefunction. Give the number of angular nodes (nodal planes) in all cases.
11. Explain the following trend in the first ionisation energies of the following ions: Be^{3+} : 217eV, B^{4+} : 340eV, C^{5+} : 490 eV.
12. Discuss the concepts of screening and penetration in many-electron atoms using the radial distribution functions you have sketched in question 9 of this problem sheet. How many radial nodes and angular nodes does each of the orbitals you sketched possess?
13. Define the term *effective nuclear charge* and discuss how it allows us to use the Rydberg formula in modified form for multi-electron atoms. Compare and contrast the energy level diagrams of hydrogen and a multi-electron atom (such as sodium).
14. Discuss the significance of the Pauli Principle, Hund’s rule and the Aufbau principle in obtaining the ground state configurations of multi-electron atoms.
15. When asked to draw the ground electronic configuration of the nitrogen atom, a student produces the following 4 sketches. Help him decide which one is the one of lowest energy (and why). Which of the configurations he has drawn is actually forbidden? Give your reasons.



16. Predict the electronic ground state configurations of Zn, Cd and Hg.
17. Predict the trend in Z_{eff} as you proceed along the second period and down Group 17.
18. Explain why the ionisation energies of O and S are lower than those of N and P.
19. (a) Define the terms *first electron affinity* and *second electron affinity* of an atom.

(b) Predict the trend in the electron affinity of the halogen atoms as you proceed down the group. Give your reasons.

(c) Account for the trends in the electron affinities (in kJ mol^{-1}) of the following atoms:

C	112	N	-7	O	141
Si	133	P	72	S	200

(d) Discuss if the electron affinity of O^- is likely to be larger or smaller than that of O.