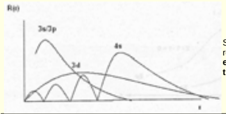
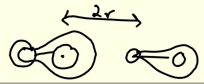
# Periodicity

- **Orbital energies**
  - **Effective nuclear charge**
    - Actual nuclear charge experienced by a certain orbital
    - Particularly interested in that of the valence orbital
    - Dictates the energy - **E = k Zeff^2 / n^2**
    - Higher Zeff means
      - **Lower** energy
      - **More compact** valence orbitals
    - Zeff = Z - shielding
      - Shielding term results from combined effect of inner orbitals
      - If electron in the **same principle quantum shell** (n) then **shielding is small**
      - The **closer to the nucleus** a shell is, the **more the shielding** (1s > 2s)
      - If order of shielding **s > p > d > f**
    - Periodicity
      - **INCREASES** across periods
        - Electrons in the same *n* don't shield each other very well
        - But *Z* increases
        - Particularly important when going across *d* and *f* orbitals
          - *d* and *f* electrons don't shield each other very well
          - So huge increase in *Zeff*
          - *f* is "core-like"?
      - **INCREASES** down groups
        - Would expect it to go down (shells added)
        - But also a large increase in *Z*
  - **Penetration**
    - 

      Some orbitals have regions of **higher e- density near the nucleus**
    - Gives them **greater effective nuclear charges** than otherwise expected
    - For example, at the *n* = *4* level
      - Maximum for 3d is lower than that for 4s
      - But 4s filled first, because of regions of probable electron density near the nucleus
      - However, most of 4s density lies above maximum of 3d, and so it doesn't shield 3d effectively
      - Therefore, once the 4s orbital is filled, 3d rapidly drops in energy and becomes core-like
      - Don't play a role in the chemistry of the *p* elements that follow
    - Penetration effect becomes more marked as *n* increases
    - So *s*-*p* separation increases
  - **Relativistic effects**
    - Both *En* and *a0* depend on the mass of the electron
    - Relativity predicts that this will change with velocity - mREL = mREST/root(1 - gamma^2)
    - Thus, as the electron goes **faster**, it's mass **increases** and this **decreases the energy and radius of the orbital**
    - Points
      - Because *s* orbitals have non-zero wavefunctions at the nucleus, they experience more nuclear charge
      - Thus, relativistic effects are greatest for *s* orbitals of large atoms - maximally at 6s, around Pt, Au (yup) and Hg
      - Since *s* orbitals shield effectively, a reduction in their radius results in a net increased shielding of *p*, *d* and *f*.
        - Can be seen in gold, where energies of *d* and *f* orbitals are high in energy
- **Atomic radii**
  - Definition
    - Hard to define because
      - Electron clouds of isolated atoms are infinite
      - The szie of an atom depends on its chemical envrionment and the nature of bonds and/or interactions it's involved in
    - So we define it in terms of the interaction we're considering
    - **Covalent radius**
      - The radius of an atom (A) within a **homoatomic bond** (A-A)
      - Half the value of the single covalent bond length (from nucleus to nucleus)
      - For elements were such a bond doesn't exist, the covalent radius can be **estimated** from a heteroatomic bond A-E (if the covalent radius of E is known)
      - Varies with oxidation state
        - Greater oxidation state means greater *Zeff* and smaller *r*
    - **Metalic radius**
      - One half of the **internuclear distance** within a metal lattice
      - Will depend on the particular packing occuring (i.e.: the **coordination number** of the metal)
        - The higher the number, the greater the length
        - Usually, coordination number of 12 listed in tables (face-centred-cubic lattice)
    - **Ionic radius**
      - The **size** of the **ion** within a **crystal lattice**
      - Can be measured directly from the lattice
      - Depends on **coordination number**
        - The higher the number, the larger the bond length
      - Depends on **charge on the ion**
        - As electrons are taken off, *Zeff* increases
        - And the radius decreases
    - **Van der Waals radius**
      - **Half the nearest contact distance between atoms in which dispersion forces only are at work**
      - Inherently loose term because there are weak and non-directional
        - Given as a range of values
      - 

        There are transient deformations and induced dipoles
  - **Across a period**
    - For *n = 1, 2, 3*
      - Increase in *Zeff* along the period
      - So decrease in size along the period
      - Total reduction of about 0.6 A per period
    - For *n = 4, 5*
      - Same
      - But *d*-block contraction results in a greater decrease in size
      - total reduction of about 0.9 A
  - **Down a group**
    - Overall trend
      - Increase in *Zeff*
      - But electrons placed further away from the nucleus (larger *n*)
      - Overall, it's an increase (about 0.2 - 0.5 A for *s*-block)
    - *p*-block elements
      - Normal for *n = 2, 3*
      - Very small increase from *n = 3 > 4* and *4 > 5*
      - Due to *d*-block contraction
        - Counteracts effects of adding another shell
    - *n = 6 p* elements
      - These are starting to involve *d* and *f* contraction
      - As well as relativistic effects
      - So they're small!
- **Electronegativities**
  - Definition
    - The **ability of an atom to attract electrons to itself within a molecule**
    - **Pauling**
      - An approximation of the **purely covalent** bond energy between A and E is the average of their homoatomic bond energies
      - However, the actual bond will be stronger, because the orbitals are different size
        - Reduction in orbtial overlap
        - But more than made-up for by electrostatic interaction
      - The difference between these two energies is a measure of the difference in ability of the two atoms to attract electrons towards them
      - We define the electronegativity of **fluorine** as **4.0**
      - And we then define that **Difference in E-negativity = root[(difference in bond strength / 95.5)]**
      - No values for elements with no compounds
    - **Alred-Rachow**
      - More theoretical
      - The nucleus exerts a force **F = e^2 Zeff / r^2** on its *s* and *p* electrons
      - Electronegativity therefore defined as 3590 * (Zeff / *Rcov*^2) + 0.74
    - **Allen**
      - Defined as the average of the one-electron energies of the *s* and *p* electrons in the ground state atom
    - All these scales standardised to fit in with the Pauling scale
      - Scales mostly follow the same trends and agree quite well
      - The main difference is that XI[Cl] > XI[N] on the pauling scale, but the other way round for the others
  - **Trends**
    - Increase across a period (increase *d Zeff*)
    - **Decrease** down a group (increased *Zeff* but valence orbitals further from nucleus)
    - Unexpected kink when entering the *4p* elements
      - *d* contraction
      - *d* orbitals don't shield very well
      - So we get an unexpectedly **high** electronegativity
      - In fact, an *increase* from the elements above
    - But the *4p* > *5p* transition is a decrease again
    - Again, the *n* = *6* elements will be more electronegative than expected (relativistic effects, *f* and *d* -block contraction)
- **Ionisation energy**
  - The **enthalpy change** when **one mole of atoms or ions** in the **gaseous state** is **oxidised by one electron**
  - **Trends**
    - **Decrease** down a group (increased *Zeff* but electrons further away)
    - **Increase** across a period (overall, see below)
    - As usual, the *4p*, *5p* and *6p* are greater than expected ( *d*-block contraction)
  - **Other factors**
    - Orbital structure
    - Completely filled shells and 1/2 filled non-*s* shells are extra-stable
    - As we go from the end of one period to the start of the next
      - Huge decrease
      - Because HUGELY favourable shell-wise
      - And HUGE increase in shielding (we're going to the next level)
- **Electron affinity**
  - The **energy released** when **one mole** of **gaseous atoms** or **ions** is **combined** with **one mole of electrons**
    - Causes a problem because is +ve if energy is released
    - Becoming common to use the "electron attachment energy"
  - **General trends**
    - Overall increase across period (increase *Zeff*)
    - Far more variable down groups
  - **Other factors**
    - Overall, it's a "fight" between *Zeff* and the added Coulombic repulsion of the added electron w/ the electron cloud
    - Greater repulsion if more compact orbitals
    - Values from Be --> F are much lower than expected, because repulsion effect wins
    - The usual *d* and *f* block and relativistic effects (more compact orbitals, so lower than expected)
      - This makes Ga = In
    - Electronic configuration also matters a lot
      - This is why carbon, for example, is so high
    - Unusually high value for Au due to relativistic effects
      - Nearly as good as halogens (which are favourable both because of high Zeff and good shell configuration)
      - Au is in fact able to form the **auride** (Au-) ion