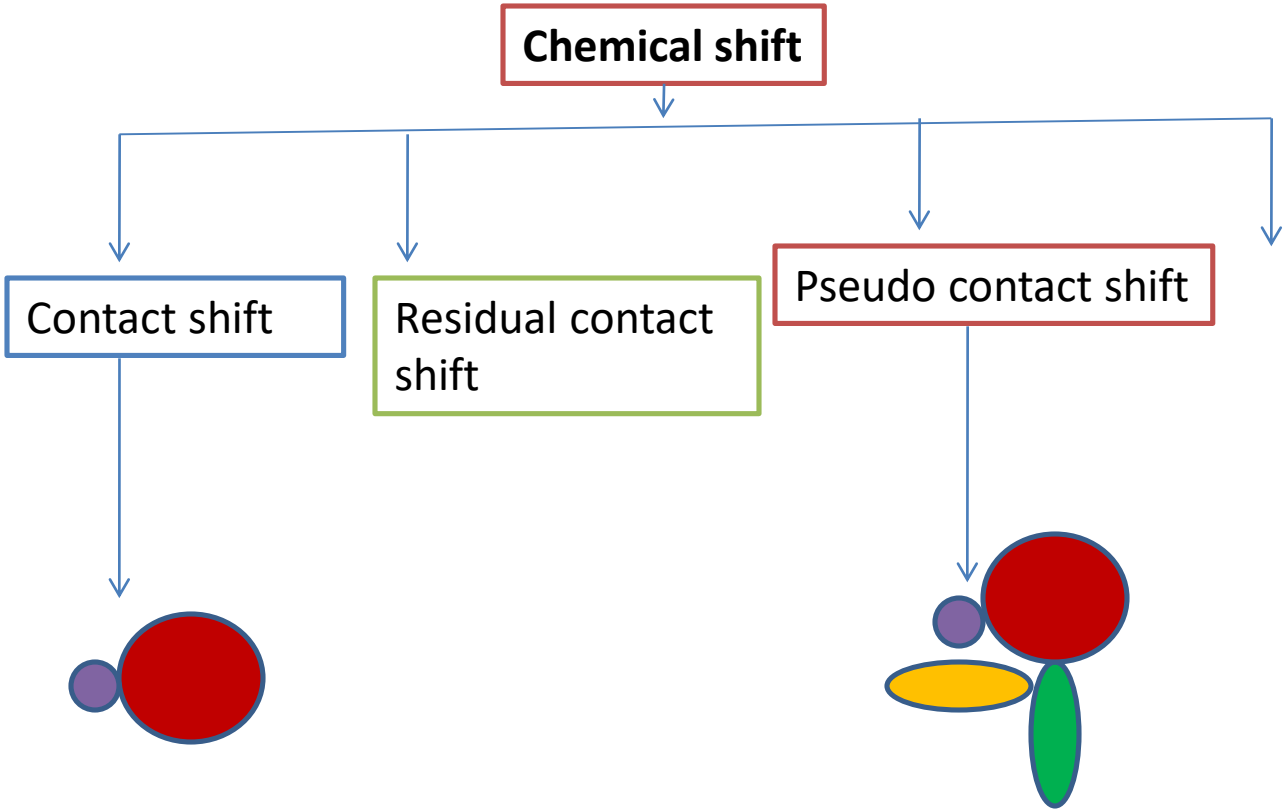
Chemical shift

- Contact shift
- Pseudo-contact shift
- Shift reagents
- Introduction to NMR of biomolecules
- Paramagnetic relaxation



• The magnetic field experienced by a nmr active nuclei is being influenced by the presence of surrounding electron cloud-termed as chemical shift

• Contact shift: Refers to influence of electron cloud present in immediate neighbour

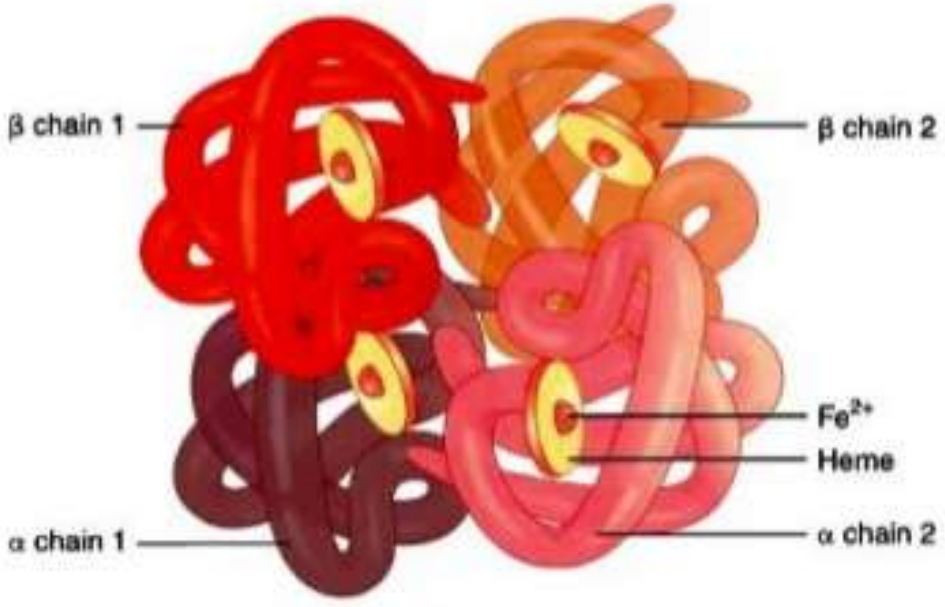
• Pseudo contact shift: Refers to presence of electron cloud in periphery/surrounding

Relevance of the subject

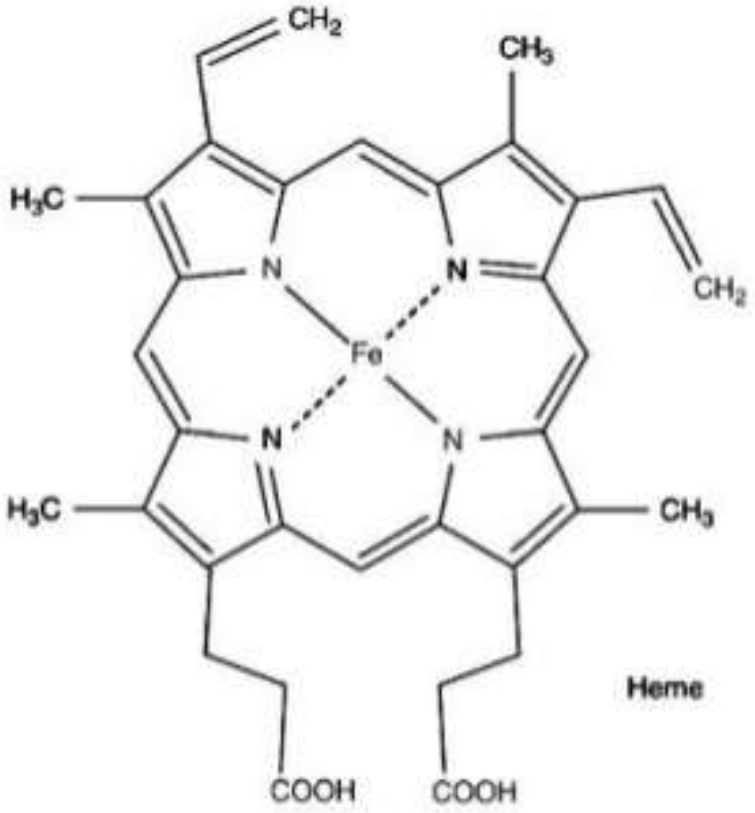
- Introduction to NMR of proteins
- Macromolecules
- NMR in 2-and 3-Dimension

- ❑ Typical example
- ❑ Structure
- ❑ Metalloenzyme

Haemoglobin

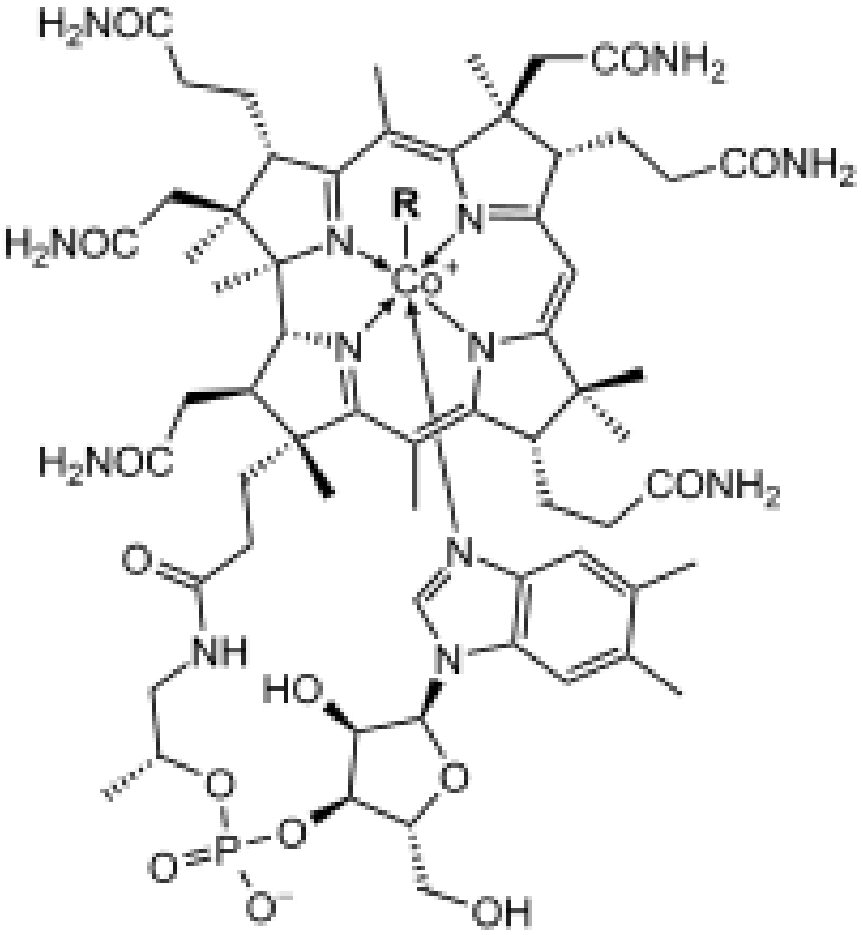


(a)

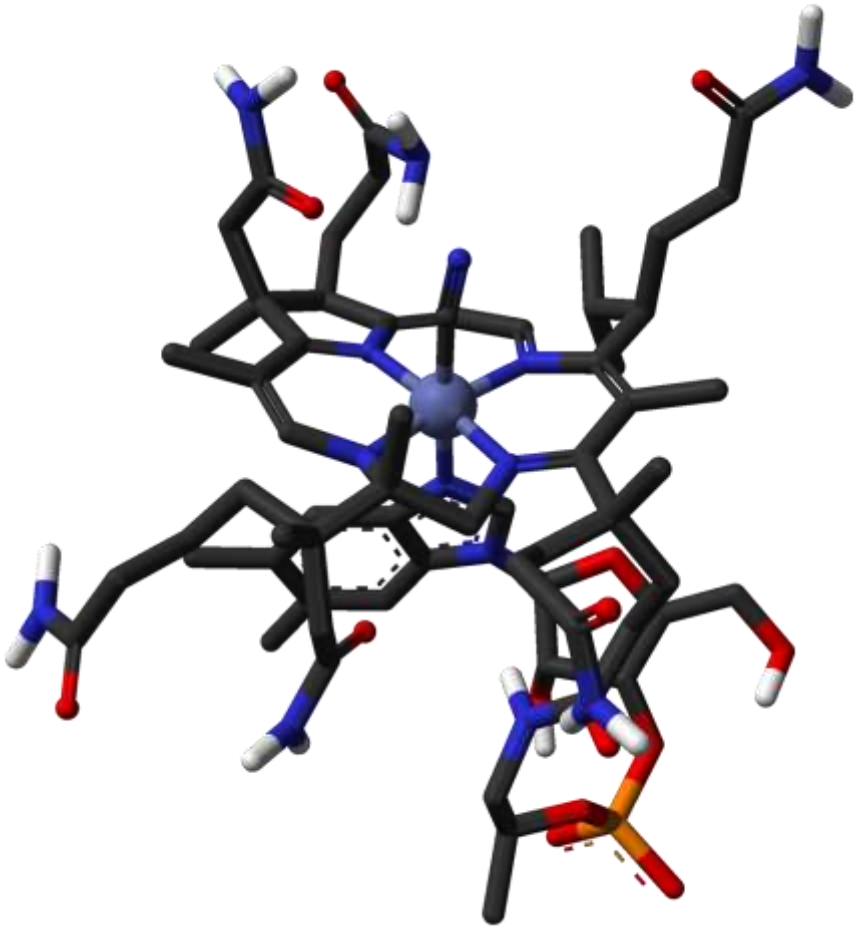


(b)

Vitamin B_{12} Cyanocobalmine



R = 5'-deoxyadenosyl, CH_3, OH, CN



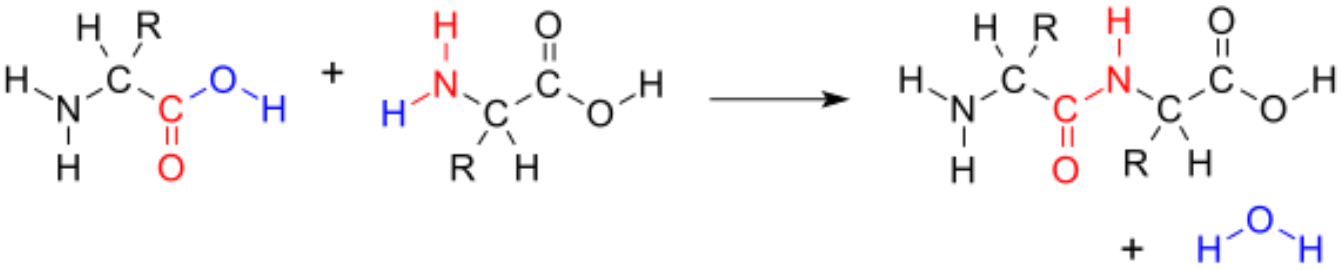
Enzymes

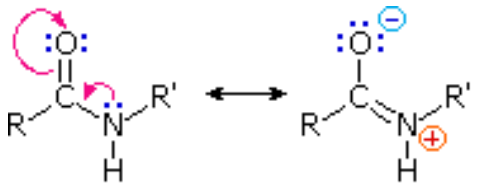
Metallo enzyme

Metal + enzyme → Polypeptide → Amide → CONH

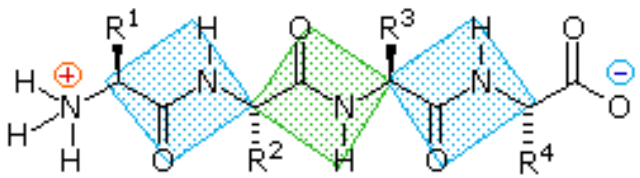
Metal + enzyme → Metal (Paramagnetic) d-or f- block

CONH → ^{13}C, ^{14}N, ^{1}H, ^{17}O





C–N double bond character in amide (peptide) bonds

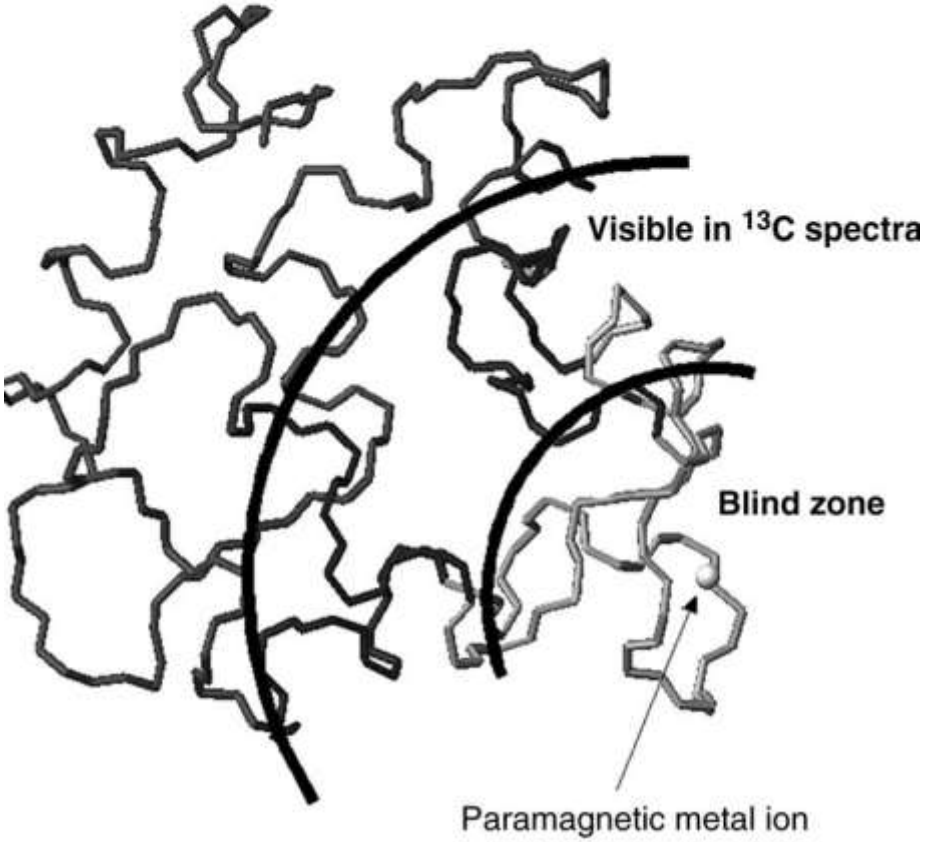


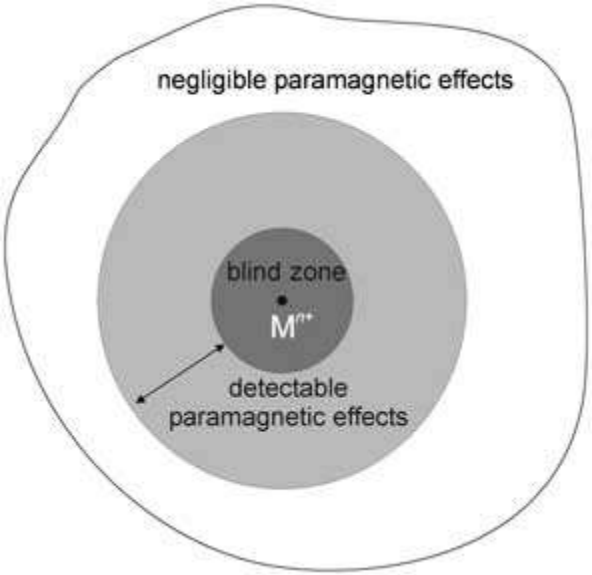
planar peptide bond segments

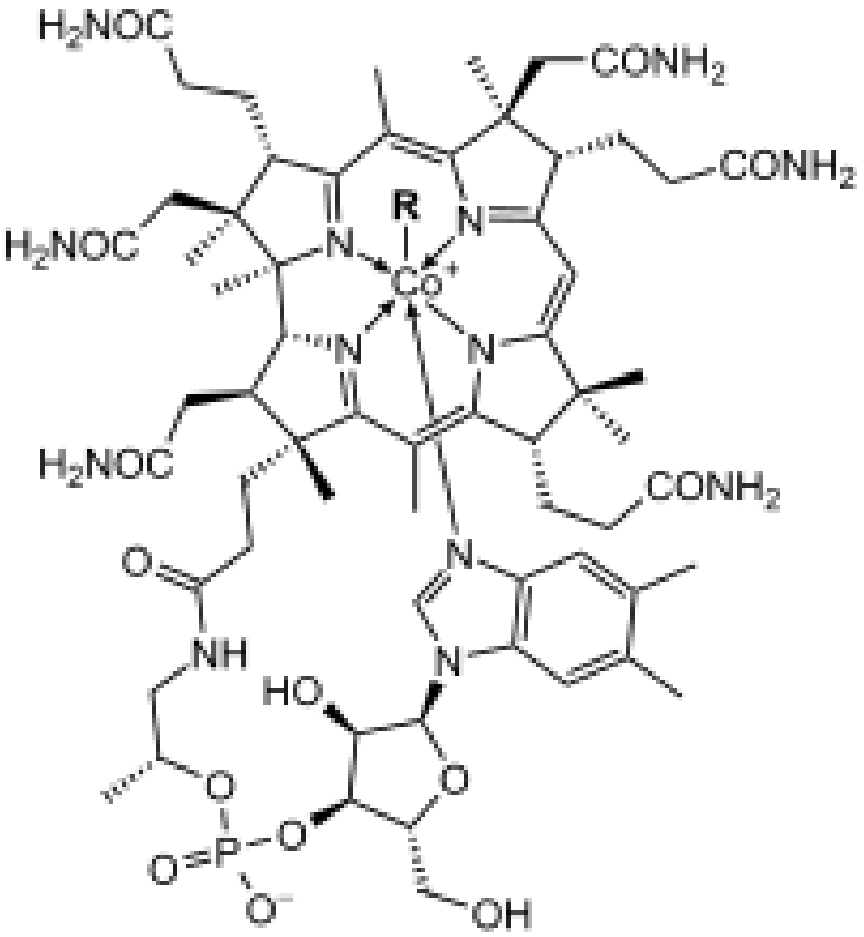
NMR Spectroscopy

What you get . . .

depends on where you look







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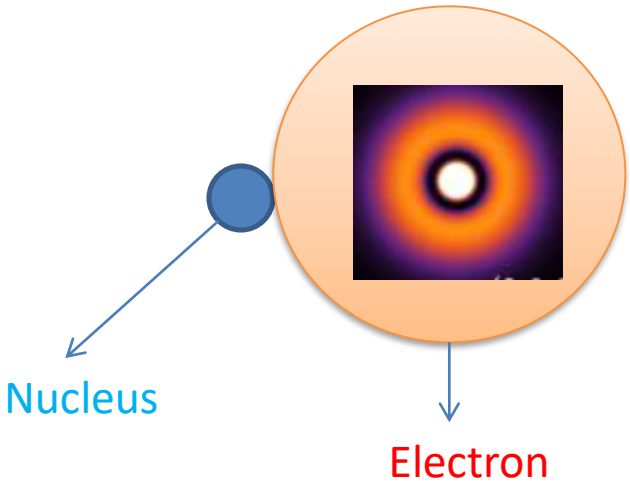
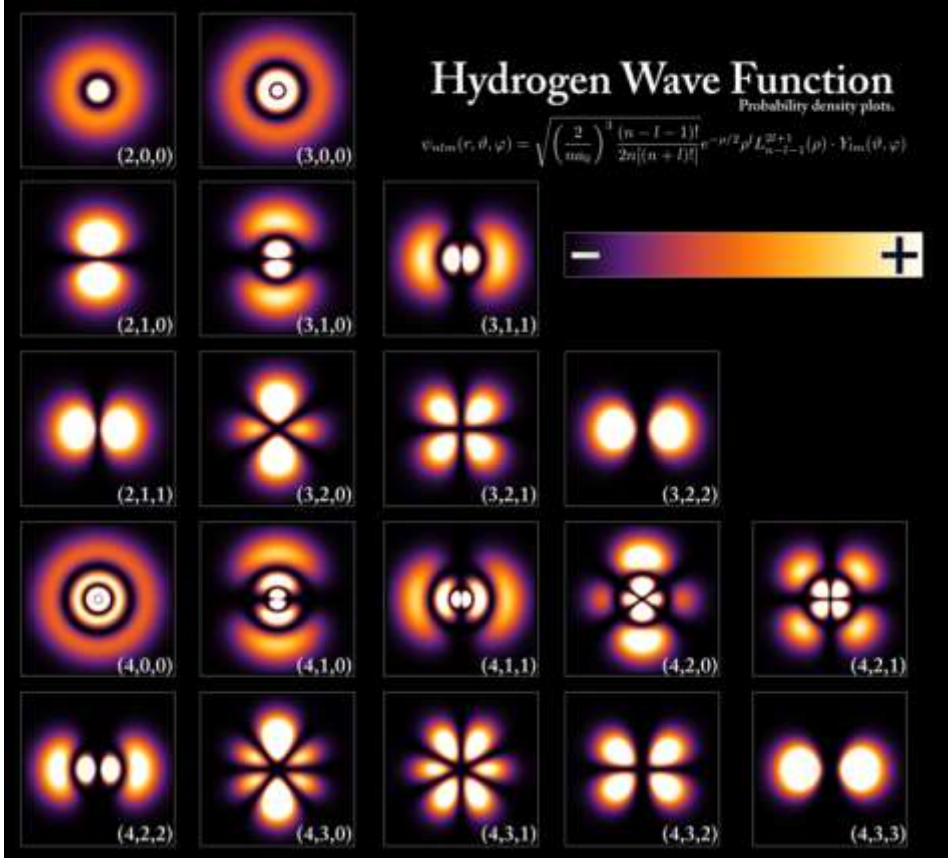
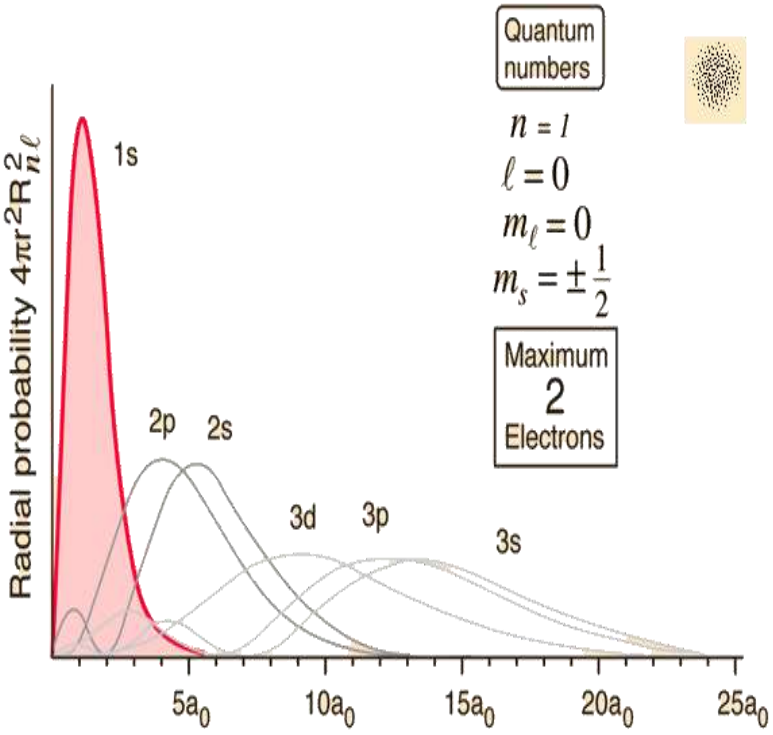
Contact shift







Pseudo contact

In H NMR, proton splits into $2m_I+1$ no. of lines in presence of external magnetic field. For a methyl group, it will split into----no. of lines

Both H and C has I value of ½, but in 1 T field ___will resonate at higher frequency and why?

Draw the nuclear spin energy levels of ^{13}C and ^{14}N in presence of external magnetic field and show possible transitions .

Both sigma and pi electrons generate secondary anisotropic fields (T/F)

Both aromatic and aliphatic alcohols show variable chemical shift values (T/F)

Free induction decay corresponds to both transverse and longitudinal decay of magnetization (T/F)