Principles of Quantum Mechanics

- indistinguishability of particles: bosons & fermions

bosons:
total wavefunction is symmetric upon interchange
of particle coordinates (space,spin)

fermions:
total wavefuncftion is antisymmetric upon interchange
of particle coordinates (space,spin)

- spin: integer (bosons) & half-integer (fermions)

Spin-Statistics theorem   (Pauli, Phys. Rev. 1940)

Schroedinger Equation
&
Exchange

Problem of two electrons (He atom or H_2 molecule):

1) H f(x1,x2) = E f(x1,x2), spatial part

2) no equation for spin part h(s1,s2)

spin and space parts are inter-dependent through Pauli Exclusion Principle:

f(x1,x2) h(s1,s2) = - f(x2,x1) h(s2,s1)

consequence: if x1=x2 and s1=s2 -> total wavefunction is zero

(I) f symmetric & h antisymmetric   (II) f antisymmetric & h symmetric
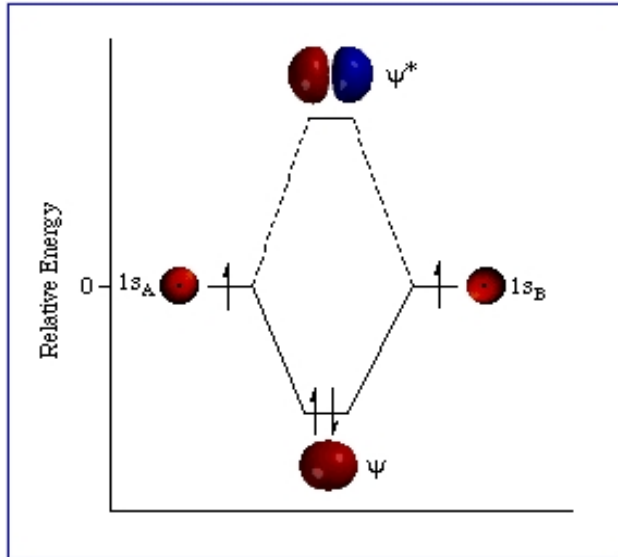
H2 molecule

(I) f symmetric & h antisymmetric   (II) f antisymmetric & h symmetric

      f has no nodes   f has nodes

electron spin ½ : s= ↑ ↓

s1,s2: four possible combinations

singlet: S=s1+s2=0

1↑ 2↓ - 1↓ 2↑   antisymmetric

triplet: S=s1+s2=1

1↑ 2↑   1↓ 2↓   1↑ 2↓ +2↑ 1↓

        symmetric

-> electrons in ATOMS:

Total Energy = electron K. E. + electron-ion Coulomb attraction
                            + electron-electron Coulomb repulsion

1s,2s,2p,3s,3p,3d, etc.: othogonal shells-> zero overlap
                      -> electrons avoid each others

nodes in spatial wavefunction:

                    spin part is of triplet or higher spin nature

                Hund's rule (ferromagnetism)

                      (atomic oxygen has spin 1)

->electrons in MOLECULES & SOLIDS:

Total Energy = (A)single-atom contributions + (B) many-atom effects

energy scales: electron K. E. (A+B, uncertainty principle) +

electron-ion Coulomb attraction (A+B)+

electron-electron Coulomb repulsion (A+B)+

ion-ion Coulomb repulsion (B)

1) e-i attraction VS i-i repulsion   (bonding)

2)   kinetic delocalisation of electrons throughout the solid
(uncertainty principle) (B)
VS
electron-electron coulomb repulsion
(electrons localise in their atomic shells) (A)

S-P BONDED SOLIDS (graphite)

s-p bonded solids: s-p orbitals are diffuse

-> inter-atomic orbital overlap is stronger than the
intra-atomic exchange coupling (Hund)

-> electrons are more delocalised than atomic-like

-> spatial wavefunction has fewest possible nodes:
symmetric-type

-> spin wavefunction is low spin: singlet-type (pairing)

DIAMAGNETISM: diamond, silicon, graphite, etc

TRANSITION METALS (Fe, Co, Ni)

3d orbital of transition metal atoms:
more localised extent compared to 3s and 3p states,
strong Hund's coupling

-> inter-atomic orbital overlap is weaker than intra-atomic
ferromagnetic coupling

-> electrons preserve part of their atomic spin moment

-> solid is magnetic

-> depending on coupling between spins:

FERROMAGNETISM, ANTIFERROMAGNETISM, PARAMAGNETISM

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to understand alignment ->   kinetic delocalisation (uncertainty principle) +
Pauli exclusion principle

ferromagnet: alignment of atomic spin

3d shell of Fe: 5 up, 1 dn   Fe↓   Fe↑   Fe↓
Co: 5 up, 2 dn   1up,5dn   5up,1dn 1up,5dn
Ni: 5 up, 3 dn

-> no electron can delocalise: unfavoured configuration

antiferromagnet: antialignment of atomic spin

3d shell of Cr : 4 up   Mn↑   Mn↑   Mn↑
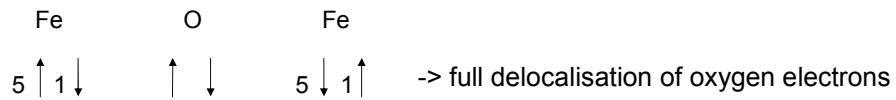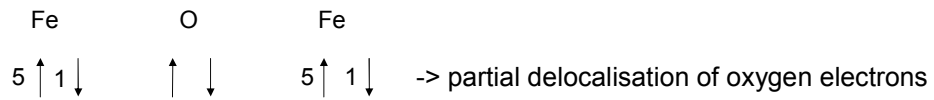Mn: 5 up   5up   5up   5up

-> no electron can delocalise: unfavoured configuration

paramagnet: no coupling between atomic spins

TRANSITION METAL OXIDES: FeO, NiO, CoO

Fe: 2+   O: 2-

-> kinetic delocalisation + Pauli principle

Fe   O   Fe

5 ↑ 1↓   ↑ ↓   5 ↑ 1↓   -> partial delocalisation of oxygen electrons

Fe   O   Fe

5 ↑ 1↓   ↑ ↓   5 ↓ 1↑   -> full delocalisation of oxygen electrons

Fe-Fe 3d orbitals overlap is strongly reduced because of O presence -> insulator

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SELF-INTERACTION ERROR IN DFT

Total Energy[n(r)]= T[n(r)]+Vext[n(r)]+Hartree[n(r)]+ Exchange-Correlation[n(r)]

Hartree[n(r)]=$\int$ dr dr' n(r)n(r') / |r-r'|

-> electron n(r) interact with itself through n(r')

Hartree-Fock theory: no self-interaction since the error in Hartree is cancelled exactly by the Fock exchange

In DFT, exchange is approximated within the LDA which is not exact
-> spurious Hartree contribution is not removed

SIE and transition metal ferro- and antiferro-magnets

effect of SIE on orbitals: interaction of electron with itself causes
the charge distribution n(r) to be more spread out,
resulting in a non physical metallisation (electron
delocalisation) of the system

* s,p metals: LDA works well since the SIE is small

* d metals: LDA still gives qualitatively good answers
because of their metallicity

Fe,Co,Ni: ferromagnetic metals:
electrons delocalise through interatomic d-orbitals overlap,
SIE is not large
i

* d insulators: FeO, CoO, NiO: antiferromagnetic insulators

Electrons keep their d-orbital
character,
interatomic d-obitals overlap is poor
and therefore SIE is large

LDA exchange is wrong:
it predicts them to be non-magnetic metals

to overcome this problem-> hybrid DFT

exchange is the problem.

B3LYP= 20 % HF + 80 % DFT(LDA, GGA)

% through fitting to large number of molecules

SUMMARY

* magnetism is due to: Spin + Pauli Exclusion Principle +
                                        Coulomb repulsion+ Uncertainty Principle

*Fe,Co,Ni: ferromagnetic metals,
                Hund's coupling of d-orbitals+ electron delocalisation

*FeO,CoO,NiO: antiferromagnetic insulators,
                        Hund's coupling of d-orbitals + electron localisation (oxygen)

*DFT works well for Fe, Co, Ni, but fails for FeO,CoO,NiO due to SIE

        possible solution is hybrid DFT: B3LYP