Chemical bonding in solids from ab-initio calculations -I

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A. Sodium and chloride ions.

B. Basic building block of the mineral halite.

C. Collection of basic building blocks (crystal).

D. Intergrown crystals of the mineral halite.
- Transfer of electron from electropositive ion to the electronegative ion
- Coulomb interactions plays an important role
- Size of the cation reduces and size of anion increases
- Electro-negativity difference between ions decide the strength of ionic bonding
Halite (NaCl) – An example of ionic bonding
ELF for NaCl

[001]

[100]
Covalent bonding

- Atoms **share** electrons to achieve electrical neutrality
- Generally stronger than ionic bonds
- Both ionic and covalent bonds typically occur in the same compound
Covalent bonding
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ELF for Diamond

[Diagram showing ELF for Diamond with [001] and [110] axes]

P.Ravindran, FME-course on Ab initio Modelling of solar cell Materials 24 February 2011 Chemical bonding in solids from abinitio calculations - I
Electron Density of Si

Electron density *difference* from sum of atoms

experiment  DFT-LDA  DFT-GGA

Electrons moved from ions and distributed uniformly in the interstitial regions.

The electrons in the interstitial regions move freely around the crystal.

Good conductors and ductile
Nonpolar Covalent Bond
Polar Covalent Bond
Polymorphs:

A. Diamond

B. Graphite
Charge Density Distribution in TiC – Mixed ionic-covalent bonding

Depleted Charge at Ti site indicate the electron transfer from Ti to C – ionic bonding

Finite charge in between atoms and their nonspherical distribution show the covalent bonding.
Charge transfer plot

Diamond (covalent)

NaCl (ionic)

Nb (metallic)
VdW forces in Biology, Chemistry and Physics
... and even in Solids

Gold – 15% \(^{(1)}\)

Silicon – 10% \(^{(2)}\)

(2) Richardson and Mahanty, *J. Phys. C* (1978)
AlP (polar)

NaCl (ionic)

Al (metallic)
elf=0.5
FIGURE 11. ELF for the diamond structure of C, Si, Ge, and Sn. The figures in the upper row are computed from the valence density, in the lower row from the total density.
\[ \text{Cs}_2\text{Pt} \]

- Ionic insulator
- \( \text{Ni}_2\text{In} \) structure type
- Affiliation to the alkali-metal monochalcogenides
- AIM charge of Pt: \(-1.6\) e\(^-\)

TB-LMTO-ASA Pt 6s fatbands

Domains of the ELF (0.35)

\( (\text{Cs}^+)_2(\text{Pt}^{2-}) \)
Formation of molecular like H-Ni-H (NiH₂) sub units
Charge transfer

\[ \Delta \rho(r) = \rho(r)_{\text{comp.}} - \rho(r)_{\text{atomic}} \]

Ionic bonding between H and the host lattice
The polarization of negative charges at H towards the electropositive La and In.
Charge density  
Charge transfer  
ELF

Ravindran et al. PRL (2002)
Chemical bonding

$KMgH_3$ – example for dominant ionic bonding

(a) Charge density
(b) Charge transfer
(c) ELF
La$^{3+}$Sc$^{3+}$O$_3^{6-}$

It is not a perfect ionic material and has finite covalency
One-dimensional Oxides

Crystal structure of Ca$_3$Co$_2$O$_6$

- Rhombohedral ($R-3c$ space group) with 22 atoms/unit cell
- Alternating face-shared octahedra and trigonal prisms form one-dimensional chains along $c$-axis
- Hexagonal with 66 atoms/unit cell
- Co spins are arranged along $c$-axis
- For every two-up spin chain, there is one down-spin chain resulting in Ferrimagnetic structure
Charge density and related features in Ca$_3$Co$_2$O$_6$

- **Very weak interaction between Co1 and Co2**
- **Magnitude of covalent interactions between Co1-O and Co2-O are different.**
- **There is strong covalent interaction within the chain and ionic interaction between Ca and the chains.**
Bonding study from *density of states* analysis

- Ca is in completely ionized state, donating almost all its valence electrons to O.
- Co is in two different oxidation and/or spin states, seen from difference in the topology of DOS curves.
- Oxygen is energetically degenerate with Co1 and Co2 forming strong covalent bond with them.
Partial Density Of States in KGaH$_4$

- Well separated Ga-$s$ and -$p$ state
- Energetically degenerated H-$s$ and Ga-$p$ states
- Strong covalent bonding Ga-H
- Ionic bonding between K and H
Charge Density Distribution in KGaH$_4$
Visualization of lone pair
From ELF
Lone pair electrons in BiMnO$_3$

Seshadri and Hill, Chemistry of Materials, 13, 2892 (2001)
ELF isosurface (0.7) show that Bi lone-pair electrons are responsible for ferroelectricity.

Ravindran et al. PRB (2006)
Chemical bonding in BiFeO$_3$ from DOS analysis

Isolated Bi-s is the lone pair electrons.

Negligible Bi electrons in the valence band indicate ionic bonding.

Degenerate Fe-d and O-p states indicate the covalent bonding.
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(a) Charge density
(b) Charge Transfer
(c) ELF