lecture 12.1.2012

we had so far:

binding in clusters and their appearances in mass spectra
 a) undirected van-der-Waals bonding

today:

b) ionic bondingc) covalent bondsd) metallic bonding

Mackay icosahedra







magic numbers



Fig. 5. The first five Mackay icosahedra. N = 13, 55, 147, 309, and 561, respectively.

geometric shell structure of rare gas clusters



undirected bonding leads to icosahedral growth



(a)



(b)

however: the rare-gas crystals are FCC !

Icosahedra maximize the number of nearest-neighbour attractive interactions: it is greater than for a FCC/HCP cluster.

e.g., for a 13-atom cluster : Icosahedra has 5 NN FCC has only 4 NN



However, packing of hard spheres as icosahedra gives frustration as N becomes large, see the gaps!

cross-over between 800 and 10000 atoms from icosahedra to fcc

geometrical packing of Magnesium clusters and electronic signatures!



Diederich et al., PhD thesis, Rostock

try to get order into the isomers: free-energy landscapes

example: protein folding



Folding occurs through the progressive organization of ensembles of structures [shown here for the src-SH3 domain (**left**)] on a funnel-shaped free energy landscape (**right**). Conformational entropy loss during folding is compensated by the free energy gained as more native interactions are formed.

application to isomerization in clusters

Visualization: Disconnectivity Graphs

At a given energy, minima can be divided into 'basins' whithin which minima are mutually accessible via transition states lying lower than this energy. Minima in different basins cannot interconvert at this energy.

Lowering the energy causes basins to split as the threshold descends below the connecting transition states.

In a disconnectivity graph, basins are calculated at a series of energies, plotted on a vertical scale. Each basin is represented by a node at the appropriate level. Lines join parent nodes to their daughters in the level below

Adjacent are some schematic potential energy curves and the corresponding graphs. Below are results for Lennard–Jones (LJ) clusters.



disconnectivity graphs



The energy scale is in units of the Lennard-Jones well-depth.

above.





http://brian.ch.cam.ac.uk/index.html





David Wales et al.

proteins



David Wales et al.

binding in clusters

a) undirected bonding (Van-der-Waals)

b)ionic

c) covalent

d)metal

additional terms to the interaction potential:



- monopole dipole interaction
- dipole-dipole interaction
- self energy of the dipole

ionic bonding in alkali halides





Ionic lattice structure

T.P. Martin

Fig. 5. Mass spectrum of $Na(NaI)_n^+$ clusters. The interval between the oscillations corresponds to the number of atoms needed to cover one face of cuboid-shaped clusters.



Stable configurations for alkali halides with a small number of atoms



conclusion: ionic clusters very soon show the bulk structure





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binding in clusters

a) undirected bonding (Van-der-Waals)

b) ionic

c) covalent

d) metal bonding

basics of covalent bonding: the Hydrogen molecule

- The classic case of <u>covalent bonding</u>, the hydrogen molecule forms by the overlap of the wavefunctions of the electrons of the respective hydrogen atoms in an interaction which is characterized as an exchange interaction. The character of this bond is entirely different from the <u>ionic bond</u> which forms with <u>sodium</u> <u>chloride, NaCl</u>. If you measure then energy balance when you form H+ and Hions and examine the attractive force between them, the energy required is positive for any value of ion separation. That is, there is no distance at which there is a net attractive interaction, so the bond cannot be ionic.
- The electron distribution around the protons of the hydrogen is described by a quantum mechanical wavefunction, and the wavefunction which describes the two electrons for a pair of atoms can be symmetric or antisymmetric with respect to exchange of the identical electrons. From the <u>Pauli exclusion principle</u>, we know that the wavefunctions for two identical fermions must be antisymmetric. The <u>electron spin</u> part of the wavefunction can be symmetric (parallel spins) or antisymmetric (opposite spins), but then the space part of the wavefunction must be the opposite. That guarantees that the entire wavefunction (the product of the spin and space wavefunctions) is antisymmetric. The two possibilities for the spatial wavefunctions for distant hydrogens are shown below.

basics of covalent bonding: the Hydrogen molecule



when the hydrogen atoms are brought close together the symmetric spatial wavefunction leads to a bonding configuration of electrons and the antisymmetric one does not. The actual electron charge density is given by the square of the magnitude of the wavefunction, and it can be seen that the symmetric wavefunction gives a high electron density between the nuclei, leading to a net attractive force between the atoms (a bond).

basics of covalent bonding: the Hydrogen molecule

The exchange interaction (an entirely quantum mechanical effect) leads to a strong bond for the hydrogen molecule with dissociation energy 4.52 eV at a separation of 0.074 nm. The potential energy of the antibonding orbital shown gives some insight into why a third hydrogen atom cannot bond to the two atoms of the hydrogen molecule. It would be in an anti-bonding situation with one of the other hydrogen atoms and would therefore be repelled. We say that the bond in the hydrogen molecule is "saturated" because it cannot accept another bond.



For larger molecules or clusters: Quantum-chemical methods, e.g., Hückel approximation

Hückel calculations for Na clusters



Carbon: a model case for covalent bonding





the fullerenes

In 1985, identification by Kroto, Smalley, Curl and co-workers of the C_{60} molecule as being a truncated icosahedron, with very high symmetry (Ih) :

all 60 atoms are equivalent, and are three-fold coordinated. Also, fullerenes with 70, 76, 78 (3 isomers), 84 (2 isomers), ... atoms.



(Named after the architect Buckminster Fuller)

Buckminster-Fulleren







"Buckminister-Fulleren"





Lanthan Atom in C_{60}

Small carbon clusters

Competition between rings and chains. Chains are more floppy (entropy favoured), but rings are energetically favoured above N=10.

Magic number for ionized carbon chains : 7,11,15 ...

Linear structures of C_3 and C_5 . The spectral lines due to the C_3 molecule were seen in 1881 in the spectrum of a comet, but not identified until 1951. C_5 identified in the infrared spectrum of a carbon star.



mass spectrum of carbon clusters by laser vaporization



Cluster Size (Atoms)

mass spectra of silicon clusters

charged Si clusters show magic number n=6, 10, 16 and 32, but a maximum in the spectrum is not followed by a deep minimum for n+1 atoms ! (Photofragmentation shows no monomer evaporation).



structure of small Si clusters















proposed basic building blocks: distorted octahedral Si₆ and adamantane (a diamond fragment) Si₁₀. The lowest energy structure for Si₁₀ is the high density tetracapped trigonal prism

Compared to carbon, reduced tendency to participate in p-bonding

structure of hydrogenated Si clusters



Hydrogen atoms saturate the silicon clusters by taking up dangling sp³ bonds: more open structures

metal chalcogenide clusters : ZnS mass spectrum



MoS platelet



Seifert et al.

Hydrogen bridge binding: molecular clusters, e.g. (H₂O)_N



Ring structures. One hydrogen per molecule involved in H bond. Near-planar structure of H bonds. Frustration for odd cycles. Tunneling splitting pattern of the vibration spectrum (like for ammonium)

Five-membered ring structure of the 20 water molecule cluster. Note that only six-membered rings are present in hexagonal ice.

structure of protonated water clusters



Most clusters consist of a number of water molecules surrounding a hydronium ion, H_3O^+ . The $(H_3O^+)(H_2O)_3$ moiety, with $C_{3\nu}$ symmetry, is the smallest unit where the inner hydronium is completely hydrogen bonded. The structure of $(H_3O^+)(H_2O)$ is however $H_2O\cdots H^+\cdots OH_2$ binding in clusters

a) undirected bonding (Van-der-Waals)

b) ionic

c) covalent

d) metal bonding

Schematics of metal binding in a cluster



A cluster of simple metal atoms can be considered as a metallic quantum dot. In the corresponding bulk materials the electrons need much more space.



the spherical jellium model: basic idea



the spherical jellium model: basic idea



the spherical jellium model: basic idea



c.f. nuclear physics

Woods Saxon potential

compare: potential energy function for atomic nucleus



Fig. 81 Realistische Darstellung der Verhältnisse beim Schalenmodell. Neutronenniveaus eines Kerns mit N=80 im Kernpotential; R und a sind Parameter des Woods-Saxon-Potentials Gl. (6.8); nach [Bei 64]

Mayer-Kuckuk

The spherical jellium model: role of the potential like in *nuclear physics*



Explains the magic numbers of neutral alkali clusters : 2, 8, 20, 40, 58, 70, 92 ...

Also explains the magic numbers for divalent metals such as zinc or cadmium, at 4,9,10,17,20,29 ... atoms.

$$2(2l+1)$$

electrons

After: Mayer-Kuckuk, Kernphysik

very important:

in the atomic nucleus: additional influence of spin-orbit interaction.

Can be neglected in clusters

Mayer-Kuckuk



The jellium model for clusters: density functional theory



(Nearly) free electrons in a small volume. The electronic properties can either be described by a simple jellium model or more sophisticated by the density functional theory. In all cases the electron distribution extends over large parts of the jellium sphere. The corresponding eigenfunctions lead to the shell structure.



larger clusters: self-consistent spherical jellium-background model



W. Ekardt Physical Review B Vol.29, Nr. 4 15Feb.1984

for very large clusters: close to bulk



compare: metal surfaces - resulting electron density

electron density n(z) shows oscillations (Friedel oszillations)
n(z) spills out beyond the ionic charge (electron spill-out)
spill-out produces a surface dipole





<u>Ursache der Oszillation:</u>

Elektronen mit festen Wellenvektor versuchen pos. Hintergrundladung abzuschirmen; hieraus folgen leichte Verschiebungen der einzelnen Atomlagen im Bereich der Oberfläche

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