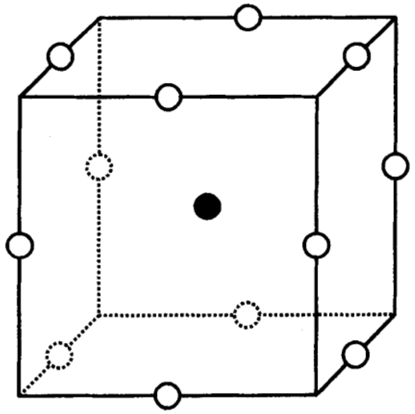
Nanoclusters and Magic Number

(Ref: Charles P.Poole Jr., Frank J. Owens; Introduction to Nanotechnology)

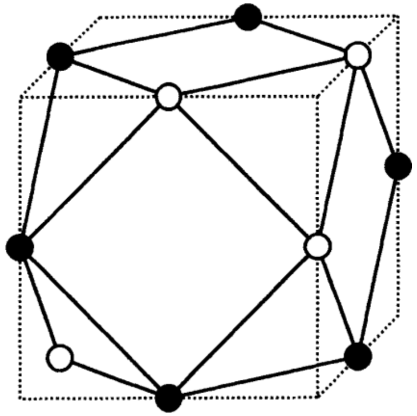
- Clusters are collections of atoms lying between individual atoms/molecules and bulk materials.
- In some materials, certain collections of atoms are more preferred due to energy minimization and exhibiting stable structures and providing unique properties to the materials.
- These collections of atom providing stable structures to the materials are called as MAGIC NUMBER.
- For example, one of the combination of 55 atoms of gold provides stable structure and hence its magic number is 55.
- For this combination, surface area is minimized. By further adding/removing any atom leads to the increase in surface to volume ratio. So, in this sense, gold prefers to form a clusters of 55 atoms which is a stable geometrical structures due to local minimum. This is called as magic number and is arbitrary number.
- These crystals have certain unique properties and can be used for certain specific applications.

- Many properties of solid depends on its microstructure.
- Most of the metallic system in solid state form close-packed lattices. For e.g; Ag, Au, Cu, Al, Co, Pb, Pt and Rh are face cantered cubic (FCC) structures.
- It can be seen that each atom has 12 nearest neighbours as shown in following figure, wherein; 12 neighbours surrounds an darkened atom located in the centre of a cube of FCC lattice.



- These 13 atoms constitute the smallest theoretical nanoparticle for FCC lattice.

- In the following figure 14-sided polyhedron, called a *dekatessarahedron*, is generated by connecting the atoms with planar faces.
- In 1998, Sugano and Koizumi call this polyhedron a *cuboctahedron*.
- This 14-sided polyhedron has six square faces and eight equilateral triangle faces.
- If another layer of 42 atoms is laid down around 13-atom nanoparticle, one obtains a 55-atom nanoparticle with the same dekatessarahedron shape.
- Similarly, larger nanoparticles with the same polyhedral shape are obtained by adding more layers, and the sequence of numbers in the resulting particles, N=1, 13, 55, 147, 309, 561, ……….. are called as *structural magic numbers.*



- For n layers the number of atoms N in this FCC nanoparticle is given by the formula

$$N = \frac{1}{3}[10n^3 - 15n^2 + 11n - 3]$$

- Number of atoms on the surface N_{surf} is given by the formula

$$N_{surf} = 10n^2 - 20n + 12$$

- For each value of n, number of atoms on the surface, as well as the percentage of atoms on the surface is listed in the table presented in next slide.

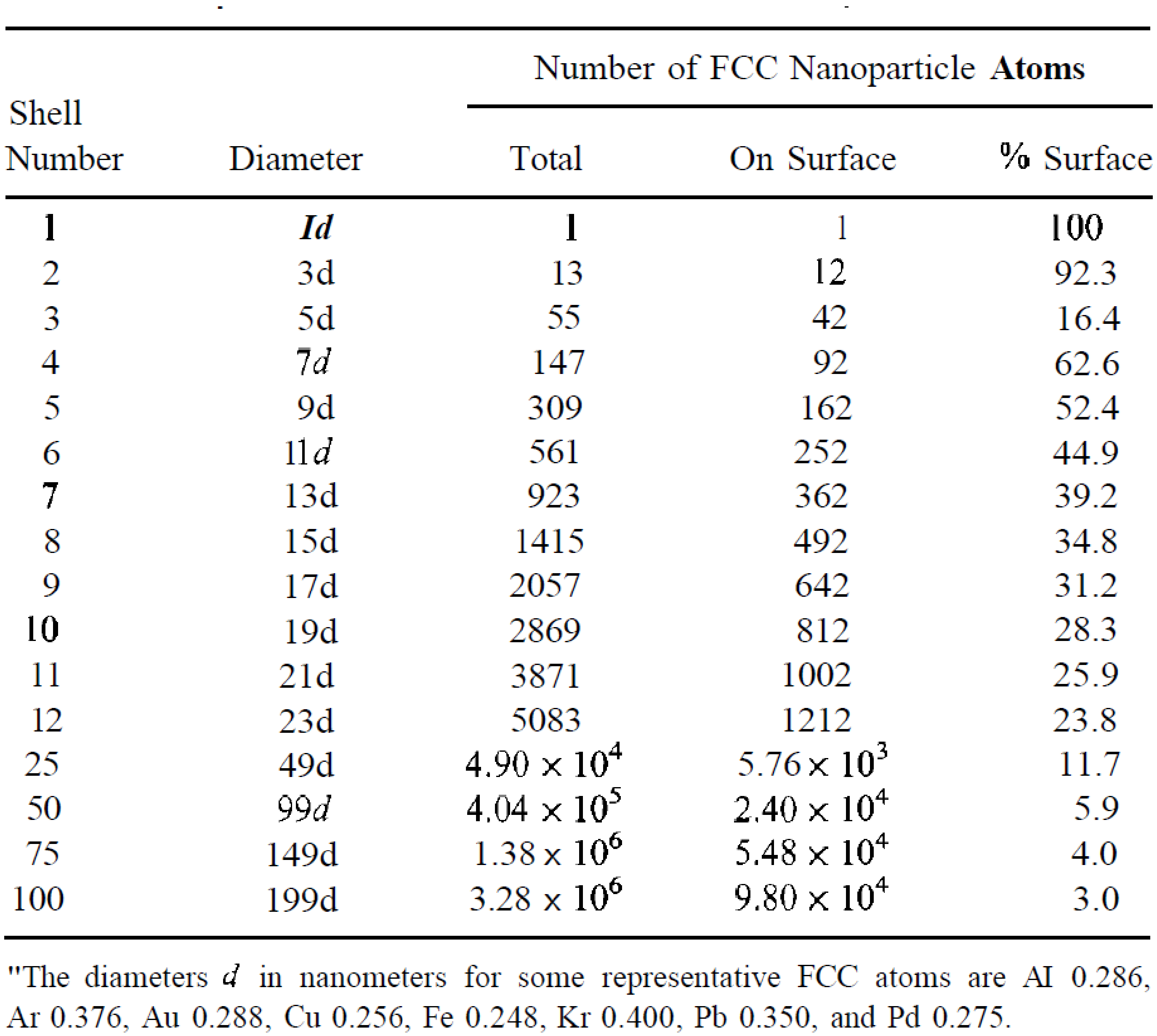
- Table also lists the diameter of each nanoparticle, which is given by the expression

  Diameter = (2n-1)d, where ‘d’ is the distance between the centres of nearest neighbour atoms.

  $d = \frac{a}{\sqrt{2}}$, where a is the lattice constant.

- If the same procedure is used to construct nanoparticles with the hexagonal close-packed structure, a slightly different set of structural magic numbers is obtained, namely; 1, 13, 57, 153, 321, 581, …..

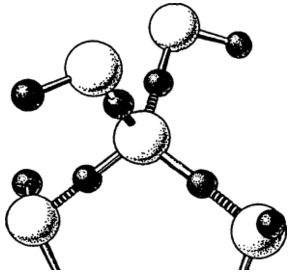
Number of atoms (structural magic numbers) in rare gas or metallic nanoparticles with face-centered cubic close-packed structure



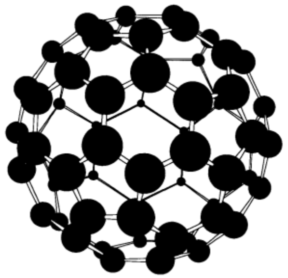
Shell Number	Diameter	Number of FCC Nanoparticle **Atoms**		
		Total	On Surface	% Surface
1	***1d***	**1**	1	100
2	3d	13	12	92.3
3	5d	55	42	16.4
4	7*d*	147	92	62.6
5	9d	309	162	52.4
6	11*d*	561	252	44.9
7	13d	923	362	39.2
8	15d	1415	492	34.8
9	17d	2057	642	31.2
10	19d	2869	812	28.3
11	21d	3871	1002	25.9
12	23d	5083	1212	23.8
25	49d	4.90×10^4	5.76×10^3	11.7
50	99*d*	4.04×10^5	2.40×10^4	5.9
75	149d	1.38×10^6	5.48×10^4	4.0
100	199d	3.28×10^6	9.80×10^4	3.0

[a] The diameters *d* in nanometers for some representative FCC atoms are Al 0.286, Ar 0.376, Au 0.288, Cu 0.256, Fe 0.248, Kr 0.400, Pb 0.350, and Pd 0.275.

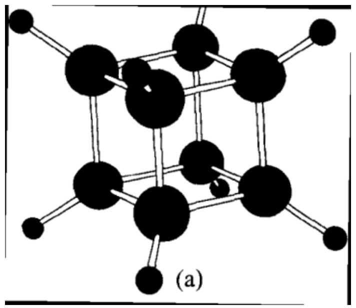
- Magic numbers that we have discussed are called structural magic numbers.
- They have been arise from minimum volume, maximum density nanoparticles that approximate a spherical shape and have close-packed structures characteristic of a bulk solid.



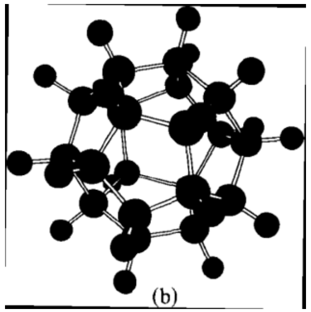
Hydrogen-bonded cluster of five water molecules



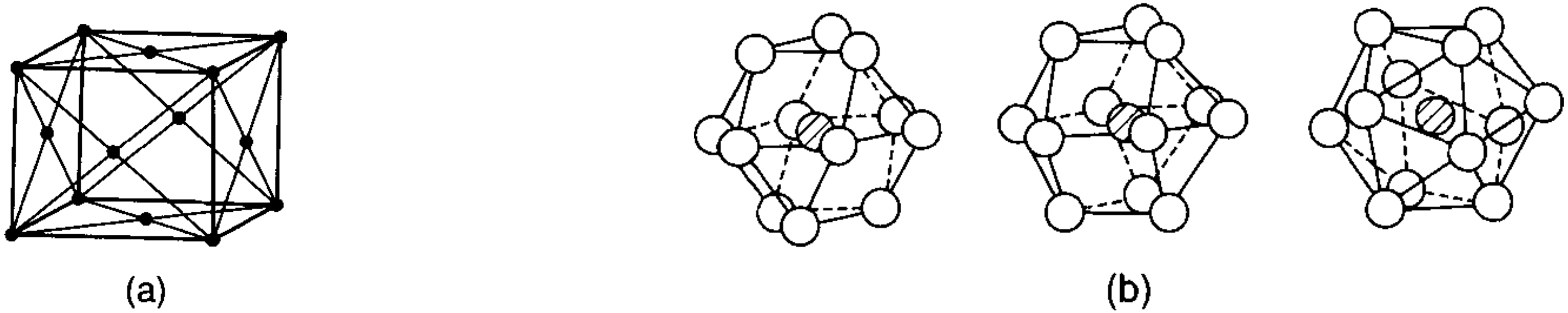
Structure of C_{60} fullerene molecule



Carbon cube structure of C_8H_8



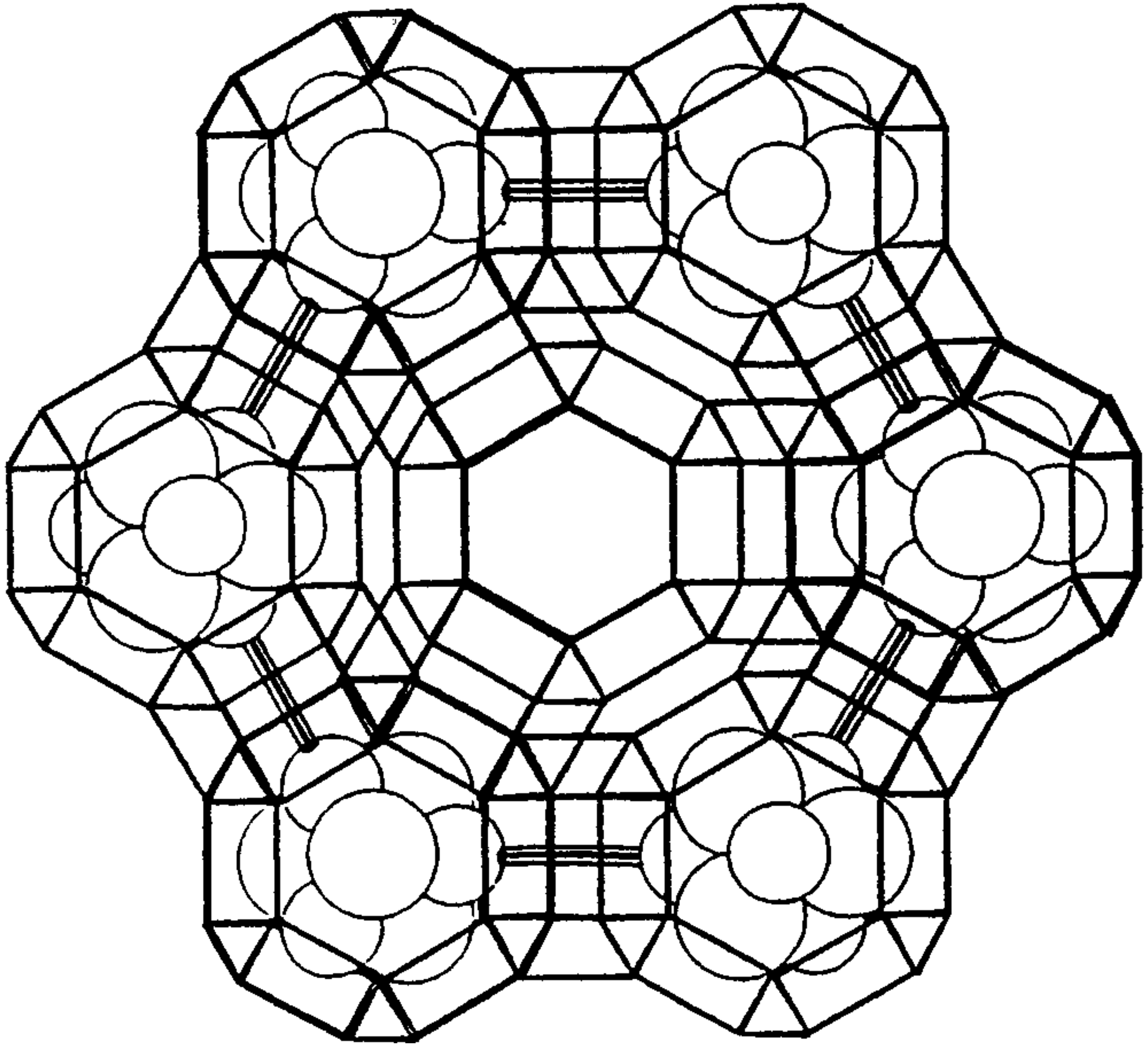
Carbon dodecahedron structure of $C_{20}H_{20}$



(a) The unit cell of bulk aluminium, (b) Three possible structures of Al13; a face-centered cubic structure (FCC), and hexagonal close-packed structure (HCP), and and icosahedral (ICOS) structure

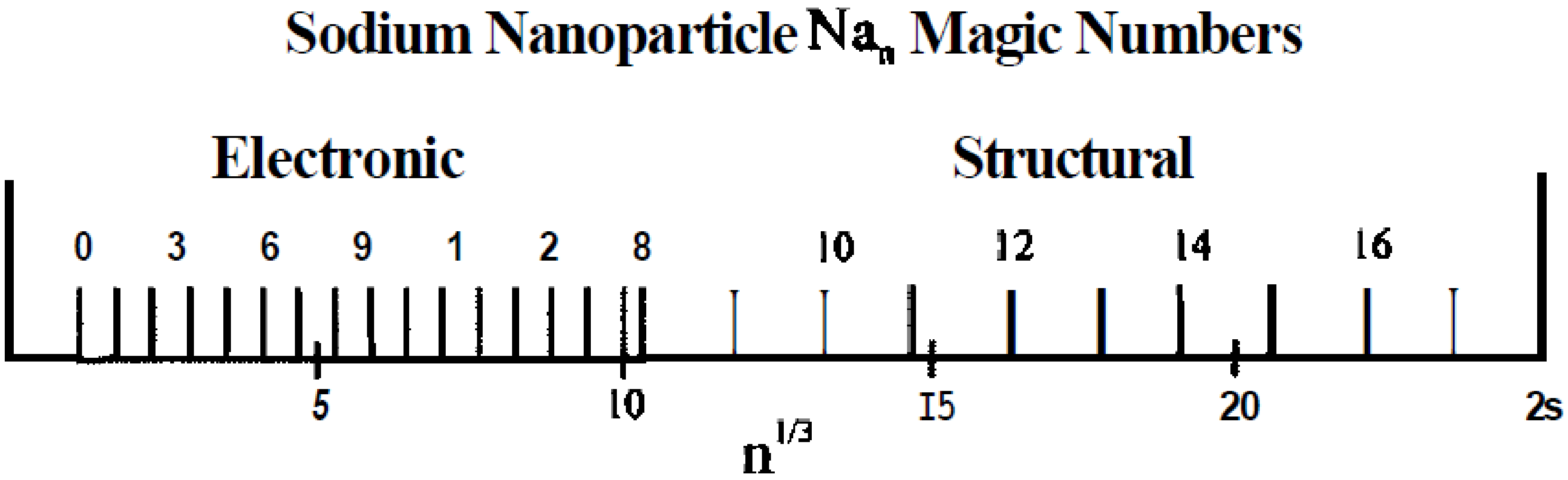
Zeolite-Y structure showing six sodalite cages (diameter-0.5 nm) occupied by Cd_4S_4 tetrahedral clusters, and one empty supercage (diameter-1.3 nm) in the center.

Ref: H.Herron and Y.Wang, Nanomaterials, Synthesis, Properties and Applications, A.S.Edelstein, ed., IOP, Bristol, UK, 1996, P.73.



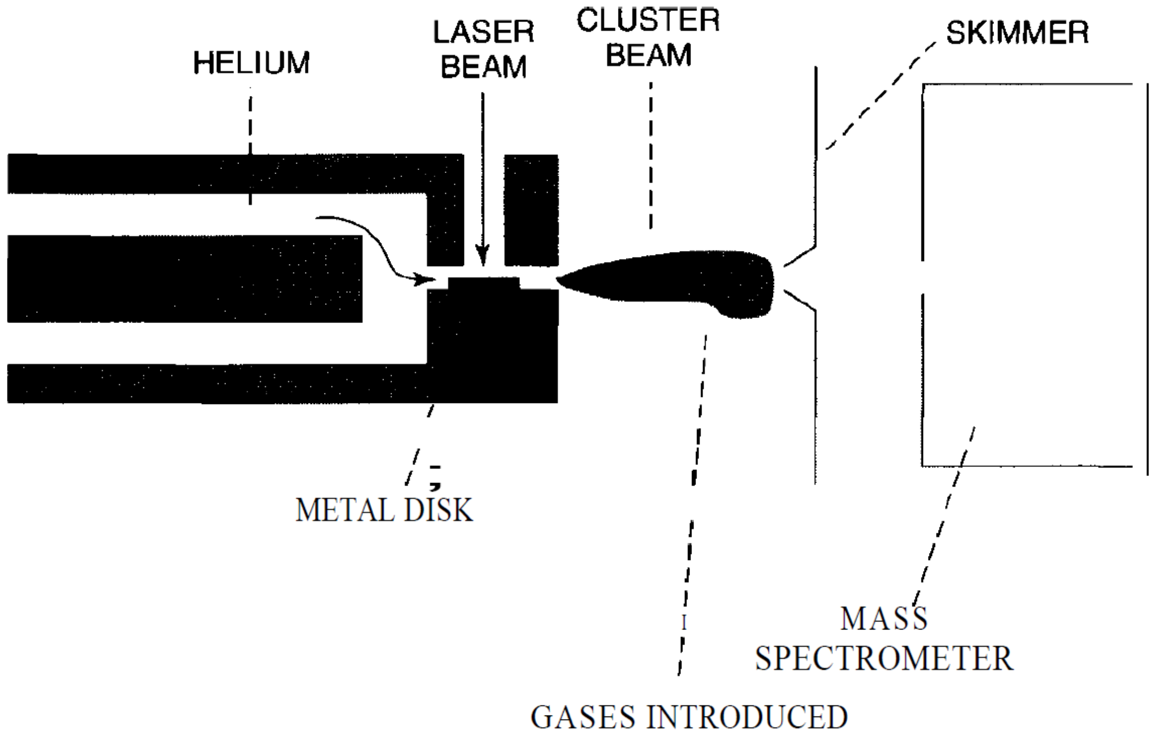
- Magic numbers as discussed above has not taken any account of the electronic structure of the constituent atoms in the nanoparticle.
- Sometimes the dominant factor in determining the minimum energy structure of small nanoparticles is the interactions of the valence electrons of the constituent atoms with an averaged molecular potential, so that the electrons occupy orbital levels associated with this potential.
- Atomic cluster configurations in which these electrons fill closed shells are especially stable, and constitute electronic magic numbers.
- Their atomic structures differ from the FCC arrangement.
- When mass spectra were recorded for sodium nanoparticles Na_N, it was found that mass peaks corresponding to the first 15 electronic magic numbers N = 3, 9, 20, 36, 61, ………………… were observed for cluster sizes up to N = 1220 atoms (n = 15), and FCC structural magic numbers starting with N = 1415 for n = 8 were observed for larger sizes [Martin et al. (1990); Sugano and Koizumi (1998), p. 90].

- Mass spectral data are plotted versus the cube root of the number of atoms $N^{1/3}$.
- It is clear that the lines from both sets of magic numbers are approximately equally spaced, with the spacing between the structural magic numbers about 2.6 times that between the electronic ones.
- This result provide evidence that small clusters tend to satisfy electronic criteria and large structure tend to be structurally determined.



Dependence of the observed mass spectra lines from N_a, nanoparticles on the cube root $N^{1/3}$ of the number of atoms N in the cluster. The lines are labelled with the index n of their electronic and structural magic numbers obtained from Martin et al. (1990).

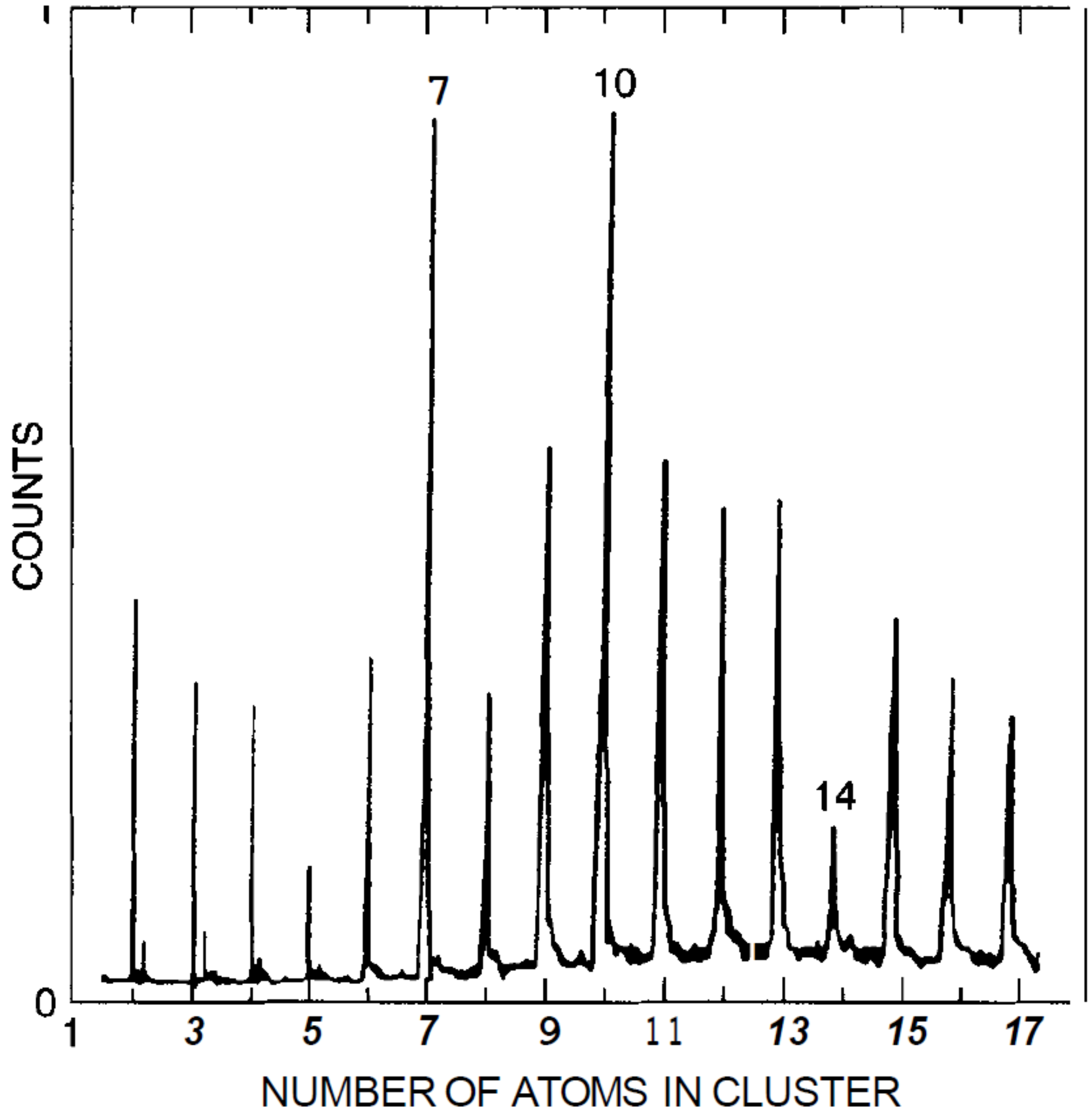
- Design of apparatus to make clusters of metal atoms are shown in next slide.
- A high intensity laser beam is incident on a metal rod, causing evaporation of atoms from the surface of the metal.
- The atoms are then swept away by a burst of helium and passed through an orifice into a vacuum where the expansion of the gas causes cooling and formation of clusters of the metal atoms.
- These clusters are then ionized by UV radiation and passed into a mass spectrometer that measures their mass/charge ratio.



Apparatus to make metal nanoparticles by laser induced evaporation of atoms from the surface of a metal. Various gases such as oxygen can be introduced to study the chemical interaction of the nanoparticles and the gases.

(Ref.: F.J.Owens and C.P.Poole, Jr., New Superconductors, Plenum Press, 1999)

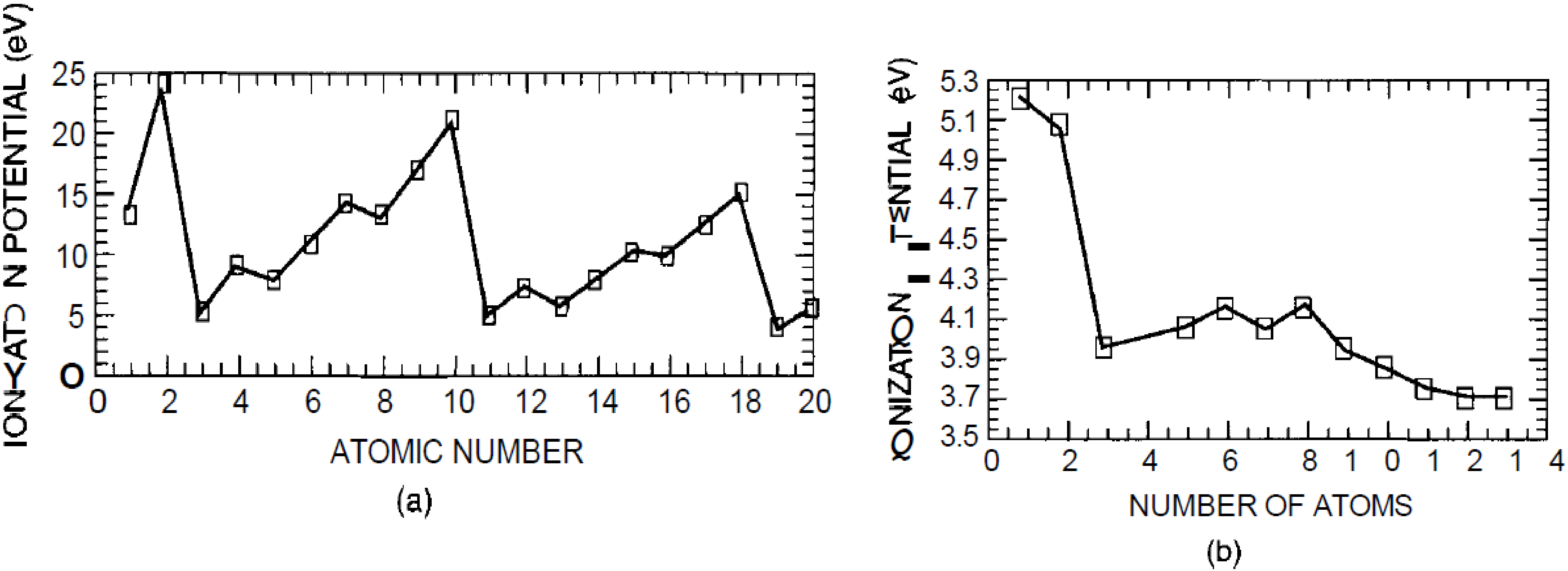
- Figure shows the mass spectrum data of lead clusters formed in such an experiment where the number of ions (counts) is plotted as a function of the number of atoms in the cluster. (Usually mass spectra data are plotted as counts versus mass over charge).
- The data shows that clusters of 7 and 10 atoms are more likely than other clusters, which means that these clusters are more stable than clusters of other sizes.



Mass spectrum of Pb clusters.

(Ref.: M.A. Duncan and D.H.Rouvray, Sci. Am. 110 (Dec. 1989)

- Figure (a) in the next slide is a plot of the ionization potential of atoms as a function of their atomic number Z, which is the number of electrons in the atom.
- The ionization potential is the energy necessary to remove the outer electron from the atom.
- The maximum ionization potentials occur for the rare gas atoms ^{2}He, ^{10}Ne, and ^{18}Ar because their outermost s and p orbitals are filled.
- More energy is required to remove electrons from filled orbitals than from unfilled orbitals.
- Figure (b) in the next slide shows the ionization potential of sodium clusters as a function of the number of atoms in a cluster.
- Peaks are observed at clusters having two and eight atoms.
- These numbers are referred to as ELECTRONIC MAGIC NUMBERS.
- Their existence suggests that clusters can be viewed as superatoms, and this result motivated the development of the Jellium model of clusters.

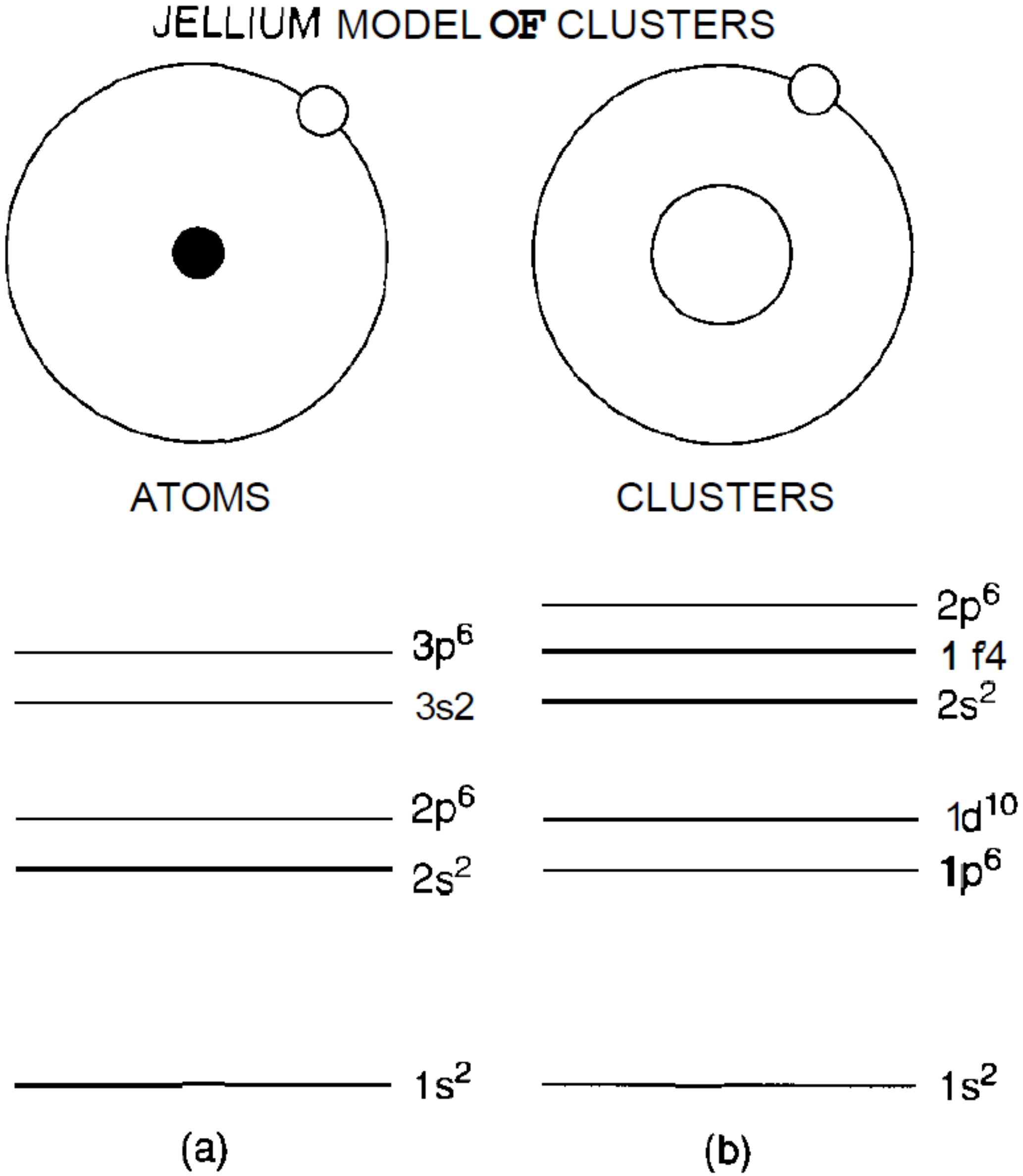


(a) A plot of the ionization energy of single atoms versus the atomic number. The ionization energy of the sodium atom at atomic number 11 is 5.14 eV, (b) Plot of the ionization energy of sodium nanoparticles versus the number of atoms in the cluster.

(Ref.: A.Herman et al., J.Chem. Phys. 80, 1780(1984))

Theoretical Modelling of Nanoparticles

- As we know from previous slides that larger clusters stability is determined by structure and the magic numbers are referred to as structural magic numbers.
- The Jellium model envisions a cluster of atoms as a large atom.
- The positive nuclear charge of each atom of the cluster is assumed to be uniformly distributed over a sphere the size of the cluster.
- A spherically symmetric potential well is used to represent the potential describing the interaction of the electron wit the positive spherical charge distribution.
- Thus the energy levels can be obtained by solving the Schrodinger equation for this system in a fashion analogous to that for the hydrogen atom.
- Figure in the next slide compares the energy level scheme for the hydrogen atom and the energy level scheme for a spherical positive charge distribution.



A comparison of the energy levels of the hydrogen atom and those of the Jellium model of a cluster. The electronic magic numbers of the atoms are 2, 10, 18, and 36 for He, Ne, Ar, and Kr, respectively (the Kr energy levels are not shown on the figure) and 2, 18, and 40 for the clusters.

(Ref.: B.K.Rao et al., J. Cluster Sci., 10, 477 (1999))

- The superscripts refer to the number of electrons that fill a particular energy level.
- The electronic magic number corresponds to the total number of electrons on superatom when the top level is filled.
- Notice that the order of the levels of Jellium model is different from that of the hydrogen atom.
- In this model the magic numbers correspond to those clusters having a size in which all the energy levels are filled.
- An alternative model that has been used to calculate the properties of clusters is to treat them as molecules and use existing molecular orbital theories such as density functional theory to calculate their properties.
- This approach can be used to calculate the actual geometric and electronic structure of small metal clusters.
- In the quantum theory of hydrogen atom, the electron circulating about the nucleus is described by a wave.
- The mathematical function for this wave, called the wavefunction ψ, is obtained by solving the Schrodinger equation, which includes the electrostatic potential between the electron and the positively charged nucleus.
- The square of the amplitude of the wavefunction represents the probability of finding the electron at some position relative to the nucleus.

- The wavefunction of the lowest level of the hydrogen atom designated the 1s level has the form

  $\Psi(1s) = A \exp(-\frac{r}{\rho})$; where r is the distance of the electron from the nucleus and ρ is the radius of the first Bohr orbit.

- This comes from solving the Schrodinger equation for an electron having an electrostatic interaction with a positive nucleus given by e/r.

- The equation of hydrogen atom is one of the few exactly solvable problems in physics, and is one of the best understood systems in the Universe.

- In the case of a molecule such as the H_2^+ ion, molecular orbital theory assumes that the wavefunction of the electron around the two H nuclei can be described as a linear combination of the wavefunction of the isolated H atoms.

- The wavefunction of the electrons in the ground state will have the form:

  $\Psi = a\,\Psi(1)_{1s} + a\,\Psi(2)_{1s}$ ………….. (a)

- The Schrodinger equation for the molecular ion is

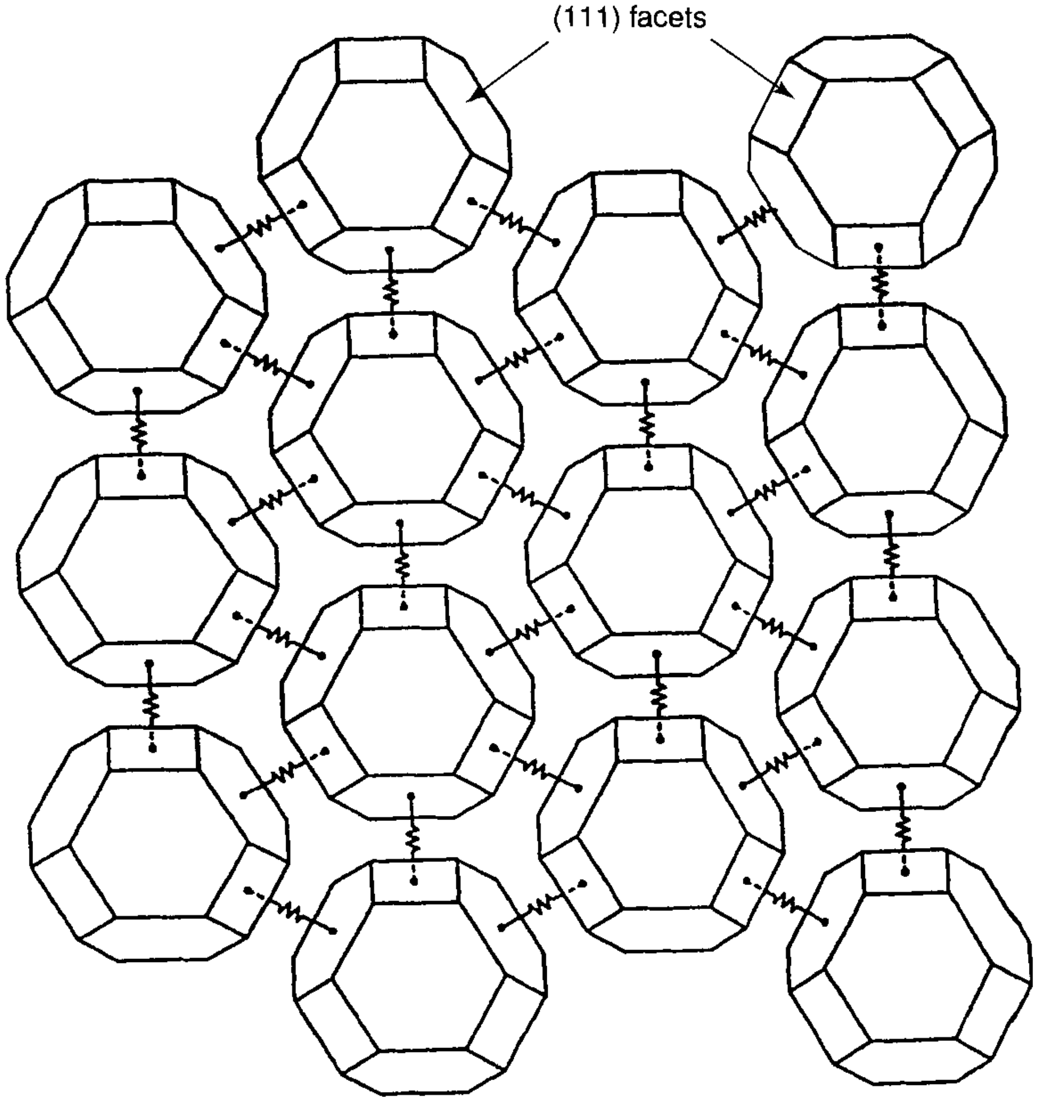
$$\left[\left(\frac{-\hbar}{2m}\right)\nabla^2 - \frac{e^2}{r_a} - \frac{e^2}{r_b}\right]\psi = E\psi$$

The symbol ∇^2 denotes a double differentiation operation. The last two terms in brackets are the electrostatic attraction of the electron to the two positive nuclei, which are at distances r_a and r_b from the electron.

- For hydrogen molecule, which has two electrons, a term for electrostatic repulsion of two electrons would be added.
- The Schrodinger equation is solved with the help of linear combination of wavefunctions as given in equation (a).
- When there are many atoms in the molecule and many electrons, the problem becomes complex and many approximations are used to obtain the solution.
- Density functional theory represents one approximation.
- With the development of new theoretical approaches and fast computer capability, it is possible to determine geometric and electronic structures of large molecules with high degree of accuracy using molecular orbital theory.

Model to explain the electrical conductivity in an ideal hexagonal array of single-crystal gold clusters with uniform intercluster resistive linkage provided by resistors connecting the molecules.

Ref: R.P.Andres et.al., Handbook of Nanostructured Materials and Nanotechnology, H.S.Nalwa, ed., Academic Press, San Diego, 2000, Vol. 3, Chapter 4, p. 221.



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