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A Few NanoComments on NanoScience and NanoTechnology

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Pitesti, September 2004

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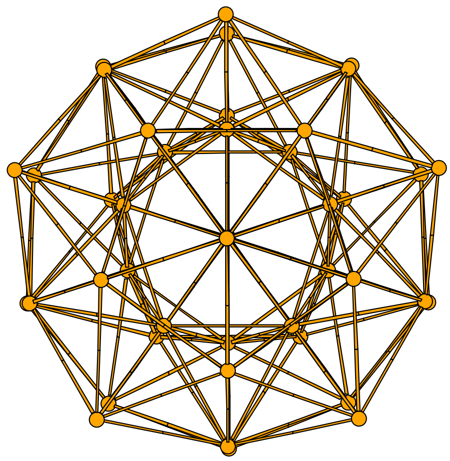


NANOME

MAPPING PROJECT

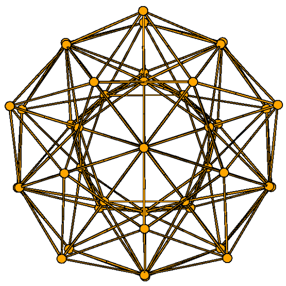
Mapping the NANOWORLD

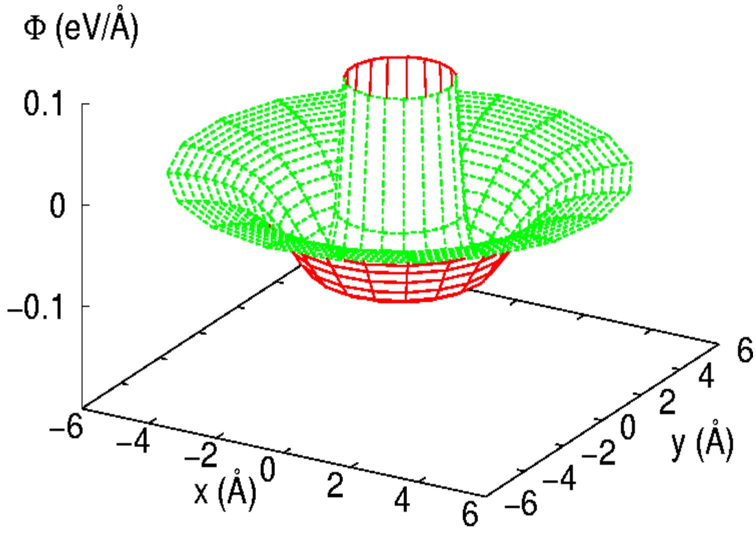
at

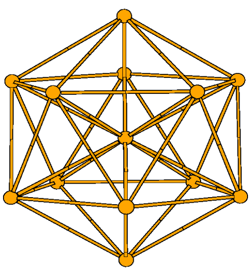
Magurele-Bucharest

<u>We are making NANO at Magurele</u>

(L. C. Cune)







Cune Potential

$$\Phi_{ij} = -\frac{1}{2} z_i^* z_j^* q \left(1 - \frac{2}{q\left|\mathbf{r}_i - \mathbf{r}_j\right|}\right) e^{-q\left|\mathbf{r}_i - \mathbf{r}_j\right|}$$

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Applications 7: $Fe_{13}(C_2H_2)_6$

Department of Energy, USA

Strategic Plan of Research 2005-2025

Priorities:

1 NanoSci & NanoTech (Electronization of Biology)

2 Complex Systems (Control of the Planet, Space, etc)

3 Astrophysics & Cosmology (New Nuclear Weapons)

(USA's 21st Century Nano Res & Dev Act, 2003)

Hierarchy in Size

Atoms, Molecules <10Å

NanoStructures 10Å—1000-1500Å

Micro-, Mini- (lower bound of today $\sim$ 900Å)

MesoStructures (1μ)

MacroStructures (Avogadro's number 10^{23}) - Universe Age ?

(1 nano=10Å $= 10^{-9}$m)

Scale

Human Hair = 800 000Å (80μ)

Red blood cell = 70 000Å

Virus = 1000Å: **Here starts Nano down to**

Fullerene molecule = 7Å

DNA = 20Å (wide)

Water molecule=3Å

What we expect from Nano

NanoElectronics (Moore's Law)

Information & Communication (NANONISATION)

Drug Development

Water (Environment) Decontamination

Stronger and Lighter Materials

"Grey Goo" ?

New Processes, Materials

Functional Nanostructures (electronic, chemical, biological, ...)

Technological Matters

Investment: $5b ($2b private)

Etching Silicon Microchips (limited); Self-assembly (bottom-up)
Displays (Se), Paints, Batteries (Ni), Catalysts
Nanowires (carbon); Optical and magnetic NanoMemories
ZnO_2 (zirconia) - ceramic plastics; Al_2O_3 (aluminium oxide) - ceramic; SiO_2(quartz) - microelectronics
Nano-Ag dresses wounds
Cosmetics (ZnO , TiO_2, FeO)

A few Examples

Nano-Au appear red, blue or gold in stained glass and ceramics, depending on its size

TiO_2-nanowires for (photo-) catalysis, H, Li storage (UV active, transparent)

Phosphorous algae

Proteins

Polymers

Romanian Advances

Cd/Se quantum nanowires (electrochemically, display)

Cu/Co multilayer nanowires (giant magnetoresistance)

Particulate alkali halogenides with Rare Earths (digital radiography)

3D Compact Disk of Ceramics with Rare Earths

NanoColoured optical crystals

Issues

- Health Risk, Social, Environmental, Safety, Regulatory, Ethical

- Toxicity - NanoBomb (DustClouds), Explosion

- Dangerous Materials: Quartz, Asbestos, Air Pollutants via Combustion (1mg per cubic metre of breathing air)

- Human Enhancement (Commercialisation of Science)

Physics

Large Surface (Finite-Size Effects)

Quantum Effects (optical, electrical, magnetic)

(El Conductance quanta *vs* Mech Tension quanta in nanowires)

NanoTech: Size and Shape Matters (Quantum Dots Optics∼Size)

New tools: STM, AFM (NanoMetrology); MBE

Chemical Binding

Dirac (˜1930) (Hartree-Fock (HF), LCAO)

1 *Ab-initio* methods (LCAO) (Pople, 1940-1998) - configuration superposition (Slater, 1929, 1930)

2 Density functional (Kohn-Sham, 1964-1998)

H_2- molecule (James-Coolidge, 1933) - energy *vs* size (He - Hylleraas, 1929, Pekeris, 1958)

Quasiclassical Description

THEORY

(L. C. Cune)

- Nanostructure (one-particle) orbital

$$\psi_s = \alpha_s \varphi_s + \beta_s \Phi_s$$

(in contrast with *ab-initio* methods' φ_s only) - Mullikan (1928)

- Cores plus valence atomic-like orbitals (upper shells) $\varphi_s = \sum c_{ia}^s \chi_{ia}$
- Minimum of atomic energy $\rightarrow c_{ia}^s$
- Minimum of extended-orbital energy $\rightarrow \beta_s$
- Coupling through $\sum \left|c_{ia}^s\right|^2 = 1$ and $\alpha_s^2 + \beta_s^2 = 1$ (self-consistency; structure dependent)
- binding effective charge z_i^* for each i - th ion

- binding ionic-hole density $\rho = \sum \beta_s^2 \left|c_{ia}^s\right|^2 \left|\chi_{ia}\right|^2$, $z_i^* = \sum \beta_s^2 \left|c_{ia}^s\right|^2$: assume spherical symmetric $\sum z_i^* \delta(r - R_i)$ (more general $\rho = \sum \beta_s^2 c_{ia}^* c_{jb} \chi_{ia}^* \chi_{jb}$)

- s - like atoms: $z_{Na}^* = 0.44$, $z_K^* = 0.34$, $z_{Fe}^* = 0.57$ $(3d^6 4s^2)$, $z_{Ag}^* = 0.19$ $(4d^{10} 5s^1)$, $z_{Ba}^* = 0.34$ (quasi-classical description of heavy atoms; atomic screning)

-(magnetic momentum, structure dependent)

Binding (cohesion) Hamiltonian

$$H = \sum_\alpha p_\alpha^2/2m - e^2 \sum_{ia} \int dR \cdot \frac{\rho_i(R)}{|R - r_\alpha|} + \frac{1}{2} e^2 \sum_{\alpha \neq \beta} \frac{1}{|r_\alpha - r_\beta|} +$$

$$+ \frac{1}{2} e^2 \sum_{i \neq j} \int dR dR' \cdot \frac{\rho_i(R) \rho_j(R')}{|R - R'|}$$

$$\rho_i = \sum \beta_s^2 \left|c_{ia}^s\right|^2 \left|\chi_{ia}\right|^2 \rightarrow z_i^* \delta(R - R_i)$$

Core-Electrons Equations

- (nano) structure orbitals

- solve iteratively for β_s and c_{ia}^s (corrections controlled by $a_{atom}/a_{structure}$, orbital-dependent)

- fractional β_s, theory of valence (donors, acceptors, etc)

- main role: actual atomic-like orbitals $\chi_{ia}(R)$ in upper shells

- (all for usual, relatively light, cohesion, upper shells!) (Pd-H problem!)

Hartree-Fock Equations (HF)

$$(p^2/2m)\Phi_s - e\varphi\cdot\Phi_s + \varepsilon_{ex}(\Phi_s) = \varepsilon\Phi_s$$

$$\varphi = e\sum_i z_i^*/\left|r-R_i\right| - e\int dr'\cdot n(r')/\left|r-r'\right|$$

$$\varepsilon_{ex} = -e^2\int dr'\cdot 1/\left|r-r'\right|\sum_{s'}\Phi_{s'}^*(r')\Phi_{s'}(r)\cdot\Phi_s(r')$$

$$n(r) = \sum_s\left|\Phi_s(r)\right|^2 \;\;,\;\; n(r,r') = \sum_s\Phi_s^*(r)\Phi_s(r')$$

- eigenfunctions for ε_{ex} - plane waves

- unknowns: $\Phi_s$and number of s (non-linear!); local changes of electron density

- s - change in electron density: no change in ε_{ex} (rigidity, non-local; Slater, 1979; Seitz, Wigner, 1934) (functional of concentration, not of density!)

- screening the Hartree (1928) potential φ untill almost constant: plane waves as eigenfunctions almost everywhere

- slow spatial variations

Solution

Hartree (1928) - Fock (1930) energy functional - variation with respect to the s - number of states

Thomas (1927)-Fermi (1928) equations (TF):

$$\hbar^2k_F^2/2m - e\varphi = 0 \;\;,\;\; \triangle\varphi = -4\pi e\sum_i z_i^*\delta(r-R_i) + 4\pi en$$

$$n = k_F^3/3\pi^2$$

plus LINEARIZATION! $n\sim\varphi$

- quasiclassical approximation $n\sim\varphi^{3/2}$- valid for $z_i^*\rightarrow\infty$, no binding (Teller, 1962)

Linearization

$$k_F^n \rightarrow \bar{k}_F^{n-1} k_F \ , \ q^2 = (8/3\pi)\bar{k}_F$$

$\bar{k_F}$ to be compared with $k_{Fav} = (1/z_0)\int nk_F = (4/3\pi^2 z_0)\int \varphi^2$; q^2 and q_{av}^2 $(z_0 = \sum_i z_i^*)$

- Poisson equation:

$$\varphi = \sum_i \frac{z_i^*}{|r - R_i|} e^{-q|r-R_i|}$$

- Thomas-Fermi screened potential
- HF energy functional (linearized):

$$E_{kin} = (27\pi^2/640)z_0 q^4 \ , \ E_{ex} = -(9/32)z_0 q^2$$

$$E_{pot} = -\tfrac{q}{4}\{3\sum_i z_i^{*2} + \sum_{i\neq j} z_i^* z_j^* [1 - \tfrac{2}{q|R_i-R_j|}]e^{-q|R_i-R_j|}\}$$

- Variational q from $E_q = E_{kin} + E_{pot}$

Cune Potential

$$\Phi(R_i - R_j) = -\frac{q z_i^* z_j^*}{2}[1 - \frac{2}{q\,|R_i - R_j|}]e^{-q|R_i-R_j|}$$

repulsive $R \rightarrow 0$, attractive $R \rightarrow \infty$, minimum at $qa \sim 2.73$

Recipee

- Minimization of E_{pot} with respect to $q\,|R_i - R_j|$
- Minimization of $E_q = E_{kin} + E_{pot}$ with respect to q
- Atomic positions (structure); vibration spectrum
- $q \simeq 0.77 z^{*1/3}$ and $q_{av} \simeq 0.9 z^{*1/3}$; 17%
- Electronic properties - "Quantum" corrections: HF eqs with screened potential (Clemenger-Nilson approximation, finite-size effects, etc)
- Correction for q (*via* linearized electron density)
- Maximal accuracy 3% (one-particle functions; lifetime)

Full Recipee

- Start with actual atomic-like potentials and $z_i^* = 1$ (normalized)
- Minimization of E_{pot} with respect to $|R_i - R_j|$and minimization of $E_q = E_{kin} + E_{pot}$ with respect to q separately
- Correct for $z_i^* < 1$ by a_{at}/a_{str}-controlled core-electrons eqs (convergence)
- Structure (atomic positions); vibration spectrum
- Electronic properties - "Quantum" corrections: HF eqs with screened potential
-Refine everything by one more iteration with the corrected q *(via* linearized electron density) (convergence)
- Stop: at about 3% accuracy

Applications 1: Atomic Clusters

- homo-atomic (δ - cores, at screening z_i^*)

- structure, magic forms and magic numbers (symmetry and space economy; entropy economy?)

- energy

- abundence $\ln(I_N^2/I_{N-1}I_{N+1}) = E_{N+1} + E_{N-1} - 2E_N$

- vibrations spectrum

- isomers

- quantum corrections (electronic), deformed cluster potentials, finite-size effects included (ionization potential, electron affinity, reactivity)

Electronic Properties

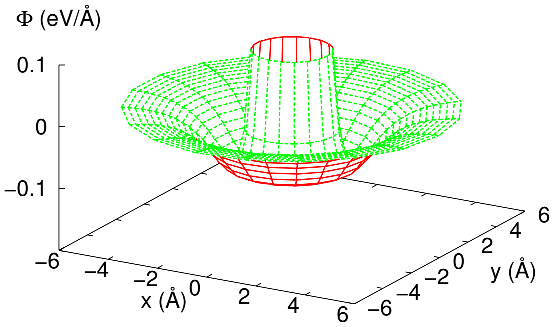
$\varphi = \sum_i \frac{z_i^*}{|r-R_i|} e^{-q|r-R_i|}$

$\varphi = \frac{4\pi z^*}{a^3 q^2}(1 - Fe^{-qR})$, $F = (1+qR)\frac{\sinh qr}{qr}$, $r < R$ (harm oscill ω^2 controlled by a/R)

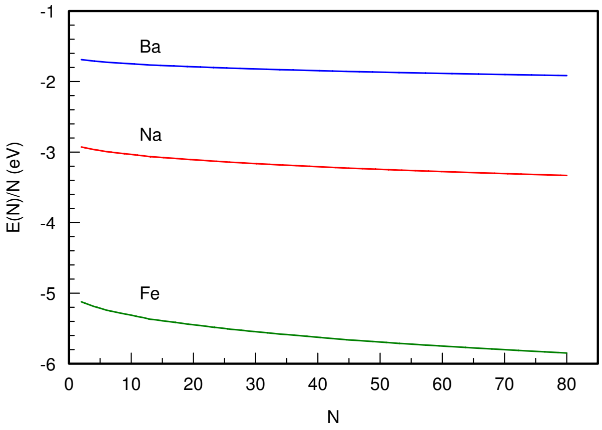
$\varphi = \frac{4\pi z^*}{a^3 q^2}(qR\cosh qR - \sinh qR)e^{-qr}/qr$, $r > R$

$E_{pot} = -\frac{3}{4} qNz^{*2}\{1 - \frac{2\pi}{(aq)^3} \cdot \frac{1}{qR}\}$

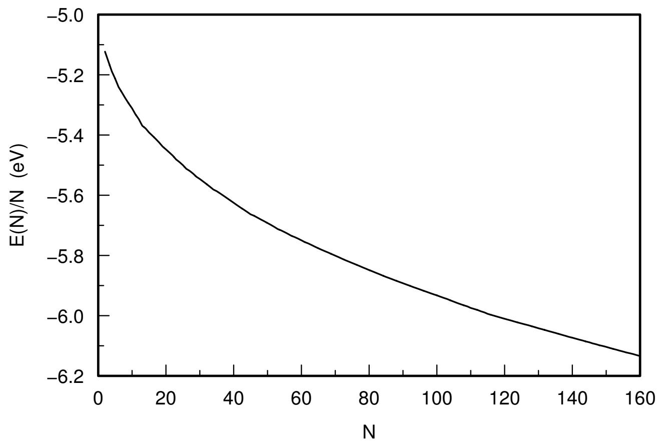
(surface tension)



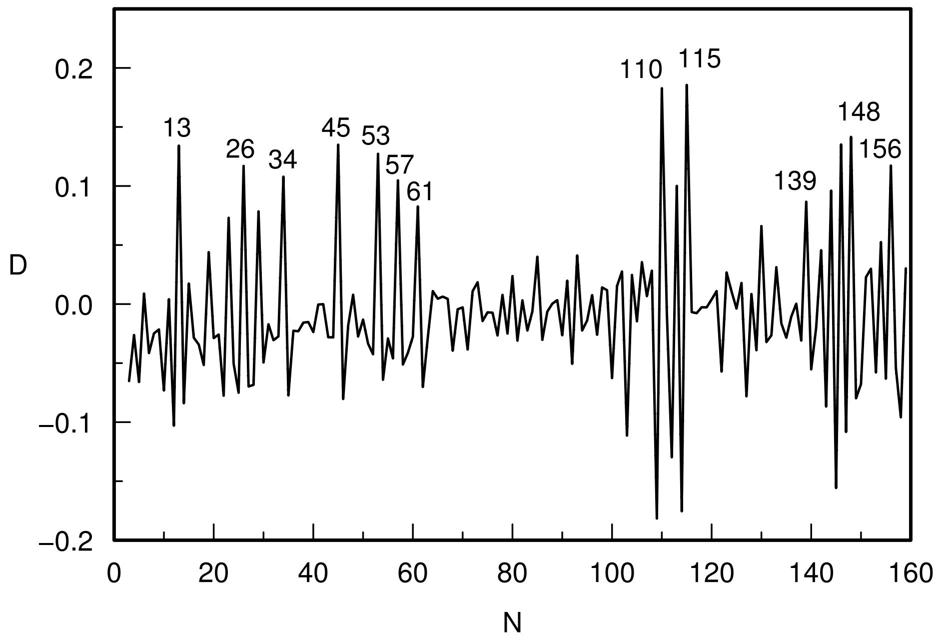
Effective inter-atomic potential



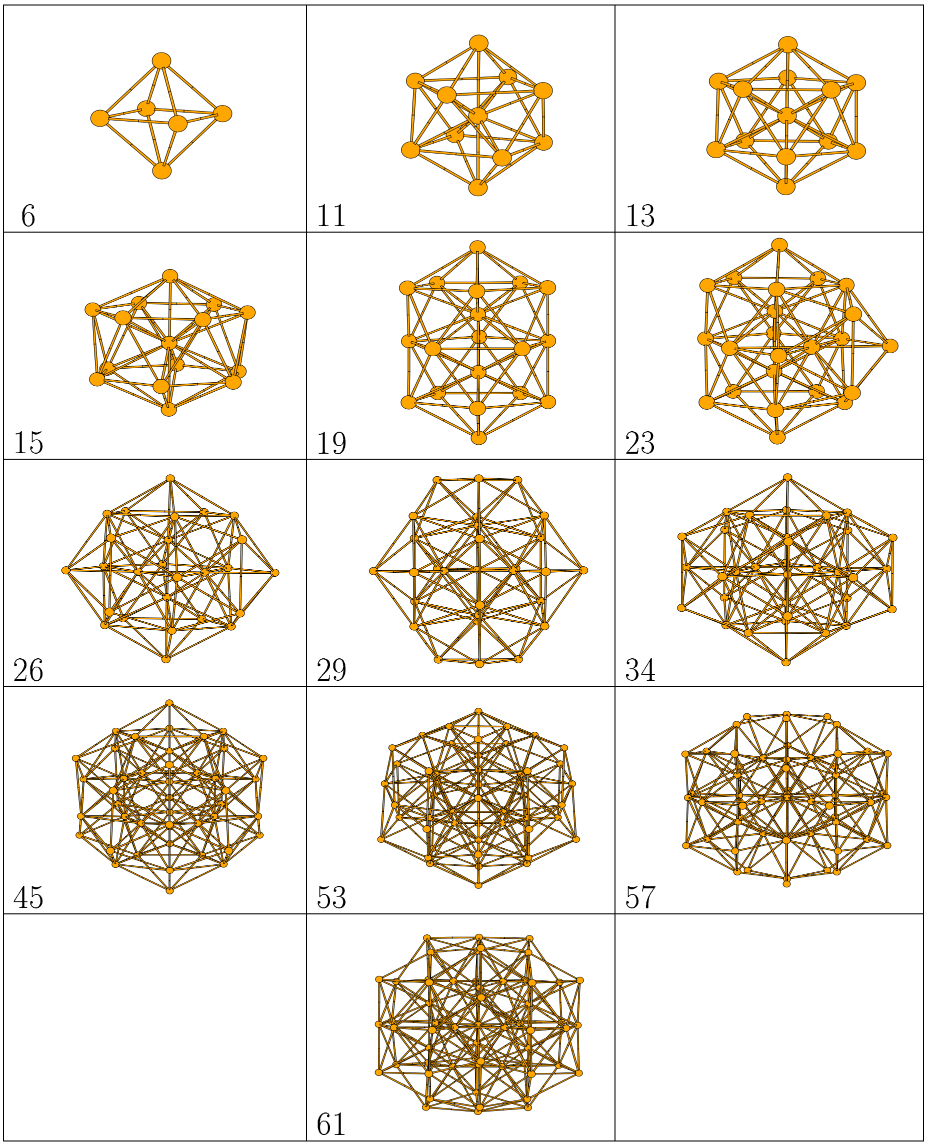
Energy per atom vs N for Ba-, Na-, and Fe-clusters (N<80)



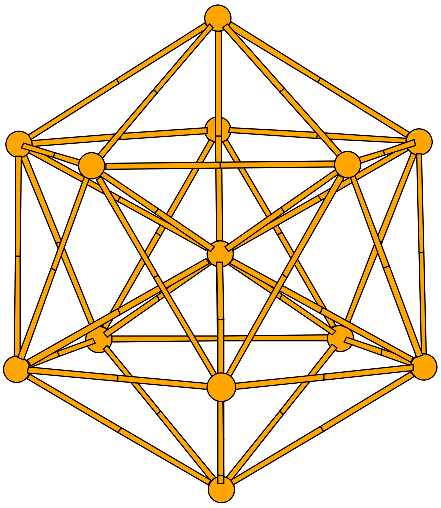
Energy per atom vs N for Fe-clusters (N<160)



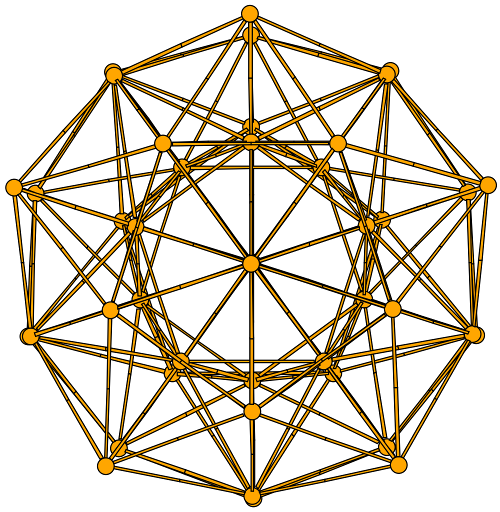
Magic Numbers



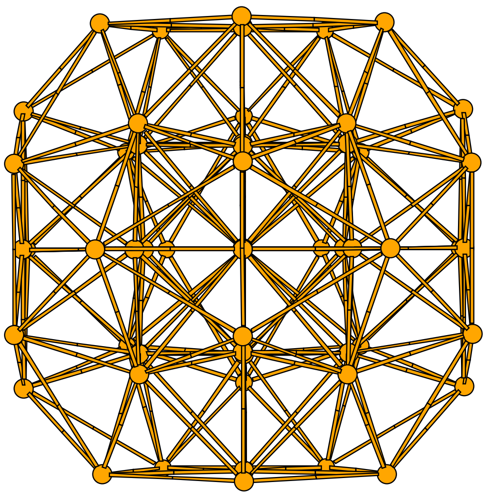
Magic homo-atomic metallic clusters



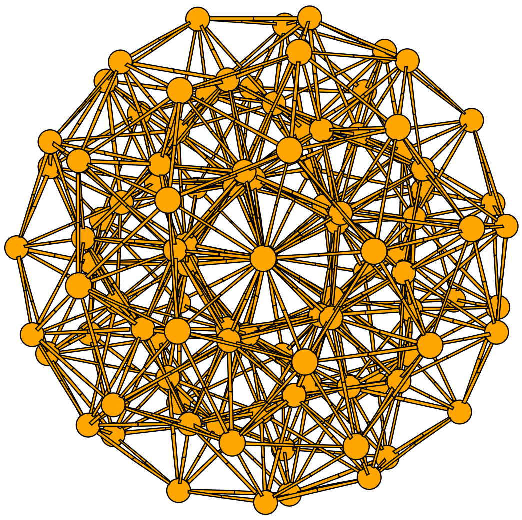
Fe_{13}



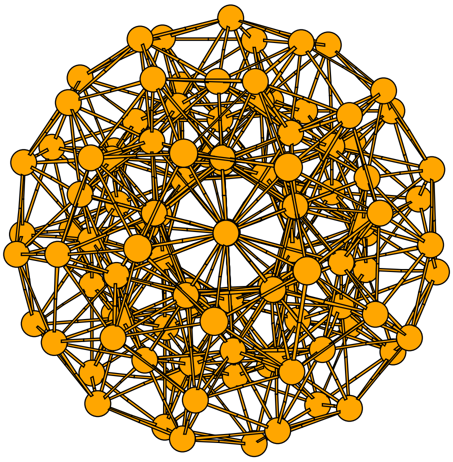
Fe_{45}



Fe_{55}

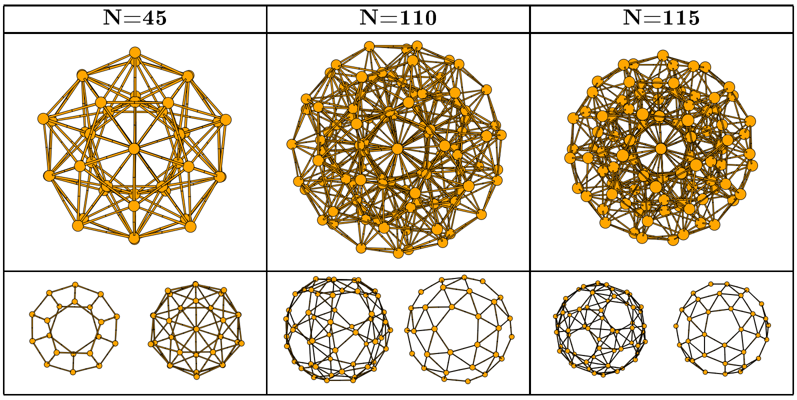


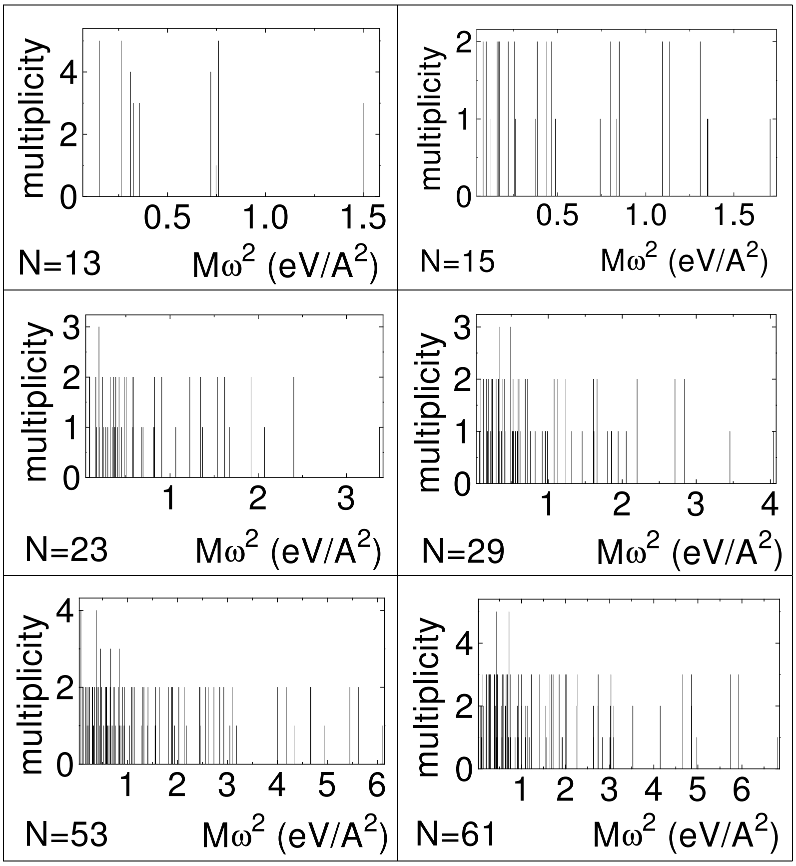
Fe_{110}



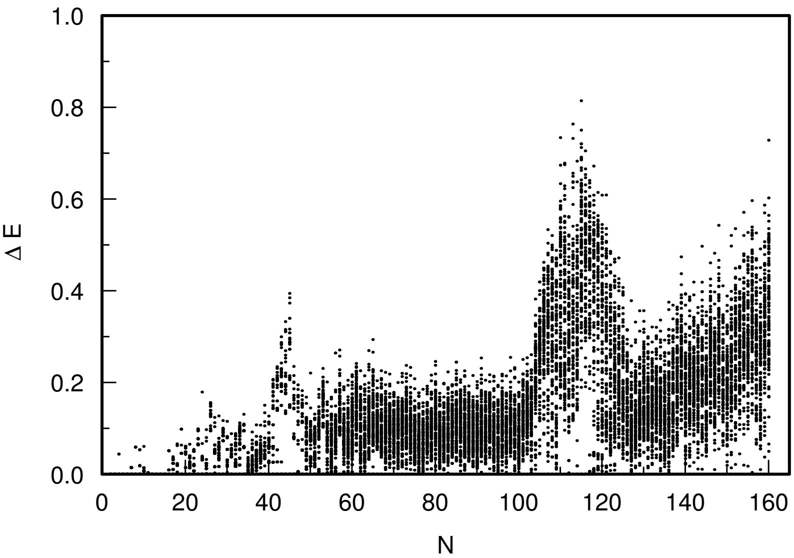
Fe_{115}

Outer atomic shells

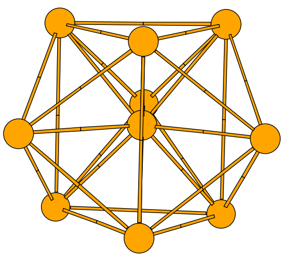




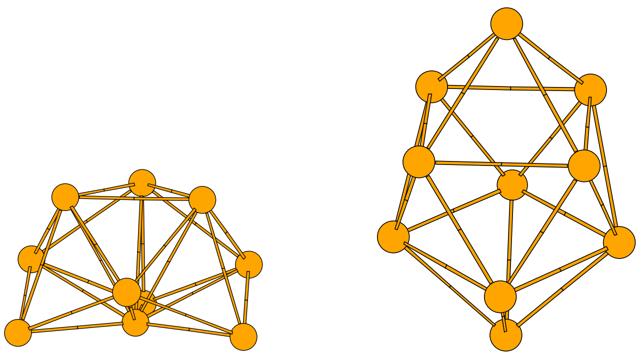
Vibration spectra for ground-state Fe-clusters



Isomers



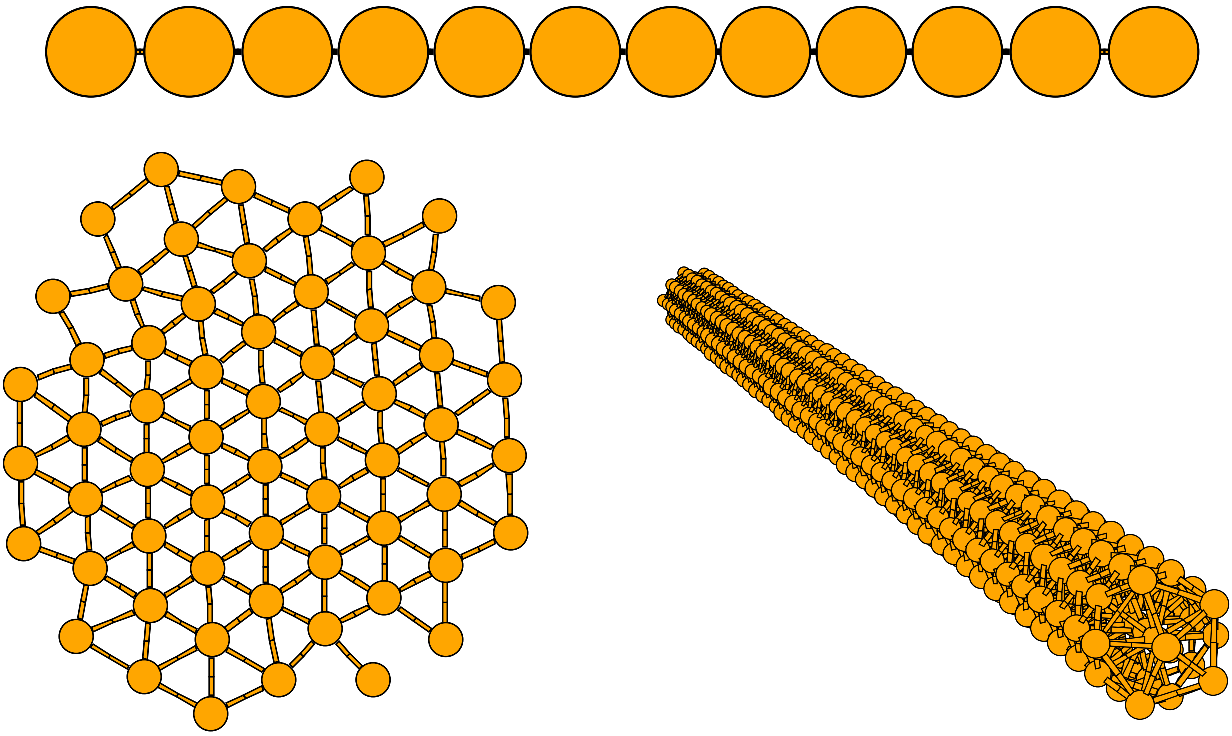
Fe_{10} ground-state



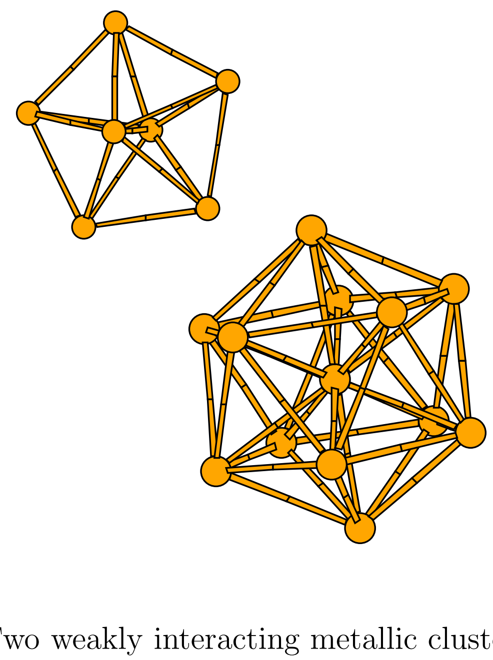
Fe_{10} isomers

Applications 2: Exotic Structures

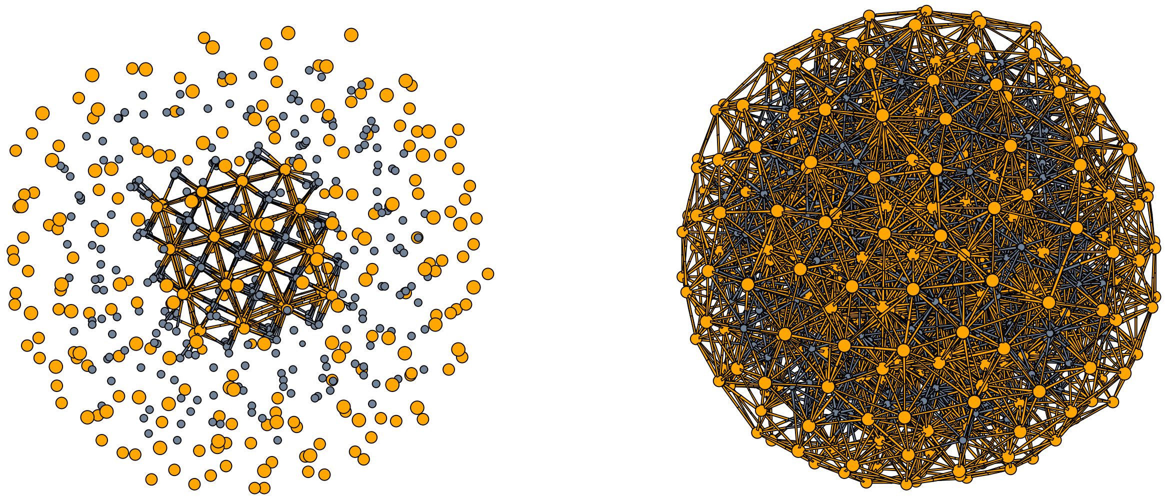
- nanowires (metallic, unstable)
- 2D atomic sheets (unstable)
- discontinuos clusters, metastability, clusters of clusters
- megaclusters
- constrained clusters



Exotic structures



Two weakly interacting metallic clusters



An 855-atoms bit of metal with a bcc-core

Applications 3: Heavy Atoms

- Experimental $E = -16Z^{7/3}$eV (empirical)

- TF model $E = -20.8Z^{7/3} + 13.6Z^2(b) - 5.98(7.3)Z^{5/3}(ex) + ...$ (Schwinger, 1980, 1981)

- $Z \to \infty$(no-binding, classical atoms)

- Linearized TF $\to -11.78Z^{7/3} - 4.56Z^{7/3} = -16.34Z^{7/3}\,(-4.53Z^{5/3}\,or\,-5.52Z^{5/3}...)$

- Quantum corrections

- (Virial theorem); molecules (statistics because linearization)

Applications 4: Universal Solid

- $E = Aq^4/4\,(kin) - Bq + q\sum_{i\neq j}F(qr_{ij})\,(pot) + E_{ex}$

- $F = \frac{1}{2q}\Phi$, $\Phi = -\frac{qz_i^* z_j^*}{2}(1 - 2/qr_{ij})e^{-qr_{ij}}$

- continuum approximation $E = -0.43Nz^{*7/3} - 0.17Nz^{*5/3}$

- Wigner universal metal; energy bands; universal solid

- compressibility ($aq = const\,,\delta a \sim \delta q$), sound waves $v_s(z^*)$; thermodynamics

- δq (δn), δR_i →vibrations ($\delta R_i \delta R_j$), el-phonon int ($\delta n \delta R_i$), el-el residual int ($\delta n \delta n$) (plasmons lifetime)

- plasmons (fractional occupancy)

-electrons: excitations (quasi-particles), $m^* = m(1 + 0.39z^{*1/3})$, lifetime, etc, all by the self-consistent potential φ

- polarizability and diamagnetic susceptibility (δn changes in energy); response in general

Applications 5: Surfaces

- Self-consistent electron potential

$$\varphi = \sum_i \frac{z_i^*}{|r - R_i|} e^{-q|r-R_i|}$$

- Continuum half-space (semi-infinite) solid

$$\varphi = \frac{4\pi z^*}{q^2 a^3}(1 - \frac{1}{2}e^{qx}) \ , \ x < 0; \ \varphi = \frac{2\pi z^*}{q^2 a^3} e^{-qx} \ , \ x > 0$$

($q = 0.77 z^{*1/3}$, $aq = 2.73$)

- surface double layer; electrons overspill (Bardeen, transistor, 1947)

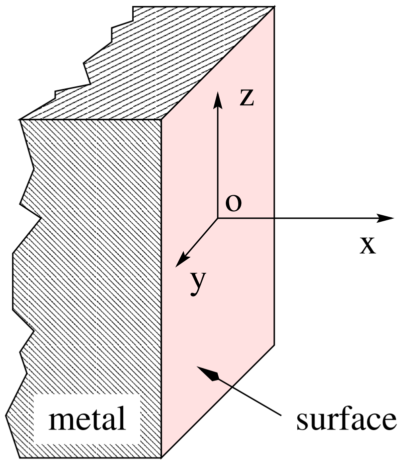
- work function φ (semi-empirical); boundary effects (finite-size quasiparticles lifetime)

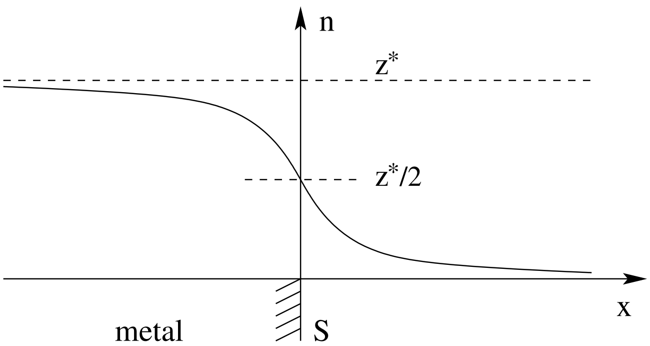
- Potential energy

$$E_{pot} = -\frac{3}{4} q \sum_i z_i^{*2} + \frac{1}{2} \sum_{i \neq j} \Phi(R_{ij})$$

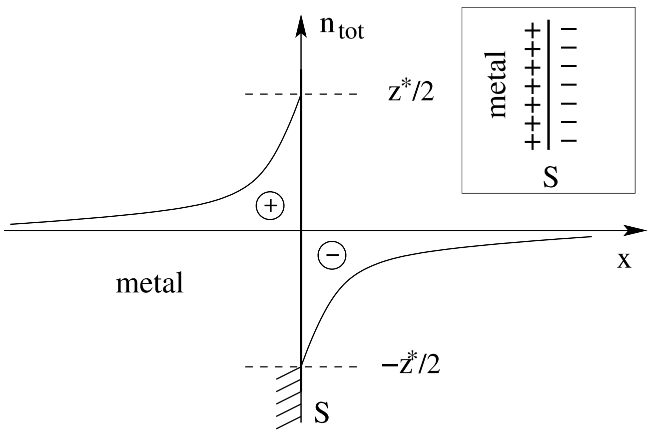
$$\Phi(R_{ij}) = -\frac{1}{2} q z_i^* z_j^* \sum (1 - \frac{2}{q\,|R_i - R_j|}) e^{-q|R_i - R_j|}$$

- Semi-infinite continuum: surface energy, surface tension (solid breaking energy)





Electron density



Charge distribution

Applications 6: Clusters Deposited on Surfaces, Contacts, Junctions and Interfaces

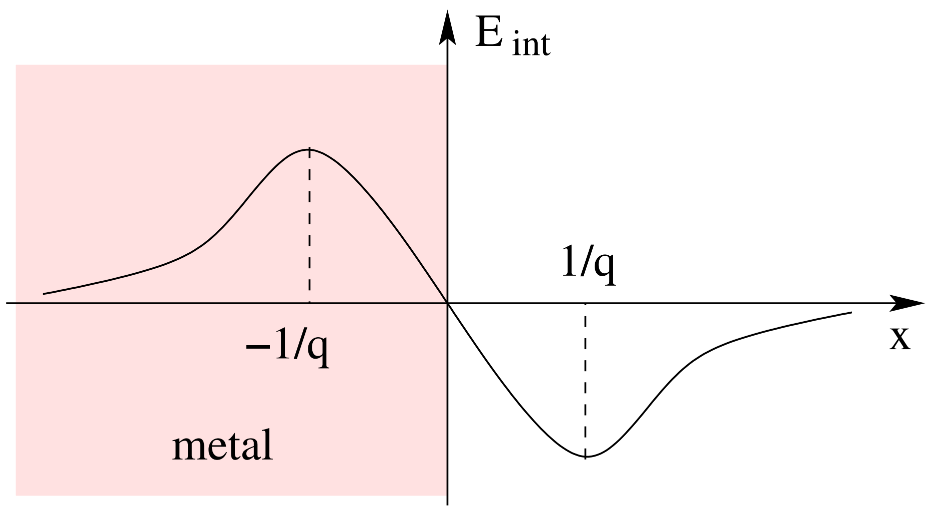
- Solid (surface) + clusters

$$E_{pot} = E_s - \frac{3}{4}q\sum_i z_i^{*2} + \frac{1}{2}\sum_{i\neq j}\Phi(R_{ij}) - \frac{\pi z^*}{qa^3}\sum_i z_i^* X_i e^{-q|X_i|}$$

- Cluster-surface interaction energy

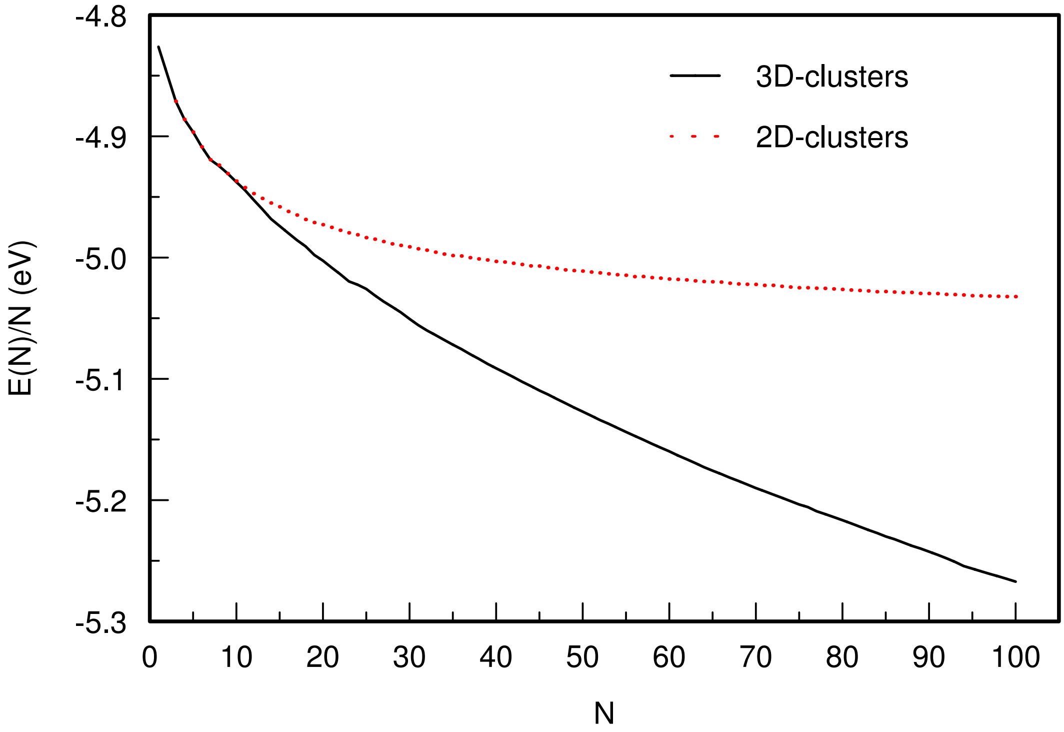
$$E_{int} = -\frac{\pi z^*}{qa^3}\sum_i z_i^* X_i e^{-q|X_i|}$$

- Two interacting semi-infinite solids: surface energy
- Clusters deposited on surfaces (Fe on Na): energy, magic forms and numbers, isomers
- monolayers, multilayers
- diffusion: contacts, junctions, interfaces

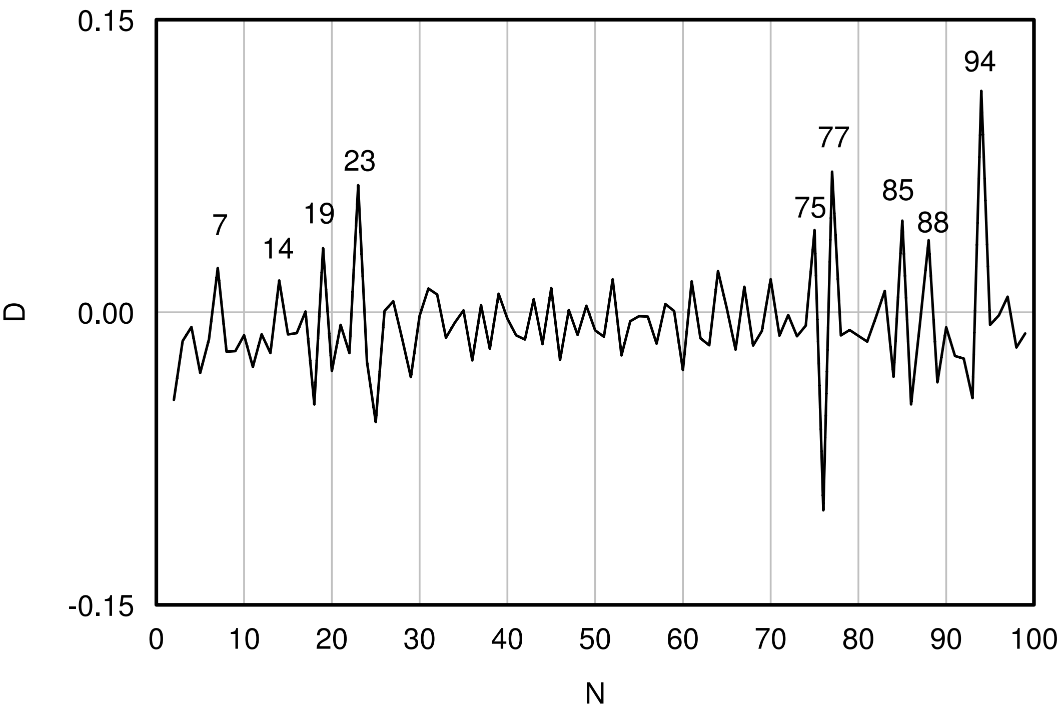


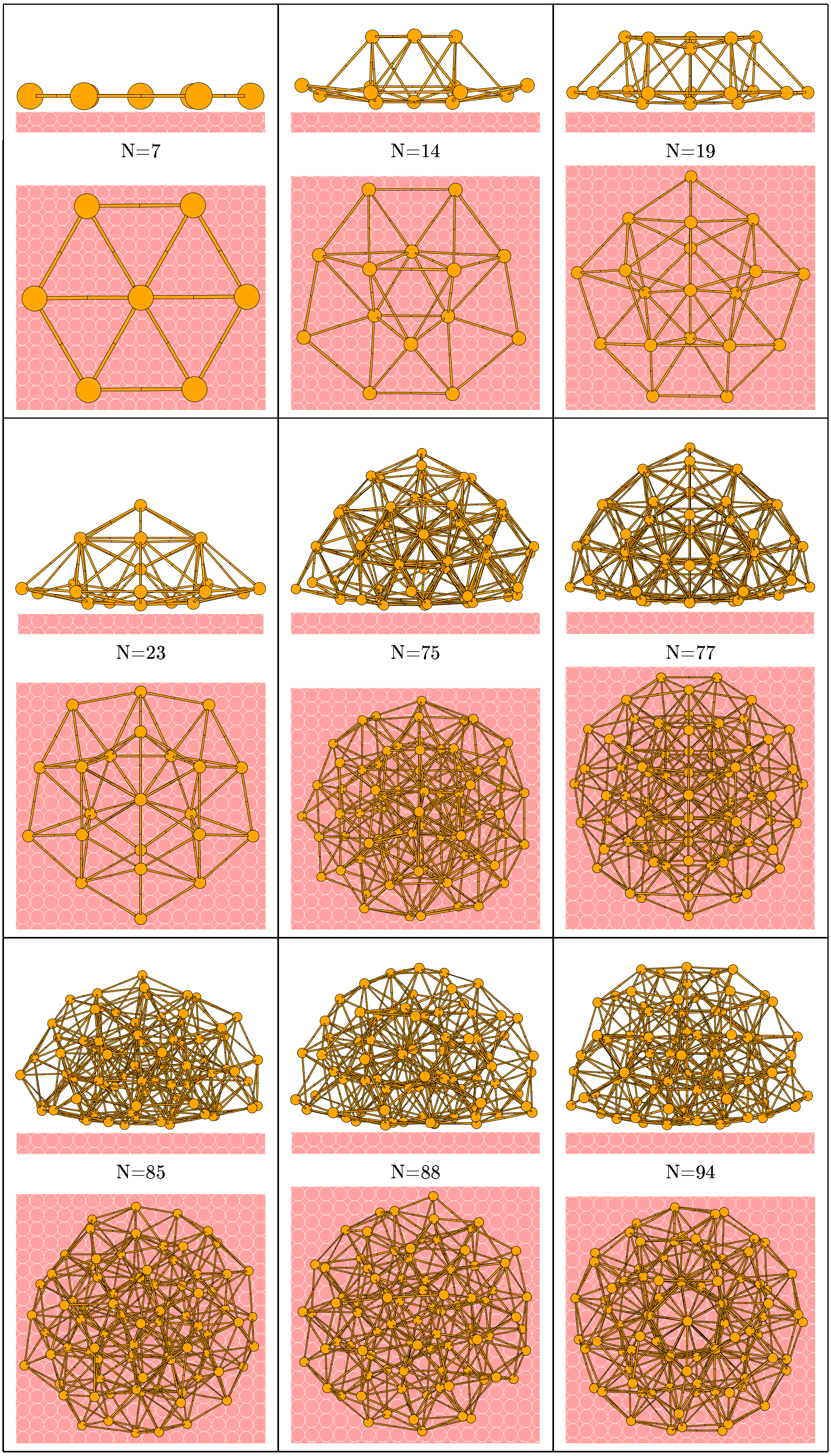
Atom-surface interaction

Binding energy

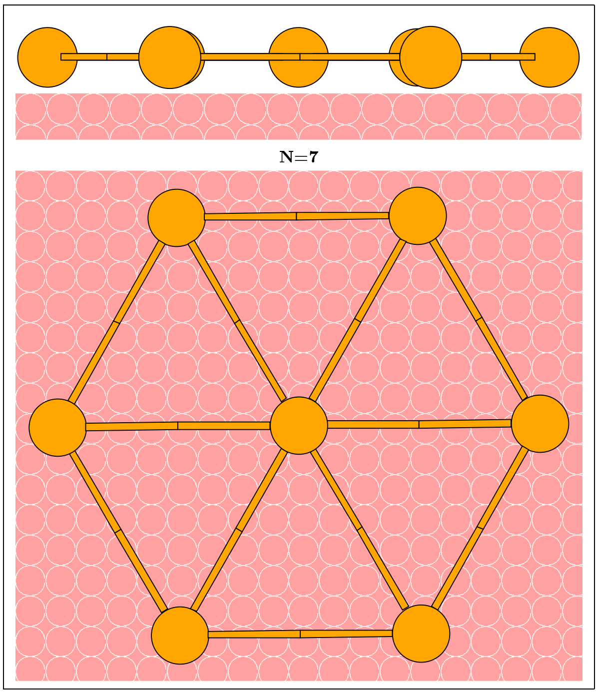


Magic numbers





Magic clusters deposited on a surface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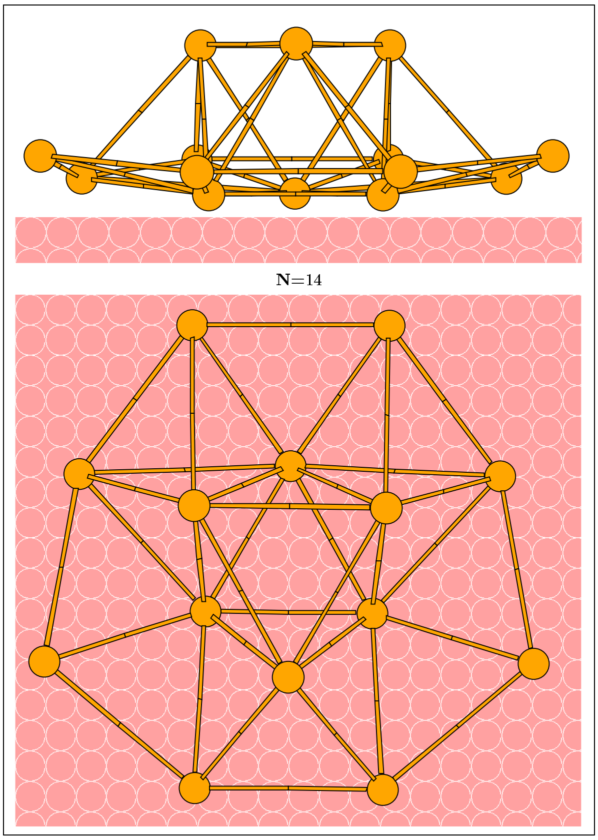
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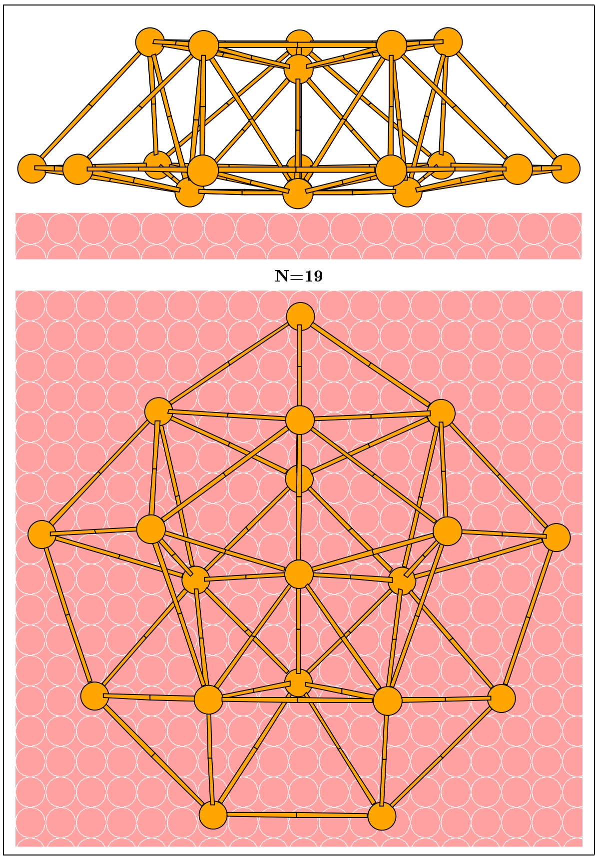
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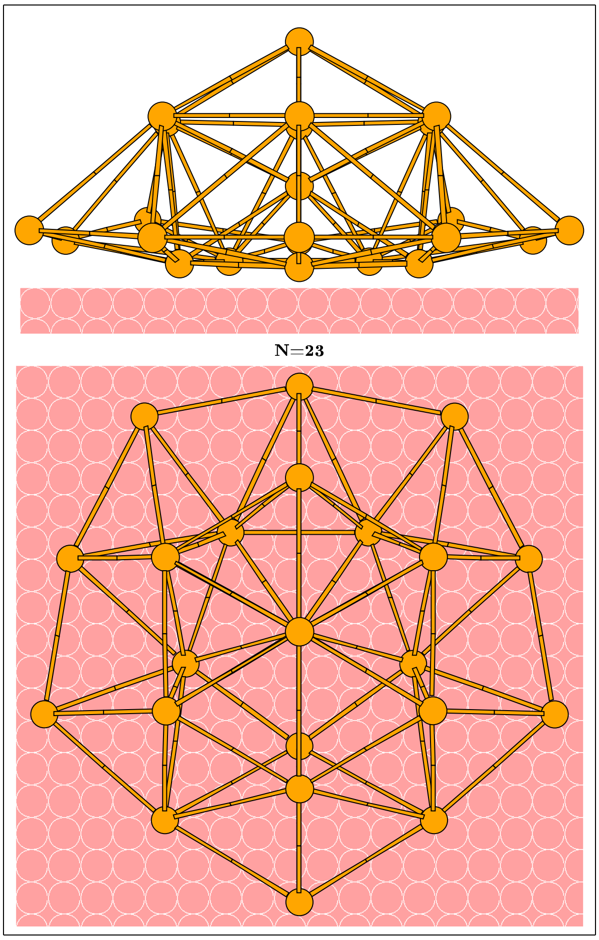
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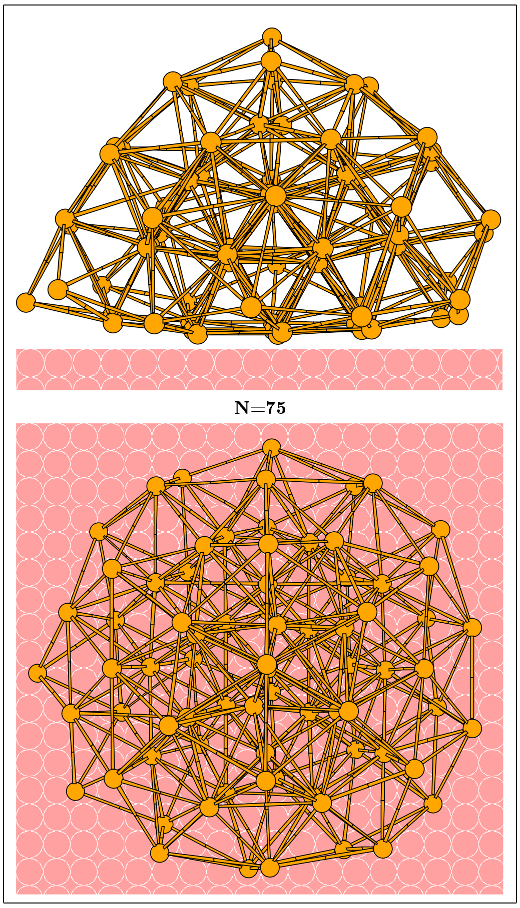

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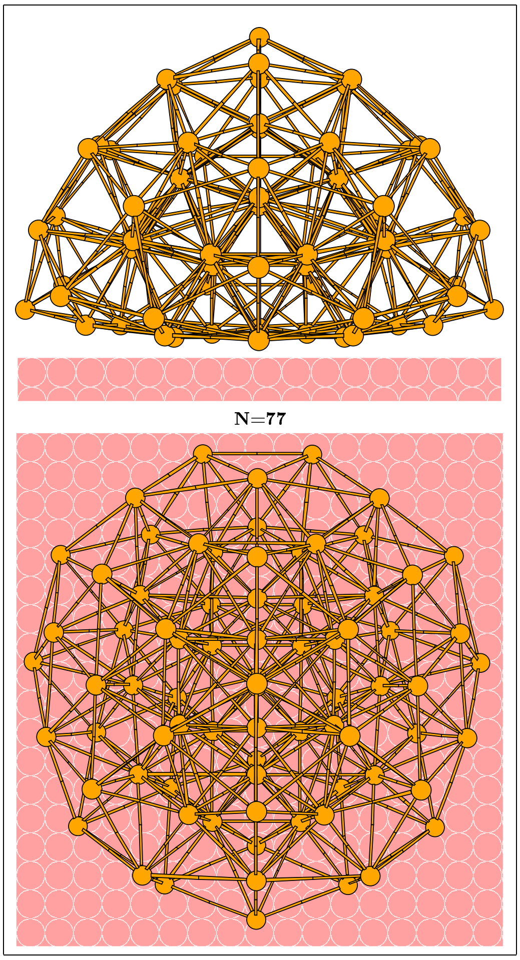

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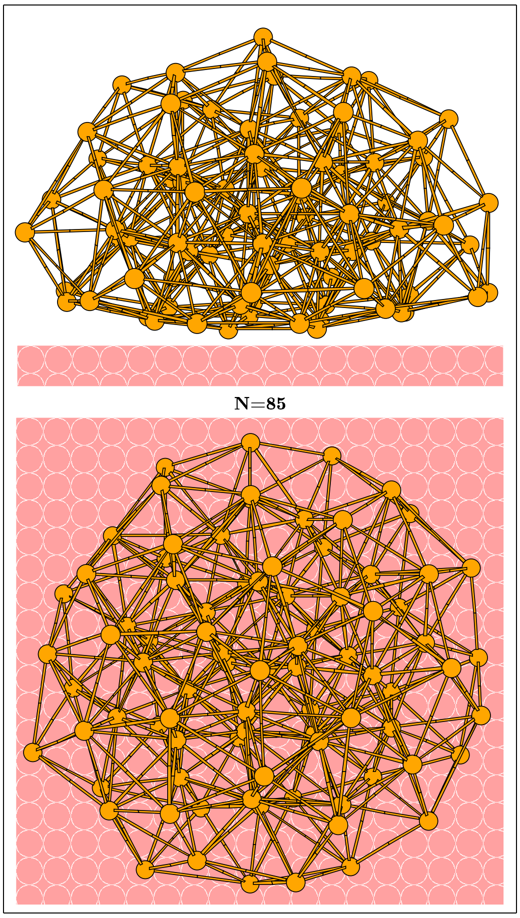

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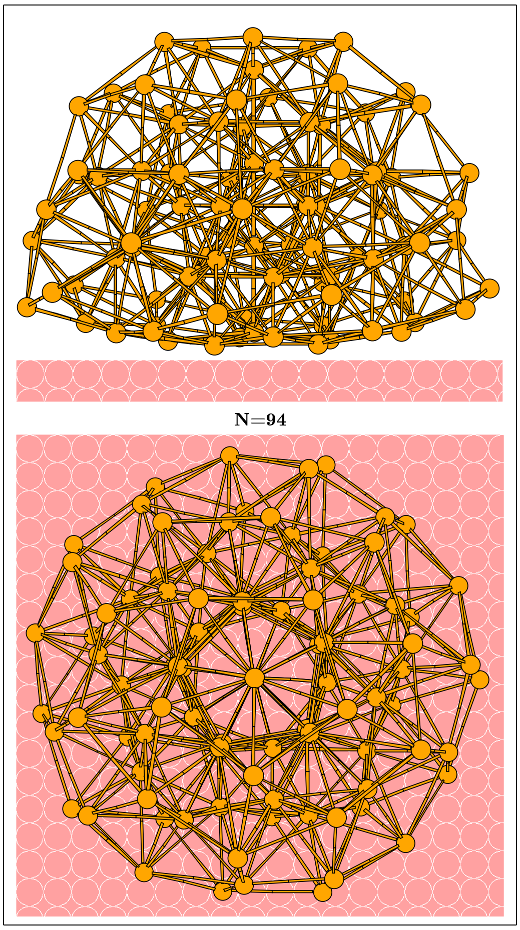

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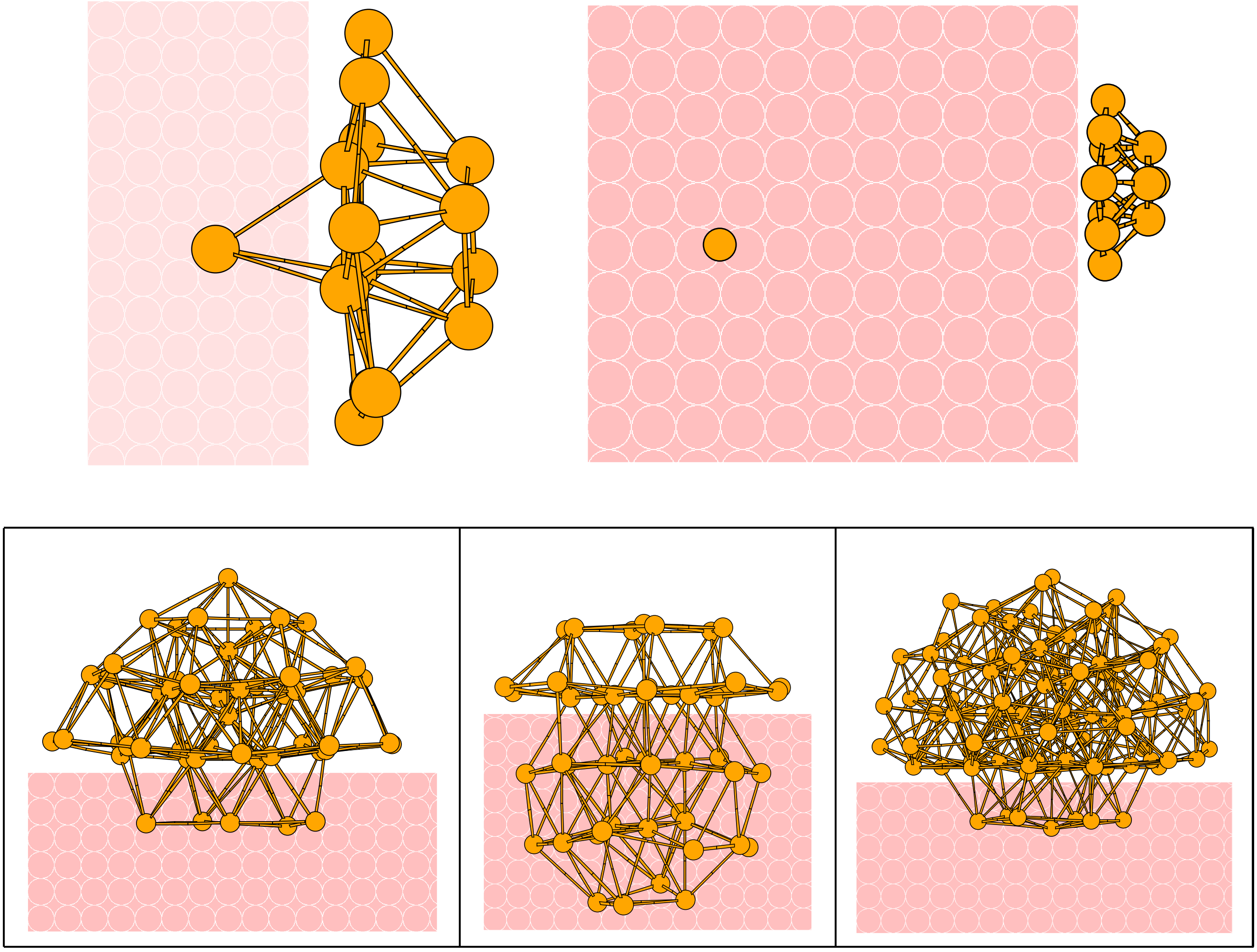
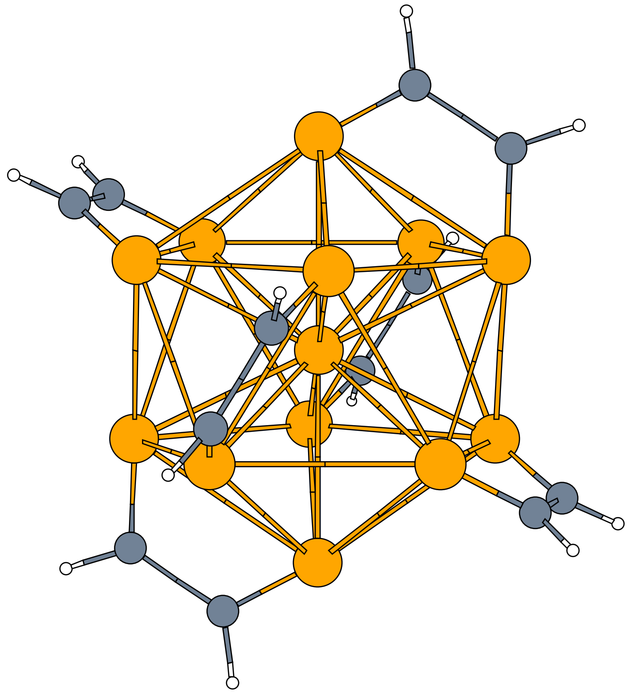


Clusters developing an interface with the solid

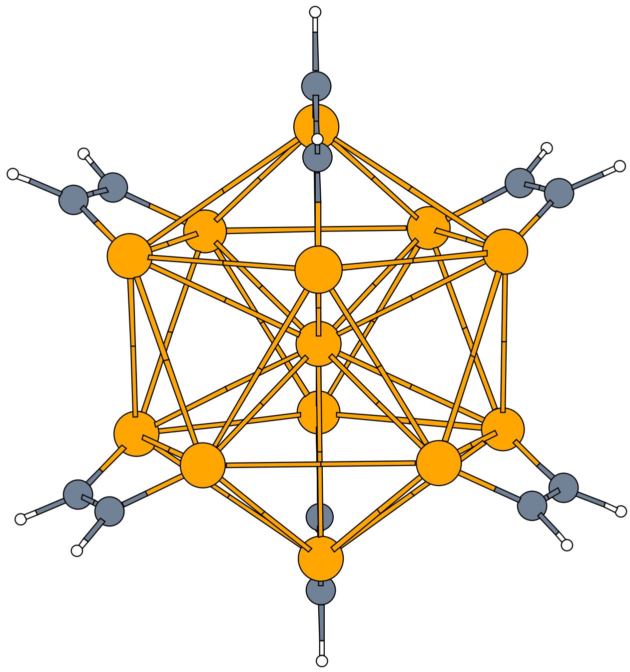
Applications 7: $Fe_{13}(C_2H_2)_6$

(Huysken & Morjan, 2003)

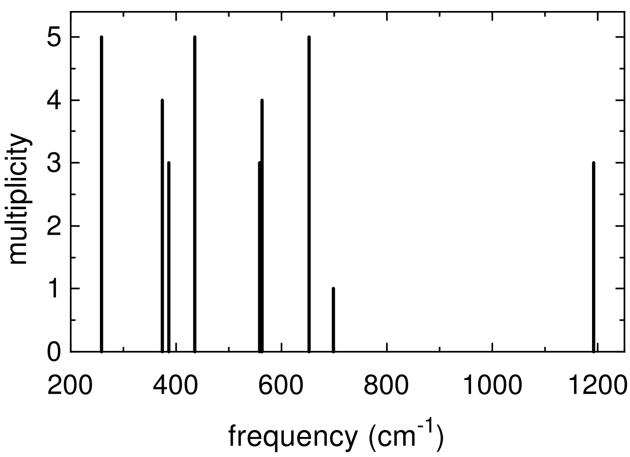
- Fe - core
- C_2H_2- ethylene clasps
- core energy, structure and vibration spectra



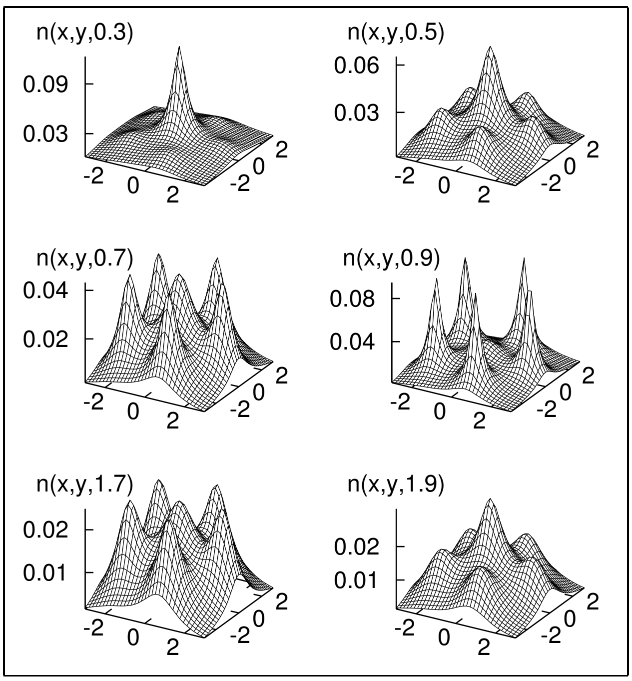
Ground-state



Isomer



Vibration spectrum



Electron density