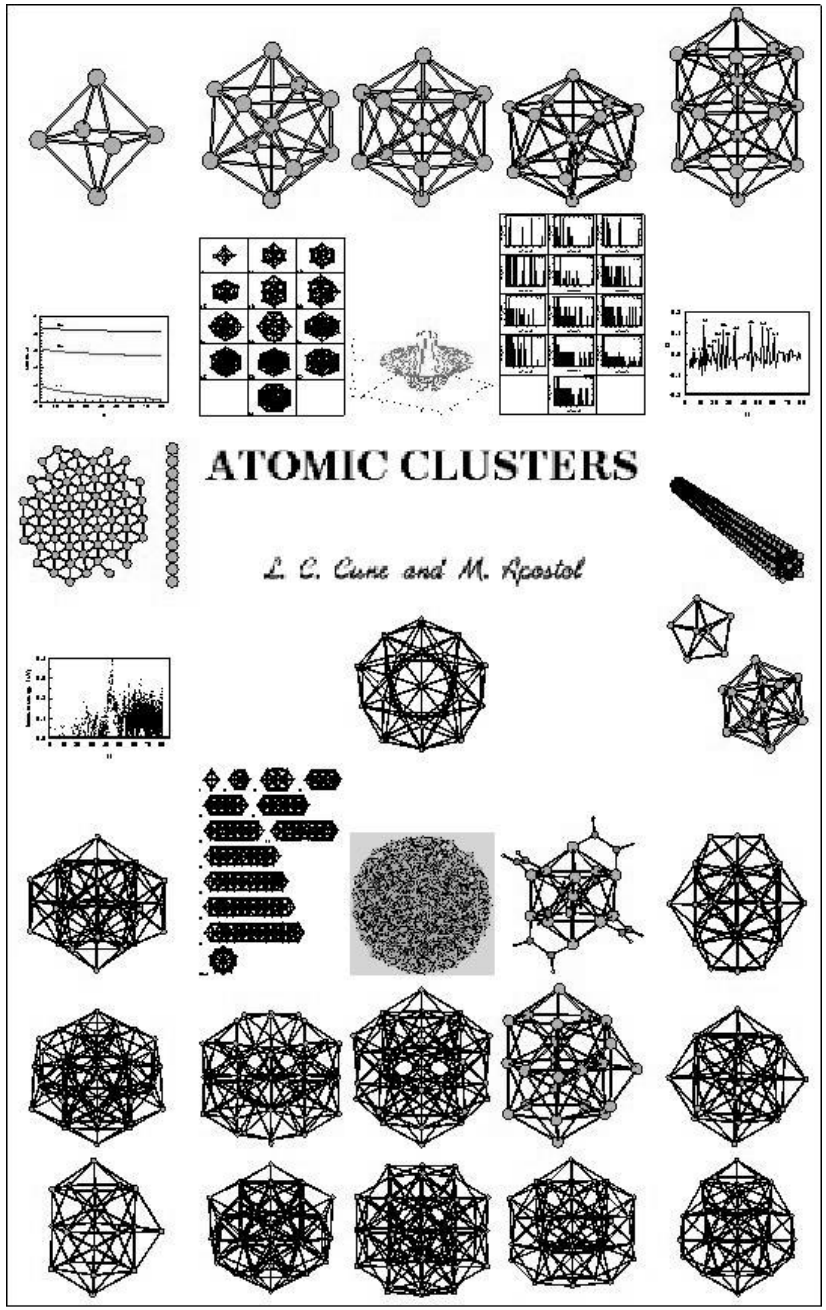

Figure 12: A shop window of clusters

$Z \gg 1$, $N \gg 1$, one-electron states, valence atomic shells, atomic-like *vs* extended (chemical bond) orbitals

$$\psi = \alpha\varphi + \beta\Phi \ , \ \alpha^2 + \beta^2 = 1$$

Ionic density

$$\rho = \sum (1-\alpha^2)\varphi^2 = \sum \beta^2 \varphi^2$$

Effective valence

$$z^* = \sum \int (1-\alpha^2)\varphi^2 \Rightarrow \beta^2 z$$

Point-like approximation

$$\rho = z_i^* \delta(\mathbf{r} - \mathbf{R}_i)$$

$$H = \sum_\alpha \mathbf{p}_\alpha^2/2m - e^2 \sum_{i\alpha} \frac{z_i^*}{|\mathbf{R}_i - \mathbf{r}_\alpha|} +$$

$$+\frac{1}{2}e^2 \sum_{\alpha\beta} \frac{1}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} + \frac{1}{2}e^2 \sum_{ij} \frac{z_i^* z_j^*}{|\mathbf{R}_i - \mathbf{R}_j|}$$

$$n(\mathbf{r}) = \sum \Phi^*(\mathbf{r})\Phi(\mathbf{r}) \ , \ n(\mathbf{r},\mathbf{r}') = \sum \Phi^*(\mathbf{r})\Phi(\mathbf{r}')$$

$$E_{HF} = \int d\mathbf{r} \cdot \sum \Phi^*(\mathbf{p}^2/2m)\Phi -$$

$$-e^2 \sum_i \int d\mathbf{r} \cdot \frac{z_i^*}{|\mathbf{R}_i - \mathbf{r}|} n(\mathbf{r}) + \frac{1}{2} e^2 \int d\mathbf{r} d\mathbf{r}' \cdot \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}) n(\mathbf{r}') -$$

$$-\frac{1}{2} e^2 \int d\mathbf{r} d\mathbf{r}' \cdot \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}, \mathbf{r}') n(\mathbf{r}', \mathbf{r}) + \frac{1}{2} e^2 \sum_{ij} \frac{z_i^* z_j^*}{|\mathbf{R}_i - \mathbf{R}_j|}$$

Hartree-Fock equation

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

Hartree field

$$\varphi = e \sum_i z_i^* / |\mathbf{r} - \mathbf{R}_i| - e \int d\mathbf{r} \cdot n(\mathbf{r}') / \left|\mathbf{r} - \mathbf{r}'\right|$$

Poisson equation

$$\Delta \varphi = -4\pi e \sum_i z_i^* \delta(\mathbf{r} - \mathbf{R}_i) + 4\pi e n$$

Exchange energy

$$\varepsilon_{ex}(\Phi) = -e^2 \int d\mathbf{r}' \cdot n(\mathbf{r}', \mathbf{r}) / \left|\mathbf{r} - \mathbf{r}'\right| \cdot \Phi(\mathbf{r}') =$$

$$= -e^2 \int d\mathbf{r}' \cdot 1 / \left|\mathbf{r} - \mathbf{r}'\right| \cdot \sum \Phi^*(\mathbf{r}') \Phi(\mathbf{r}) \cdot \Phi(\mathbf{r}')$$

Quasi-Classical Description

-$\epsilon_{ex}(\Phi)$ admits plane waves as eigenfunctions

-"rigidity" of the $\epsilon_{ex}(\Phi)$ under local variations of electron density (non-locality); a new parameter $k_F(\mathbf{r})$

-use this parameter to screen off the Coulomb interaction, and to get Hartree equation

$$(\mathbf{p}^2/2m)\Phi - e\varphi \cdot \Phi = \varepsilon\Phi$$

admit quasi-plane waves solutions; therefore, the Hartree-Fock equation admits (quasi-) plane waves as solutions, to the first approximation

-variation with respect to $k_F(\mathbf{r})$

$$\hbar^2 k_F^2/2m - e\varphi = 0$$

-$n = k_F^3/3\pi^2$, $n \sim \varphi^{3/2}$, classical 3/2-Thomas-Fermi model in Poisson equation; valid for $z_i^* \to \infty$, "no-binding" theorem ("quasi-classical approximation")

Linearized Thomas-Fermi theory

$$k_F^2/2 \to \bar{k}_F k_F/2 = \varphi$$

$$n = \bar{k}_F^2 k_F/3\pi^2 = (2/3\pi^2)\bar{k}_F\varphi = (q^2/4\pi)\varphi$$

$$\Delta\varphi = -4\pi \sum_i z_i^* \delta(\mathbf{r} - \mathbf{R}_i) + q^2\varphi$$

→**binding**; $\bar{k}_F$ (q) , variational parameter

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

$$\begin{aligned} E_{pot} &= \int d\mathbf{r} \cdot (-\varphi n + \tfrac{1}{2}\varphi_e n) + E_{ion-ion} = \\ &= -\tfrac{1}{2} \int d\mathbf{r} \cdot (\varphi + \varphi_i) n + E_{ion-ion} = \\ &= -\tfrac{q^2}{8\pi} \int d\mathbf{r} \cdot (\varphi + \varphi_i) \varphi + E_{ion-ion} \end{aligned}$$

$$\varphi_i = \sum_i \frac{z_i^*}{|\mathbf{r} - \mathbf{R}_i|}\ ,\ E_{ion-ion} = \frac{1}{2} \sum_{ij} \frac{z_i^* z_j^*}{\left|\mathbf{R}_i - \mathbf{R}_j\right|}$$

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

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

$$E_{pot} = -Bq \ , \ r_{ij} \sim a \sim 2.73/q$$

$$T = \frac{V}{10\pi^2} k_F^5 \rightarrow \frac{\overline{k_F^4}}{10\pi^2} \int d\mathbf{r} \cdot k_F = \frac{27\pi}{40 \cdot 64} q^6 \int d\mathbf{r} \cdot \varphi$$

$$= \frac{27\pi^2}{640} z_0 q^4 = Aq^4/4 \ , \ z_0 = \sum_i z_i^*$$

$$E_q = T + E_{pot} = Aq^4/4 - Bq$$

$$\rightarrow q = (B/A)^{1/3} = 0.77 z^{*1/3} \ , \ a \sim 3.5/z^{*1/3}$$

$$E_q = -0.43 N z^{*7/3}$$

$$E_b = E_q + E_{ex}$$

$$E_{ex} = -\frac{Vk_F^4}{4\pi^3} \to -\frac{\overline{k_F^3}}{4\pi^3} \int d\mathbf{r} \cdot k_F =$$

$$-\frac{9}{128} q^4 \int d\mathbf{r} \cdot \varphi = -\frac{9}{32} q^2 N z^* =$$

$$= -0.17 N z^{*5/3}$$

Plane-waves, Average field

$$\varphi_0 = \overline{\varphi} = \overline{\sum_i \frac{z_i^*}{|\mathbf{r} - \mathbf{R}_i|} e^{-q|\mathbf{r}-\mathbf{R}_i|}} =$$

$$= 4\pi z^* / a^3 q^2 = 0.48 z^{*4/3}$$

Quantal corrections

$$(-\hbar^2/2m)\Delta\Phi - e\varphi \cdot \Phi = \varepsilon\Phi$$

perturbation (off-diagonal exchange):

$$\varepsilon_{ex}(\Phi)$$

$$\overline{k}_F = \frac{3\pi}{8} q_{av}^2 = \frac{1}{z_0} \int d\mathbf{r} \cdot k_F n = \frac{16}{3\pi z_0} \int dr \cdot r^2 \varphi^2$$

$$q_{av} = 0.9 z^{*1/3} \Leftrightarrow q_{var} = 0.77 z^{*1/3} \text{ , } 17\%$$

Lifetime effects; $\delta\varepsilon \sim \delta\varphi$, $(\delta\varphi)^2 \Rightarrow 0.17 \cdot 17\% = 3\%$

Atom

$$\varphi = Z e^{-qr}/r$$

Quasi-classical energy $-11.78 Z^{7/3}$eV (exchange $-4.6 Z^{5/3}$eV), $q_{var} = 0.77 Z^{1/3}$, $q_{av} = 0.9 Z^{1/3}$; $\overline{q} = 0.84 Z^{1/3}$; Quantal corrections (Hartree) $-4.56 Z^{7/3}$eV $\Rightarrow E = -16 Z^{7/3}$eV

$$N_{out} = \int_{r>R} d\mathbf{r} \cdot n = Z(1+qR)e^{-qR}$$

$$z^* = z(1+qR)e^{-qR} = z(1+0.84 Z^{1/3})e^{-0.84 Z^{1/3}}$$

$(R = 1)$; $\Rightarrow z^*_{Fe} = 0.57$ $(Z = 26,\ z = 2)$

-Magic forms, magic numbers (ground state)

$N = 6, 11, 13, 15, 19, 23, 26, 29, 34, 45, 53, 57, 61, ...$

-Isomers, statistical magic numbers; quadrupole potential, electronic magic numbers

-Ionization potential ($I = (1 - \beta^2)I_a + \beta^2 I_b$), electron affinity

-plasma frequency (fractional occupancy)

-quasi-classical quasiparticles, Fermi liquid, $f = (4\pi N z^*/q^2)((2\pi\hbar)^3/V)\delta(\mathbf{p} - \mathbf{p}')$; $m^* = m(1 + 0.39 z^{*1/3})$; no 0-sound, no renormalized spin paramagnetism

-phonons, electron-phonon interaction, sound velocity $v_s = [(0.43 z^{*7/3} + 0.68 z^{*5/3})/A]^{1/2}$m/s

-response, polarizability, diamagnetic susceptibility

-magnetic moment, Hund's rule; e.g., 6d, Fe$\Rightarrow$ $4\mu_B$; 0.57, 0.43$\Rightarrow$ $4.57\mu_B$

-quantal corrections

-spatial structure of the ionic cores

-hetero-atomic clusters

-solids

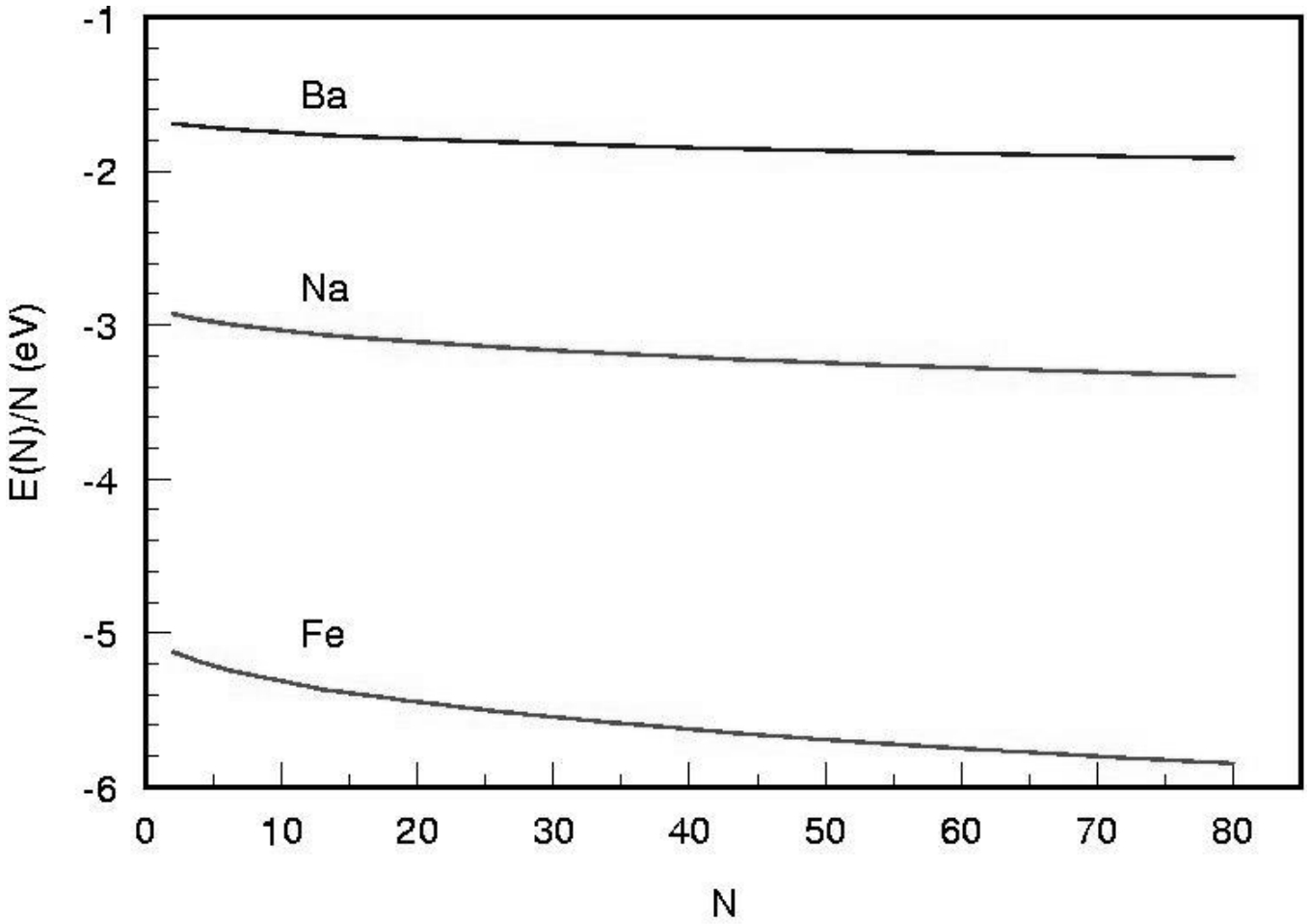

Figure 1: Ground-state energy per atom $E(N)/N$ *vs* cluster size N for Na ($z^* = 0.44$)), Fe ($z^* = 0.57$) and Ba ($z^* = 0.34$)

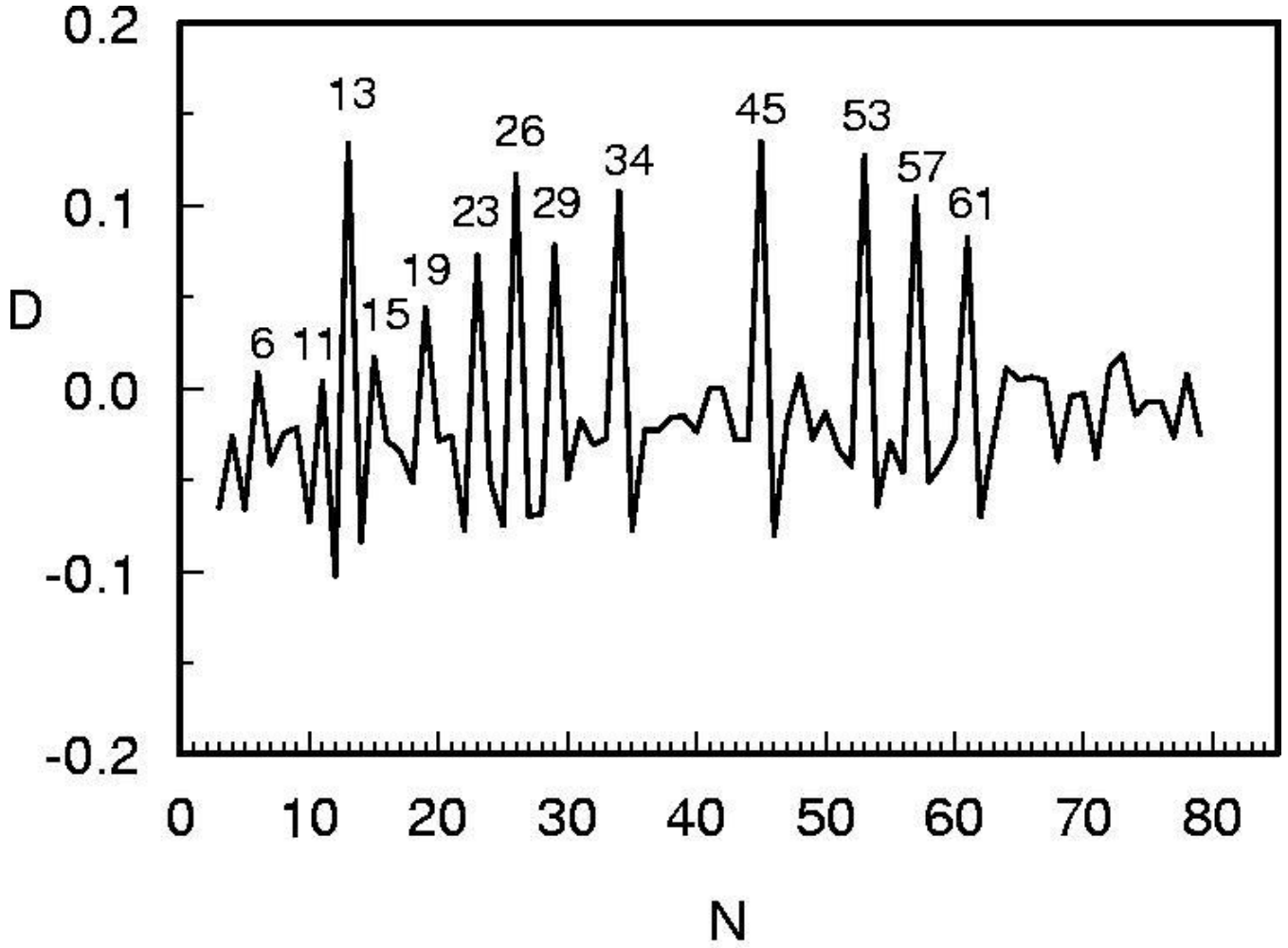

Figure 2: Geometric magic numbers for homo-atomic metallic clusters

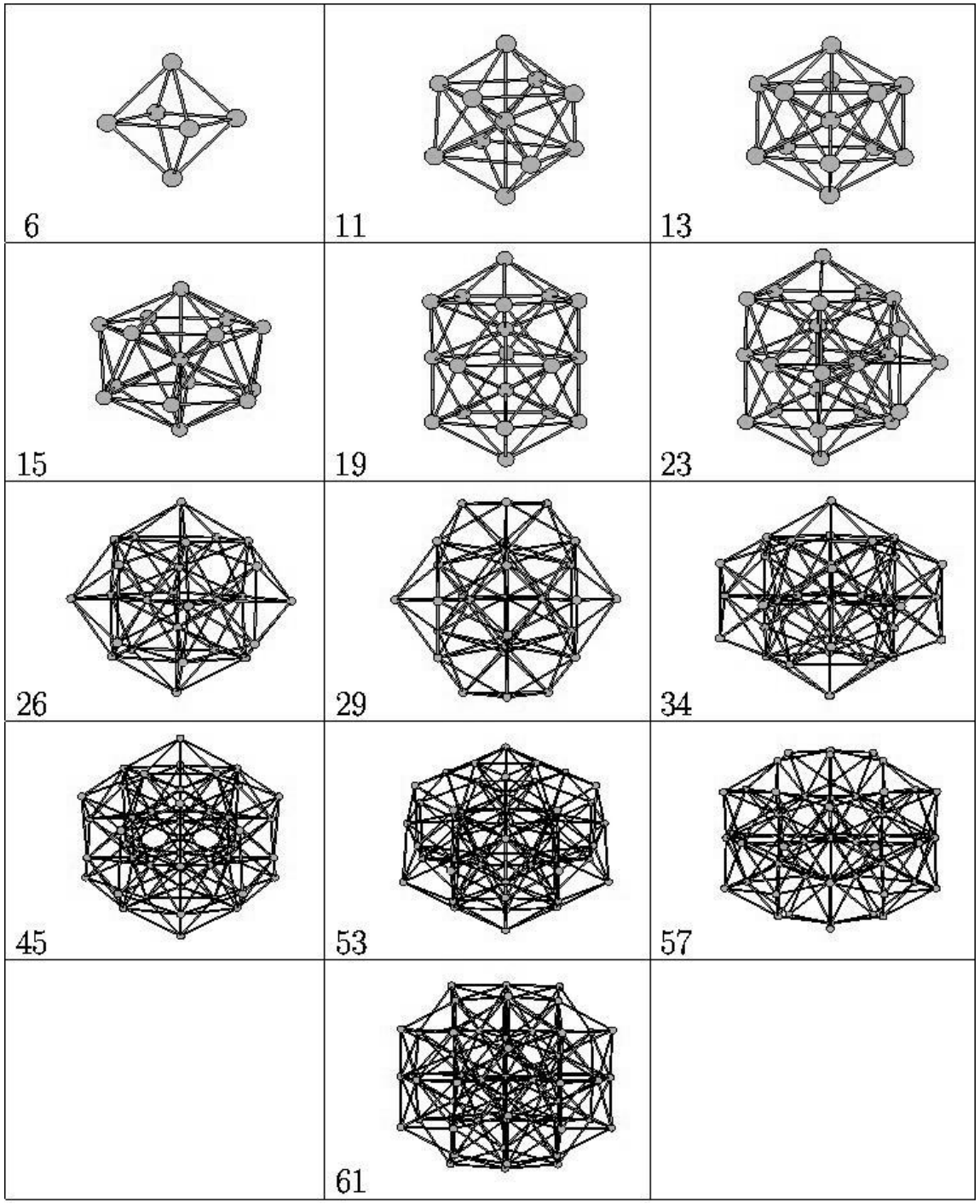

Figure 3: Magic homo-atomic metallic clusters

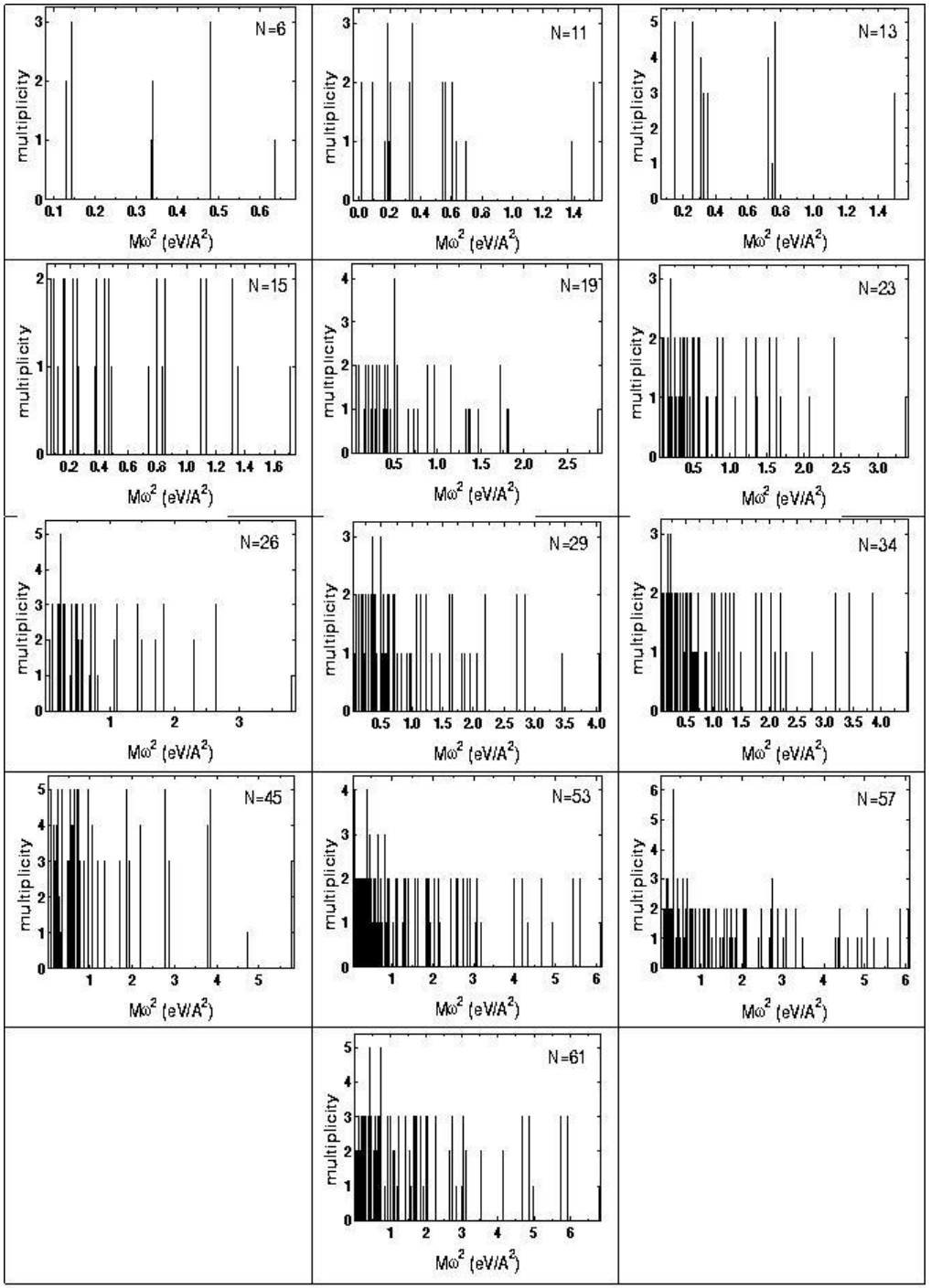

Figure 4: Vibration spectra for magic Fe-clusters ($z^* = 0.57$)

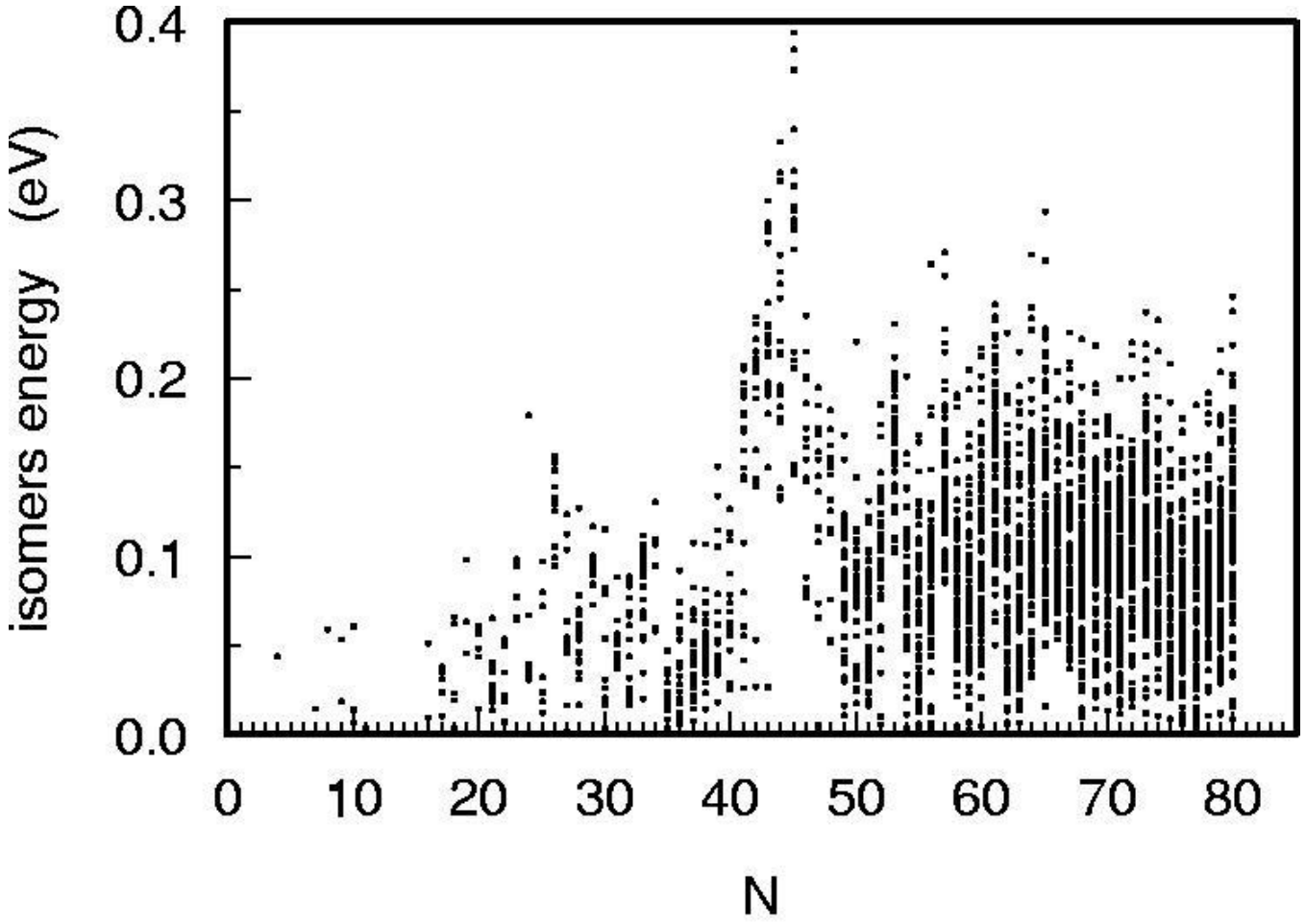

Figure 5: Isomer table for Fe-clusters ($z^* = 0.57$; errors less than 10^{-2}eV)

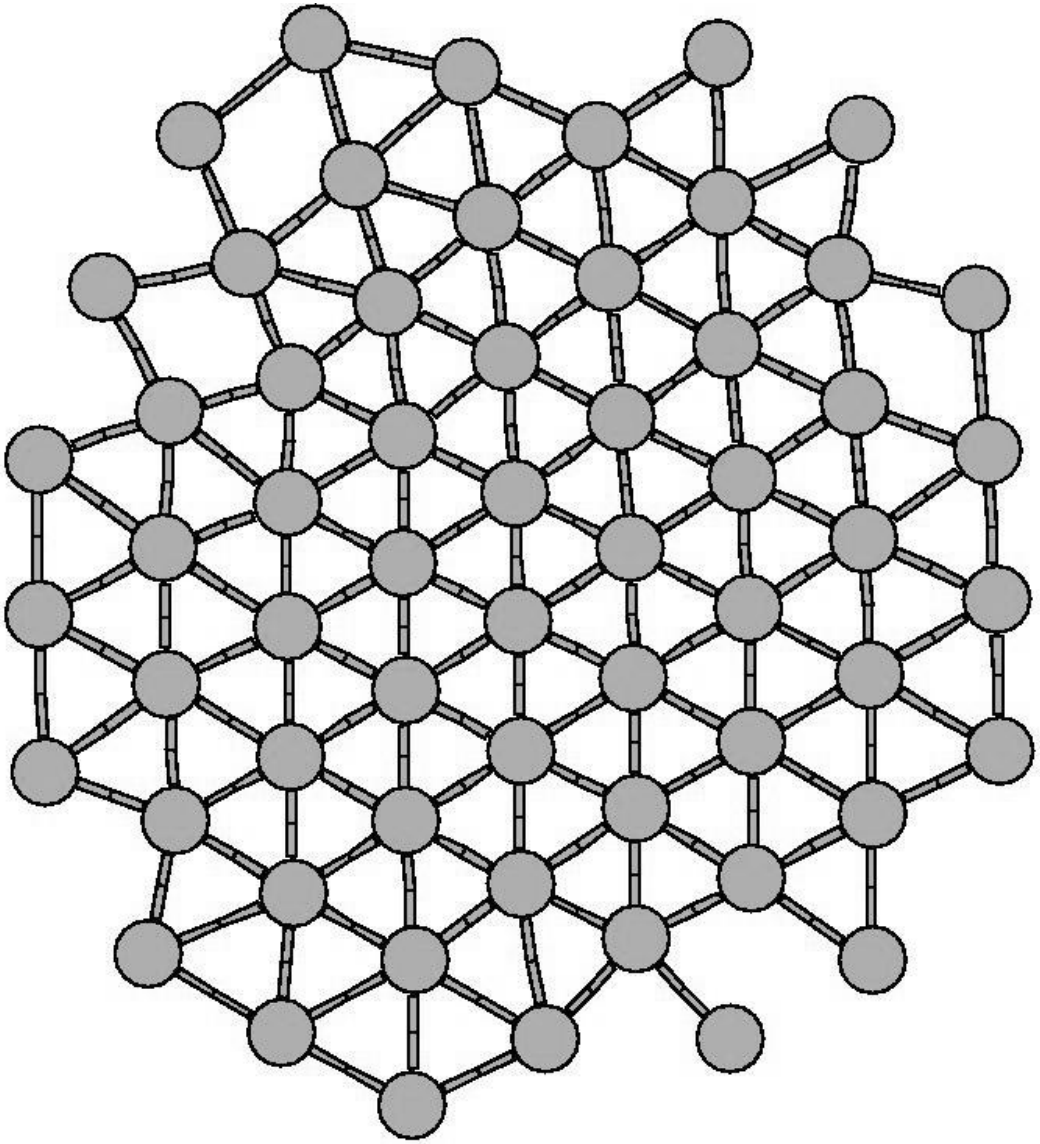

Figure 6: A hexagonal atomic sheet obtained from a saddle point of the potential energy

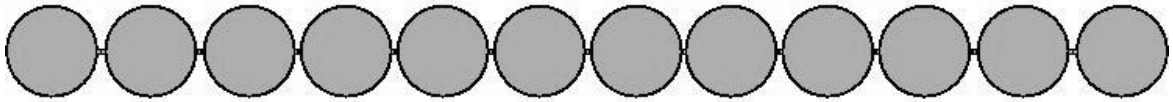

Figure 7: An (unstable) atomic chain

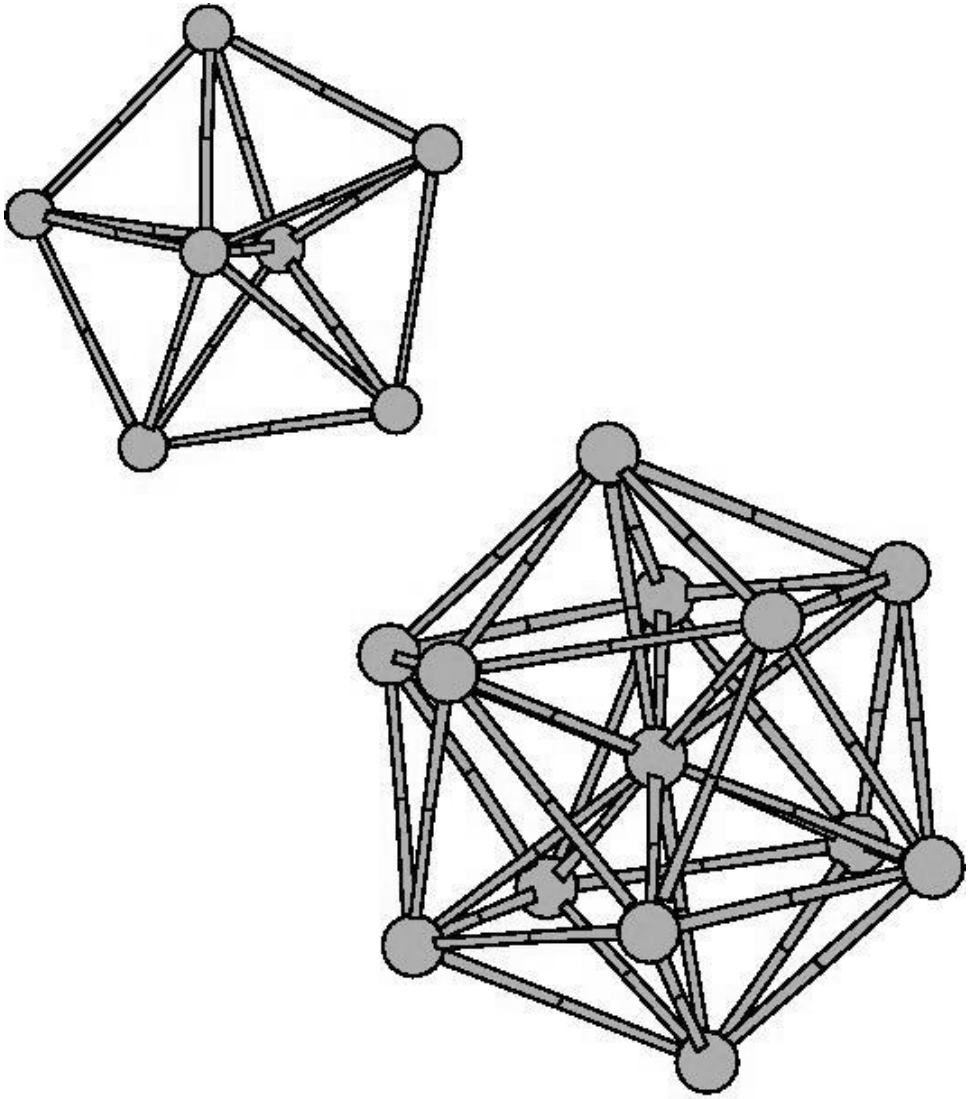

Figure 8: Two atomic fragments in quasi-equilibrium

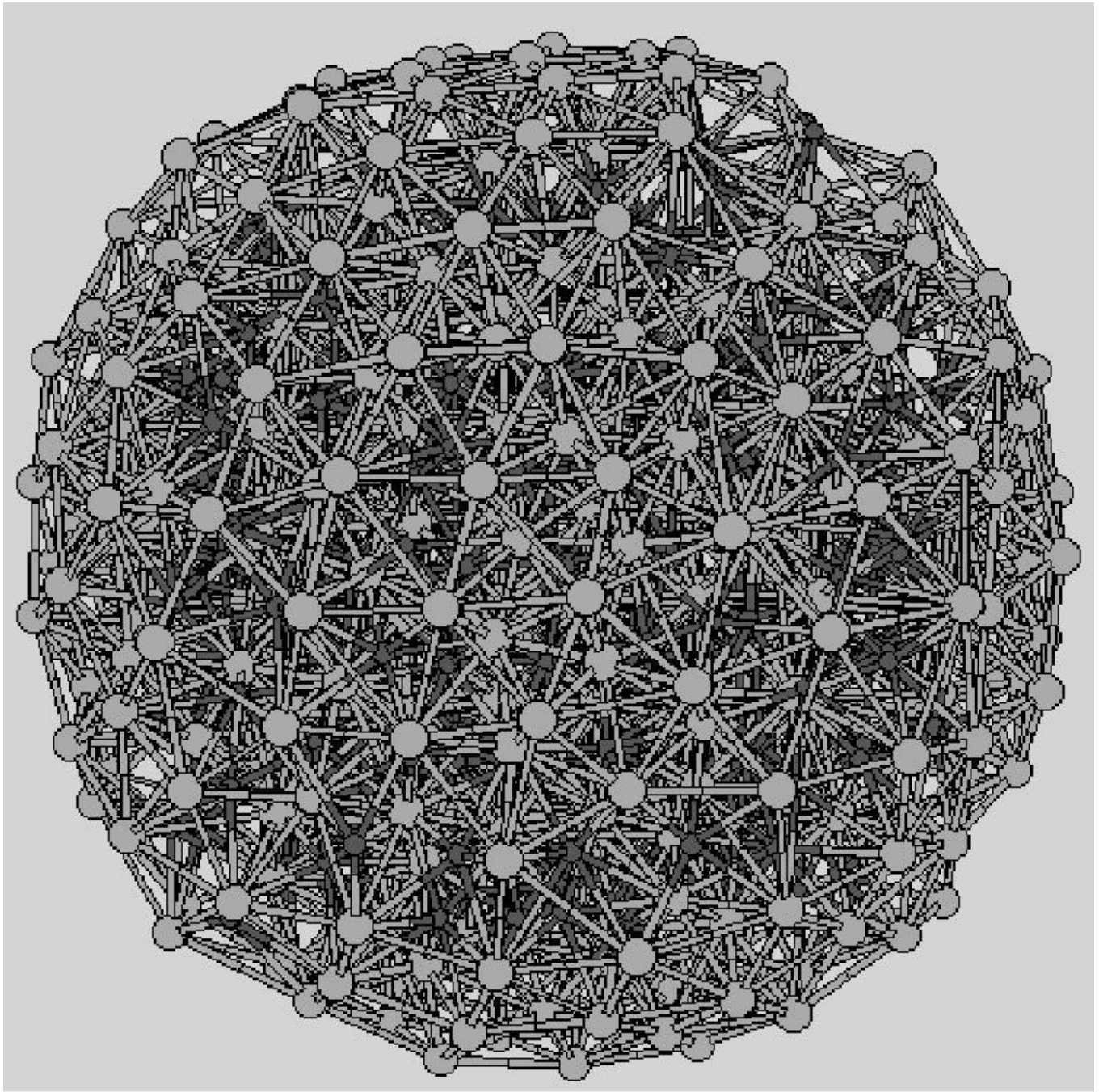

Figure 9: A bcc-core solid of 855-atoms

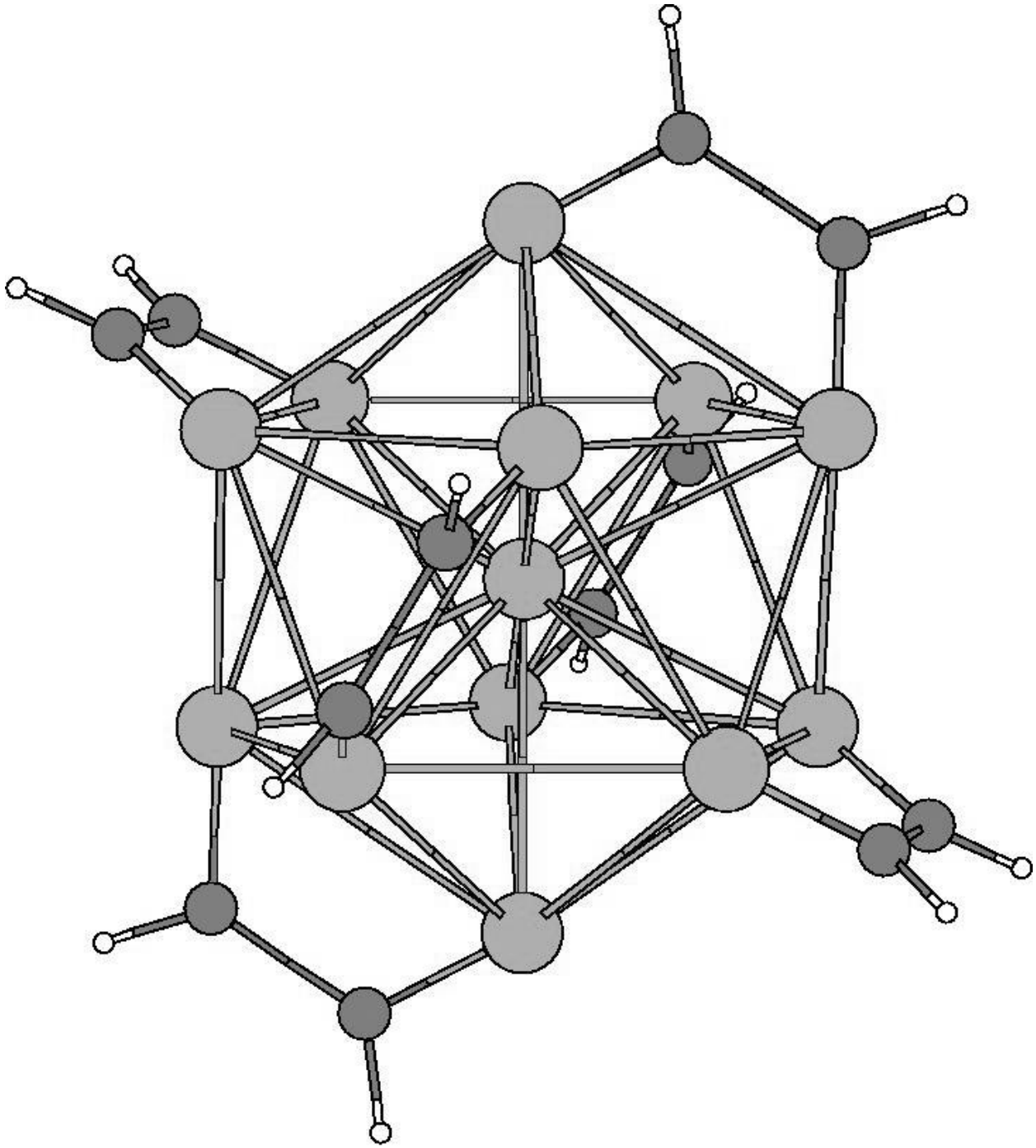

Figure 10: $Fe_{13}(C_2H_2)_6$ with Fe_{13} in the icosahedron vertices and $(C_2H_2)_6$ on sides

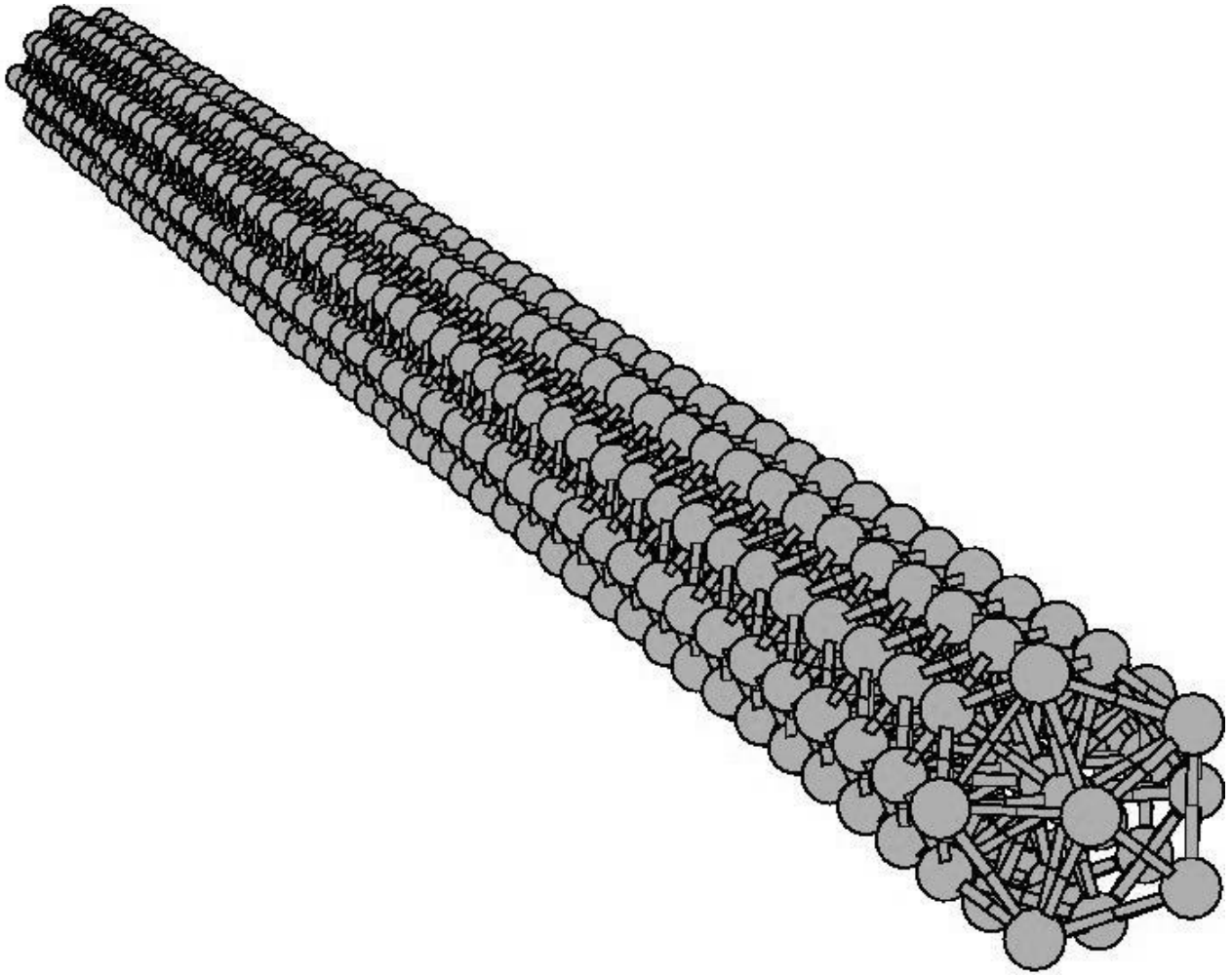

Figure 11: A "popcorn" metallic wire (unstable), single-wall nanotube, made of intertwined icosahedra