Atomic Clusters
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tomic clusters are the smallest bits of solids, the tiniest parts of our atomic world. I prefer to call them the nuclei of the condensed matter. Here are a few examples of atomic clusters. One can see a 13-atoms cluster with an icosahedral symmetry, which is characteristic of such atomic structures. It consists of two rotated pentagons, one atom at the bottom, one on the top and another in the centre. On increasing the size of the clusters one gets more and more complex aggregates, like the 45-atoms cluster which is highly symmetric, or the 80-atoms cluster with an intricate symmetry. These are homo-atomic clusters, but here is a hetero-atomic cluster consisting of a 13-Fe core covered with 6 C_2H_2 radicals, synthesized recently by dr. Huisken in Gottingen; we helped in assessing its wonderful, highly-symmetric structure. One can also see an unstable hexagonal two-dimensional atomic sheet, as well as a metallic nanowire, made out of intertwined icosahedra. This nanowire is unstable, but its diameter fits perfectly the inner diameter of a carbon nanotube, which is stable; so, we may think of introducing it into a carbon nanotube, leaving outside just one metallic atom protruding from the end icosahedron, making thus a perfect, ideal tip for electron microscopy. Here are two atomic fragments, in a metastable state. attracting each other with an extremely weak force; after 4 days of running our computer we found the two fragments got together in one, stable aggregate. Finally, we have here a large atomic structure of 855 atoms, obtained by relaxing a bcc-structure; its surface is quite disordered and goes pretty farther in depth, but the core still preserves the bcc structue over cca $4-5$ unit cells; we hope this way to understand the way the translational symmetry grows up.

We posed to ourselves the following problem. Suppose we take a number n_1 of atoms of one kind, n_2 atoms of another, n_3 of another, and so on, in a finite sequence; do these atoms bind together, and how does the aggregate looks like, and what are its physical and chemical properties? We found the answer by means of the so-called quasi-classical theory of atomic binding, and we are able to know everything about such clusters: their cohesion, or binding, energy, their geometric forms, their ground-states and excited states, the inter-atomic distances, vibration spectra, the one-electron energy levels, ionization potentials, chemical affinities, plasmons, electron-phonon interaction, electric polarizabilities, diamgnetic susceptibilities, response to external perturbations, magnetic momenta, etc. For the time being our calculations are restricted to homo-atomic clusters made out of metallic ions with s-, d- and f-valence shells, whose ionic cores can be approximated by point-like charges; and our scheme of computation involves a two-, three-steps of iterations, the first one being the main quasi-classical contribution, the latter involving the quantal corrections, which amount to cca $15-17\%$ of the main contribution; and we are at the quasi-classical contribution at this moment, the quantal corrections being under way. The way we perform the computations is based on the fact that we know, from first principle, the effective inter-atomic potentials, which
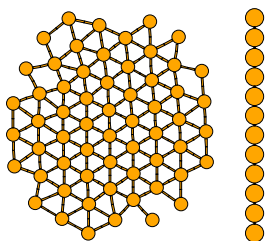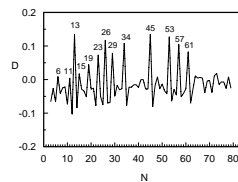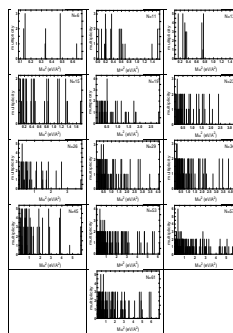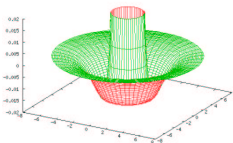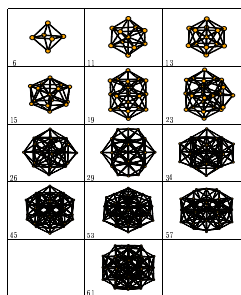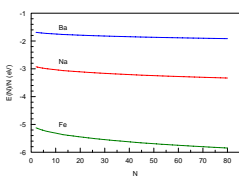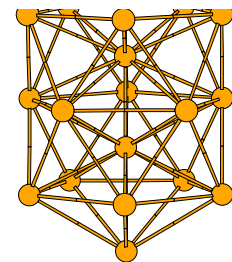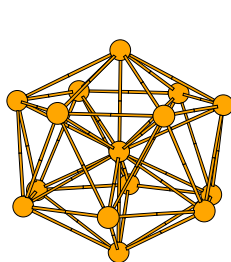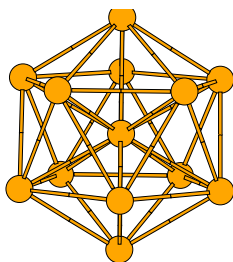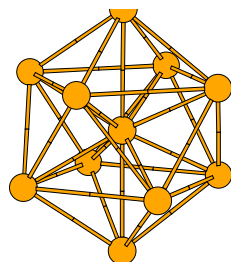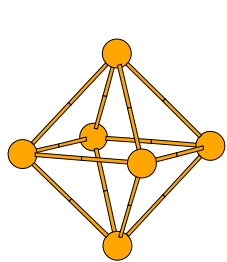
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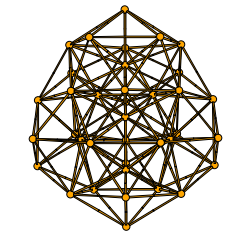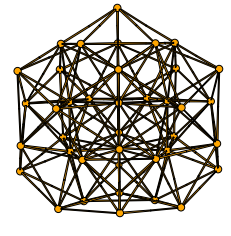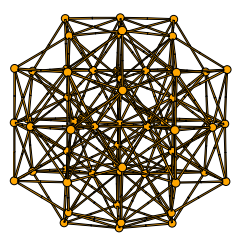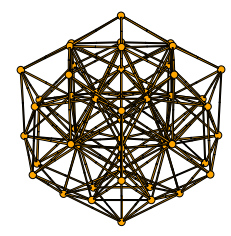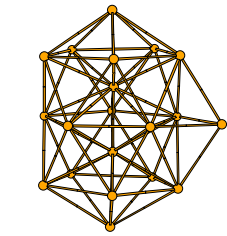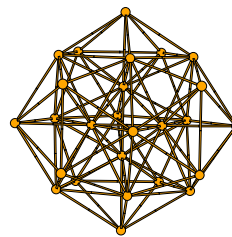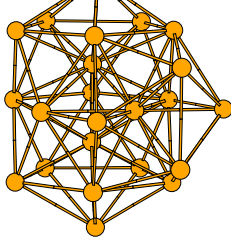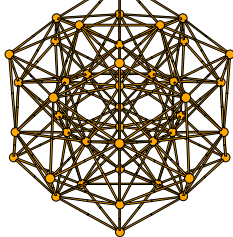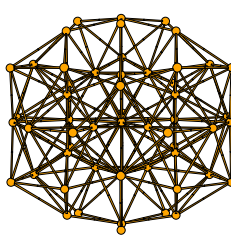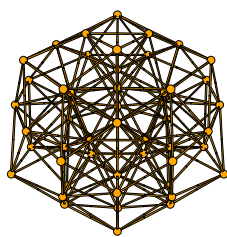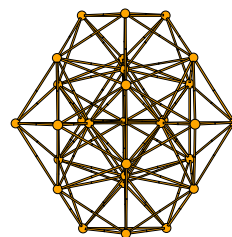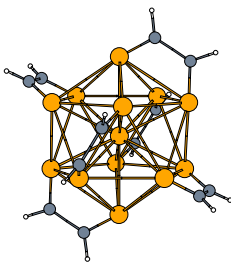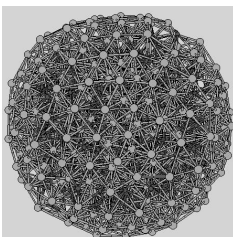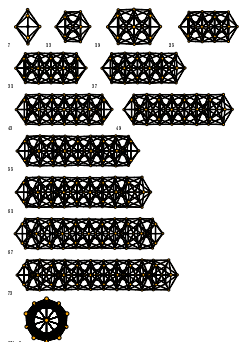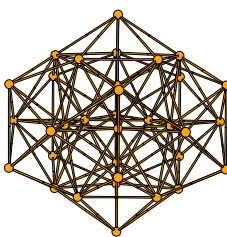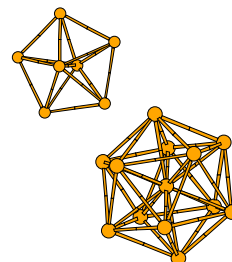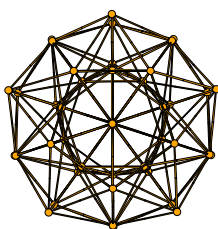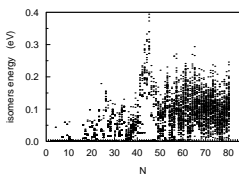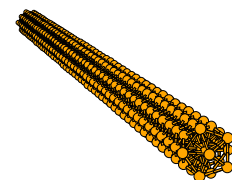
of course is attractive at long distances and repulsive at short distances. One can see it depicted here, in the wind show of clusters. For point-like ionic charges it looks like a screened Coulomb potential multiplied by a polynomial of the first rank, the only input parameter it contains being the effective charge z_i^* of the i-th ion. Actually, we can derive, in some cases, this parameter from the atomic screening theory, as depending on the atomic number Z_i and the nominal valence z_i (for instance $z_i^* = 0.57$ for Fe). In fact, our more general theory of chemical bond allows also the derivation of the nominal valence, while the charge density of the ionic cores look more complicate, like

$$\rho(r) = \sum \alpha_{ia} \left| \chi_{ia}(r - R_i) \right|^2 \quad ,$$

where χ is the a-th valence atomic orbital of the i-th ion, R_i is the psoition of this ion, and $z_i^* = \sum \alpha_{ia}$; or, even more, it is given by a pair-wise

$$\rho(r) = \sum \alpha_{ia;jb} \chi_{ia}^*(r - R_i) \chi_{jb}(r - R_j)$$

distribution of charges. The coefficients $\alpha_{ia;jb}$ are determined both by linear combination of atomic orbitals and by variational minimizing of the whole energy functional with respect to the (fractional) occupancy of the chemical bond orbitals. However, here we restrict ourselves to point-like ionic cores with the charge density

$$\rho(r) = \sum z_i^* \delta(r - R_i) \ .$$

We start with a random space distribution of ionic cores, and, knowing the effective inter-atomic forces, we let these ions to move step by step toward their equilibrium positions; we repeat this computer experiment many times, and thus we are able to get both the ground-state and the shape isomers states. these isomers differ slightly in energy with respect to the ground state, for larger sizes they are very numerous, for smaller sizes there are "white islands" of isomers corresponding to magic clusters. The isomers have the surface atoms in a rather disordered state, their statistical ensemble being much alike to a liquid; while the cluster cores are solid, so that we are in the presence of a new state of matter, where the cores are solid and the surface is liquid, whose properties we do not know yet. In the wind shop we can see the isomer table for Fe-clusters, as well as some magic numbers in the sequence from vanishing size to 80-atoms clusters, together with the corresponding mass spectrum of the ground states, where one can see sharp peaks at 13 atoms and 45 atoms. Here, a nice coincidence occurrs, consisting in that one of the most stable cluster is made of 13 atoms, while the magic clusters are also in number of 13, up to very large cluster size, where they approach the bulk behaviour. The geometric shapes obtained for various clusters are additionally tested for stability by computing the frequency spectra, and here one can see such vibration spectra for magic clusters of Fe, where the multiplicity of the vibrational modes are plotted *vs* frequency, and one can see the vibration frequencies getting denser toward long wavelengths on increasing the cluster size, as expected. The numerical values of the ground-state energies are also given here for various clusters of Fe, Ba and Na, and they agree well with other calculations, where the latter are available, up to the $15 - 17\%$ accuracy of the quasi-classical description, as mentioned above.

Now, here are a few magnified pictures of the ground-state energiesthe corresponding mass spectrum of the geometric ground-statesmagic homo-atomic metalic clusters with wonderful symmetriesvibration spectra for magic Fe-clustersisomer table for Fe-clustersa hexagonal atomic sheet (unstable)an unstable atomic chaintwo atomic fragments in quasi-equilibriuma 855-atoms piece of solid with a bcc-corethe $Fe_{13}(C_2H_2)_6$ clustera "popcorn" metallic wire (unstable)as well as many other curios atomic aggregates.

Now, in closing this talk I give a few technical details of the theory we use to get all this aggregates.
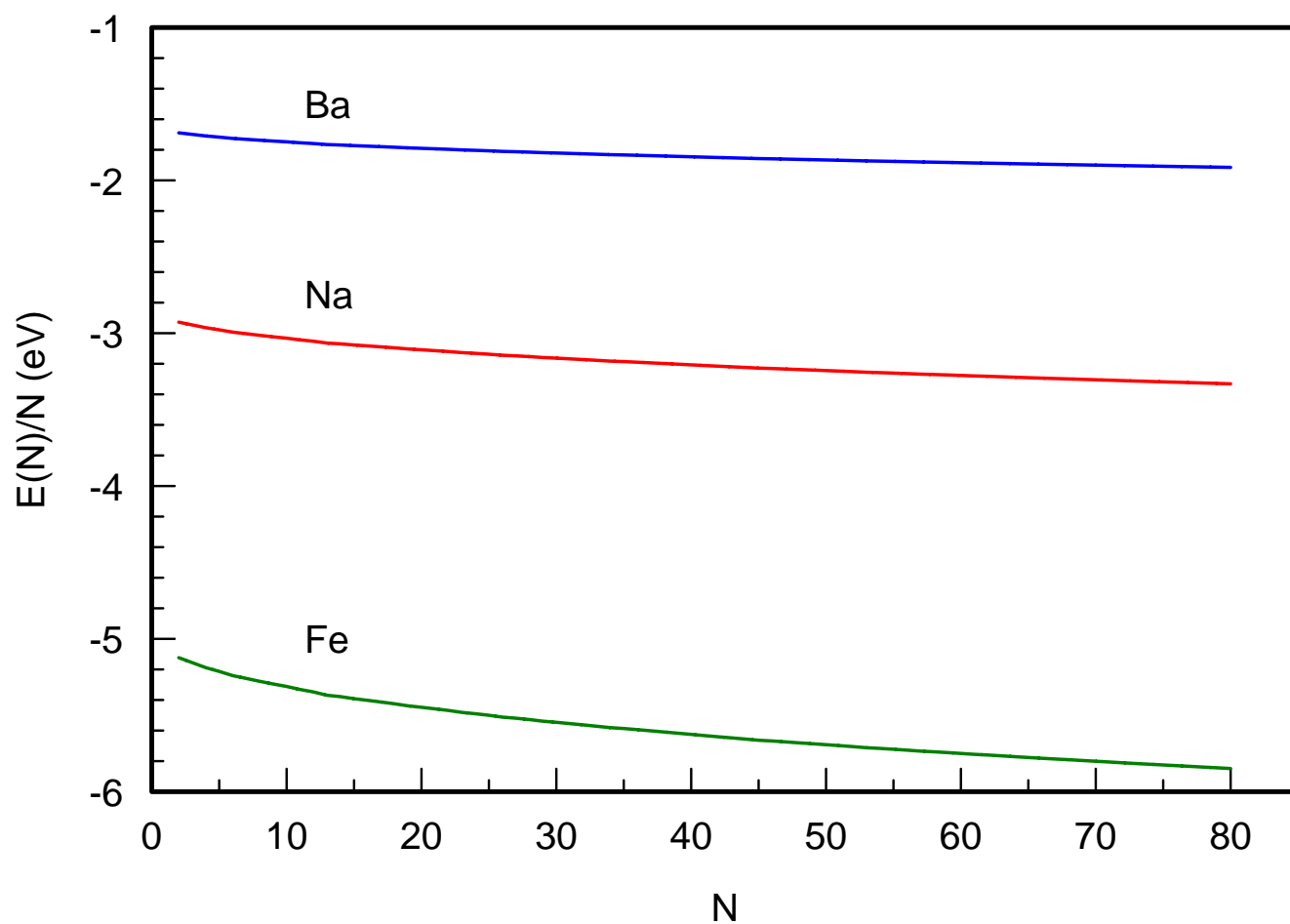
Figure 2: Ground-state energy of Ba ($z = 2$, $z^* = 0.34$), Na ($z = 1$, $z^* = 0.44$) and Fe ($z = 2$, $z^* = 0.57$) clusters.
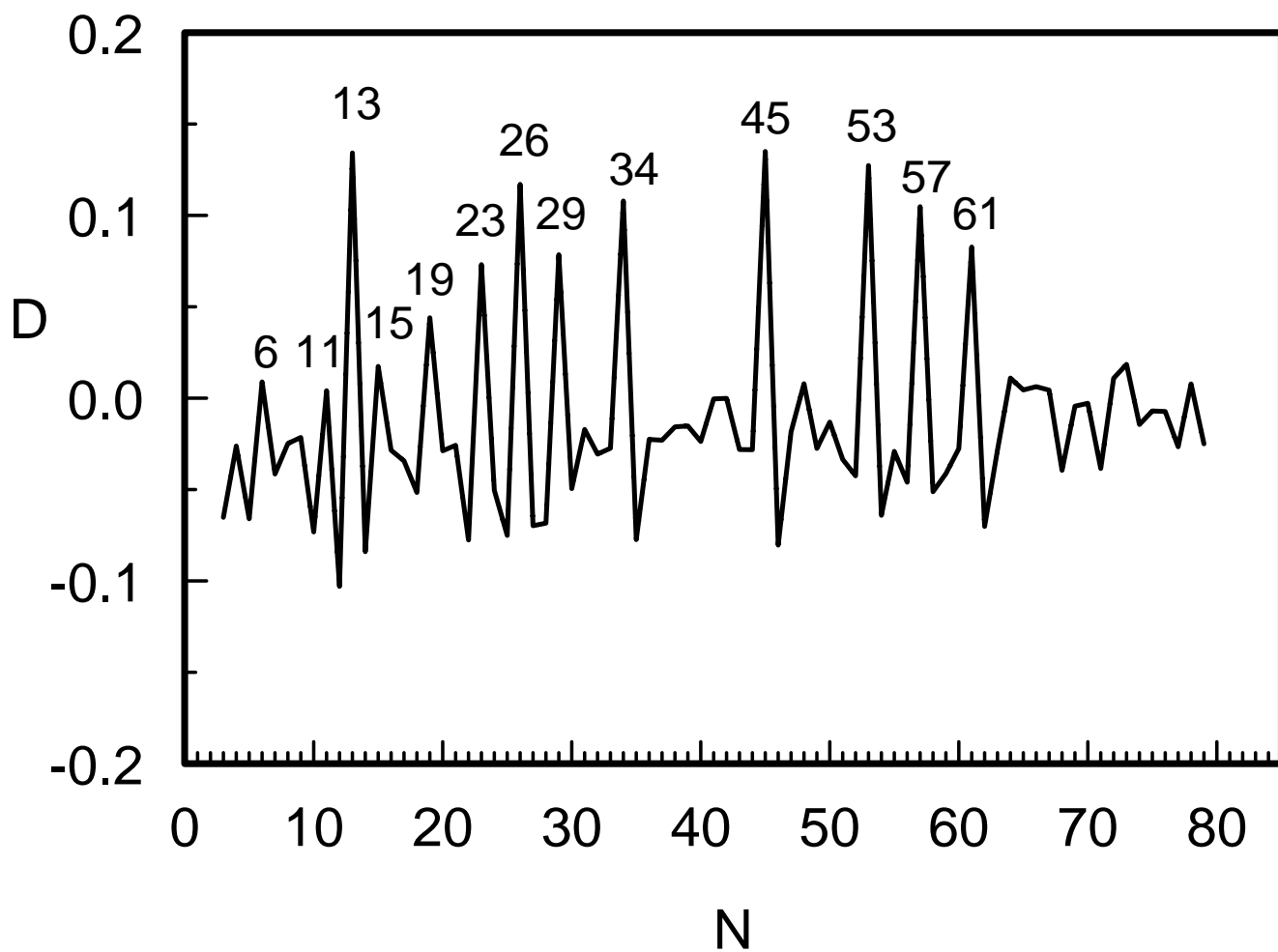
Figure 3: Geometric magic numbers for homo-atomic metallic clusters
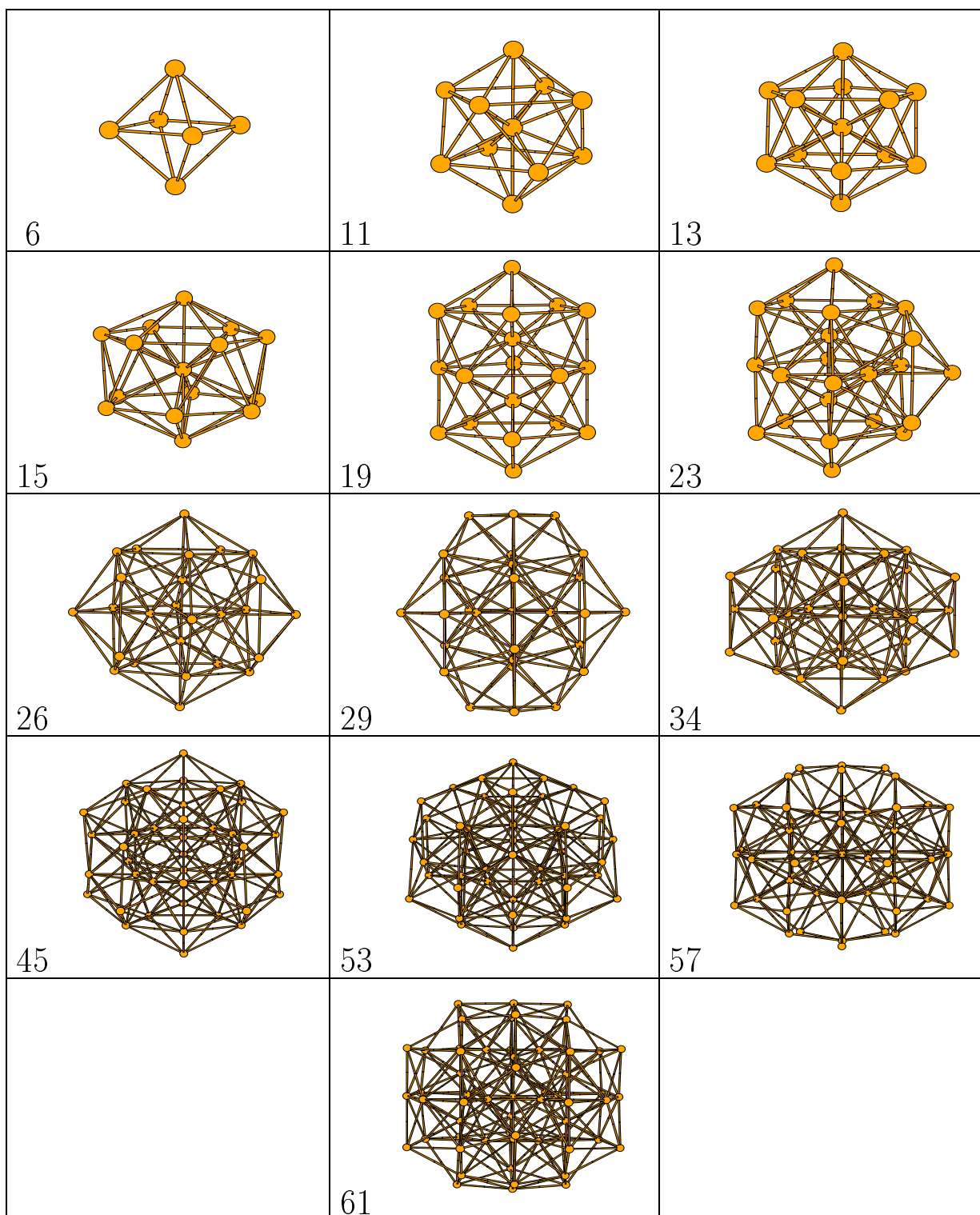
Figure 4: Magic homo-atomic metallic clusters
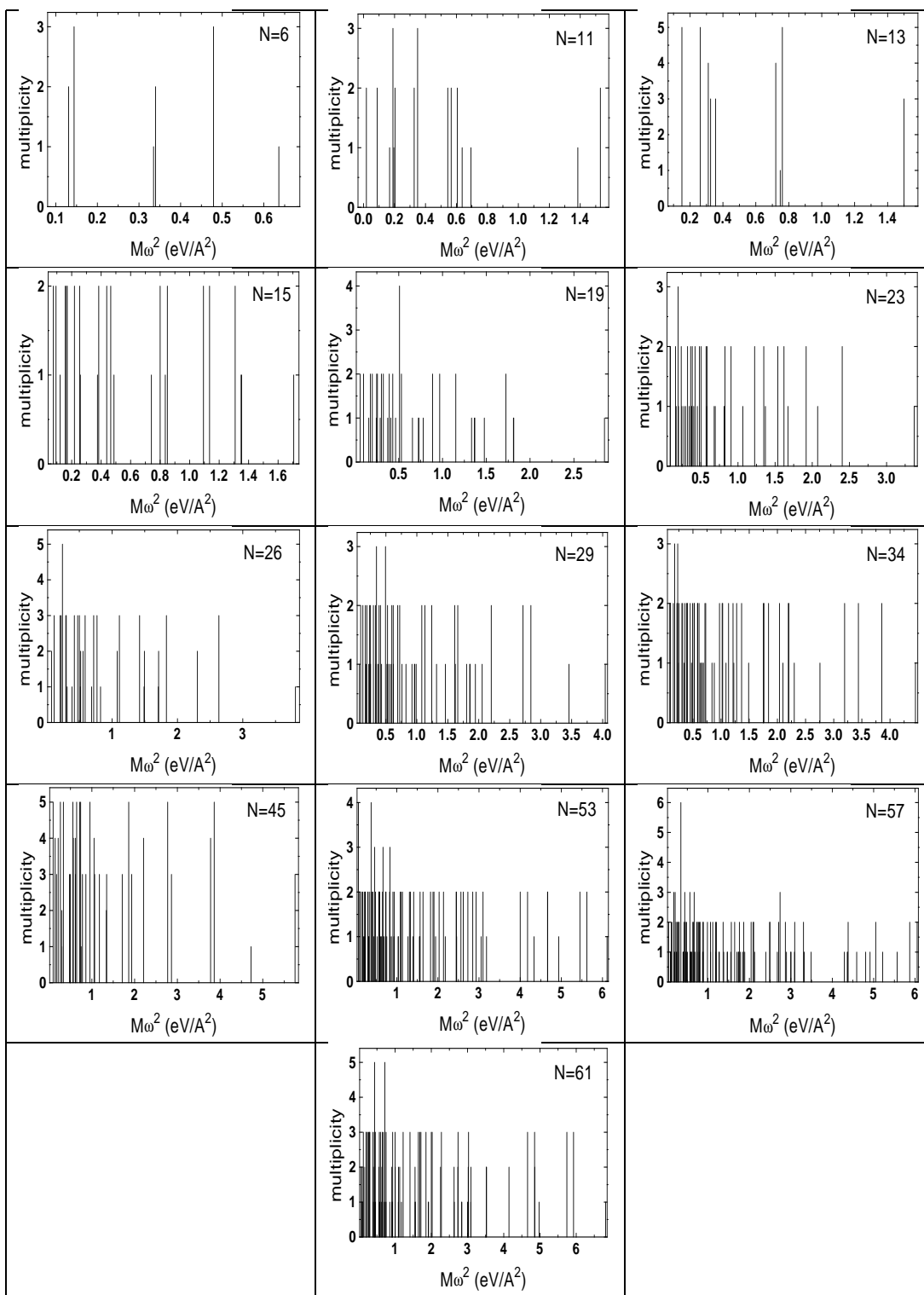
Figure 5: Vibration spectra for magic Fe-clusters
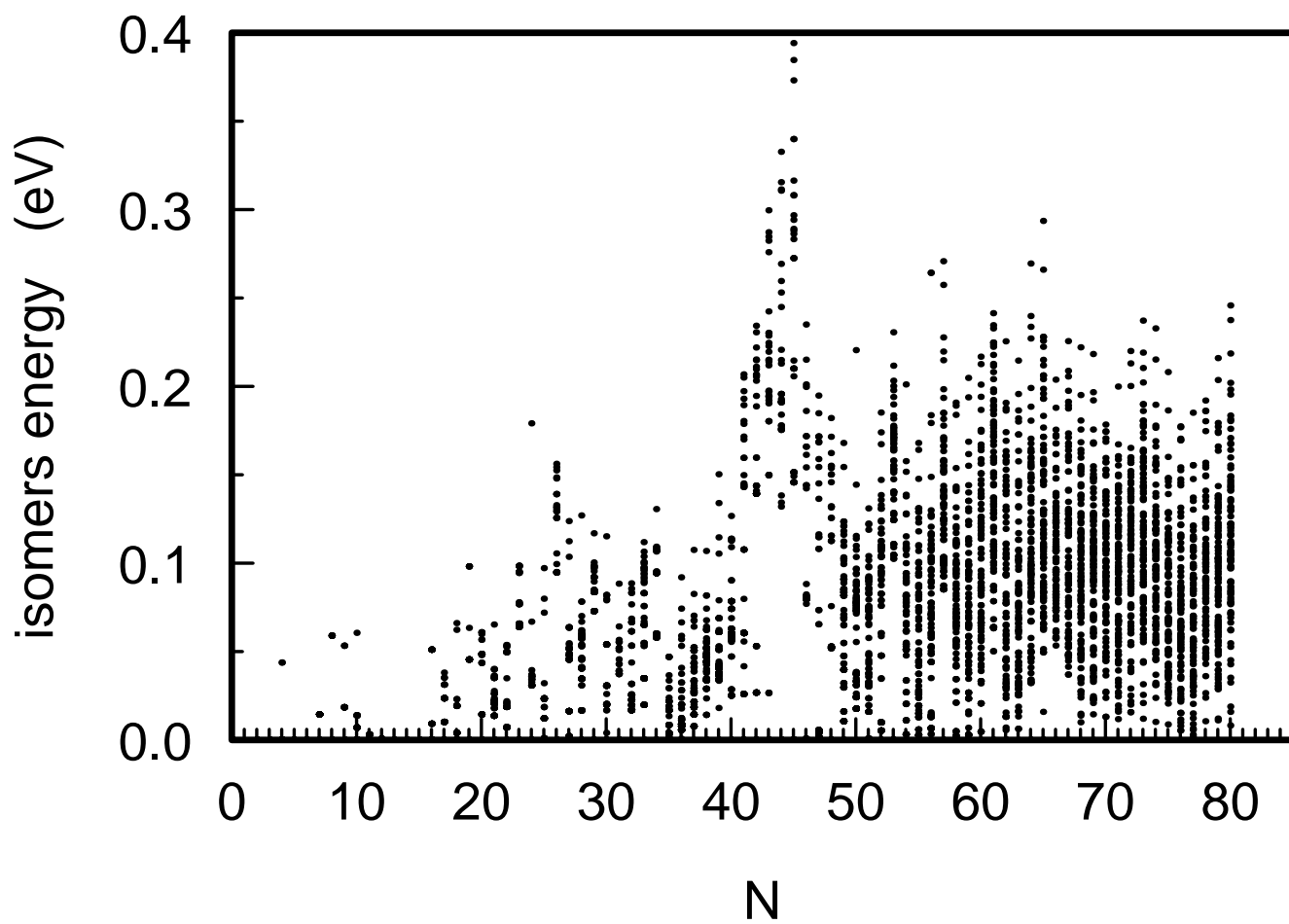
Figure 6: Isomer table for Fe-clusters
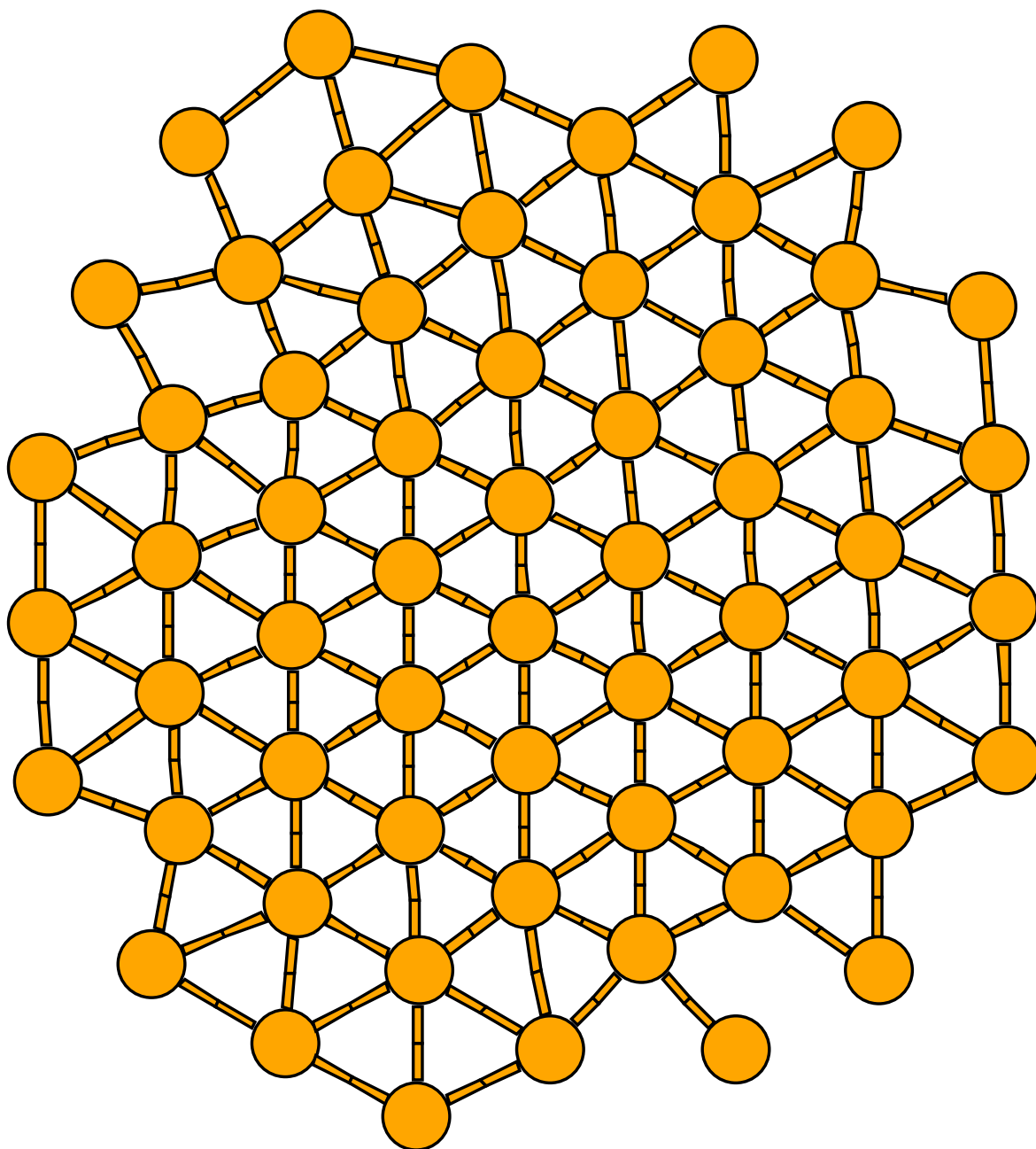
Figure 7: An unstable hexagonal atomic sheet
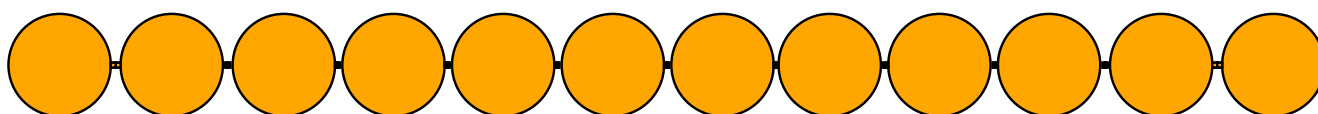
Figure 8: An unstable atomic chain
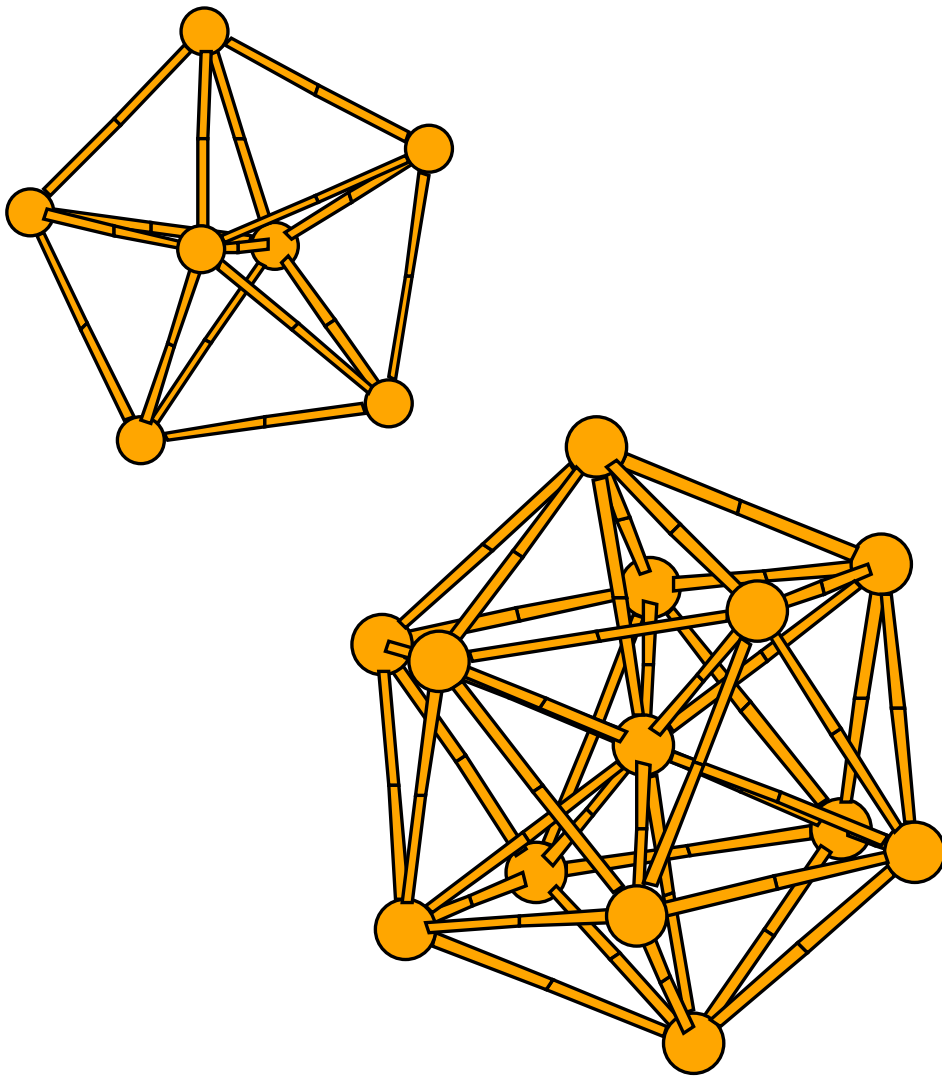
Figure 9: Two atomic fragments in quasi-equilibrium
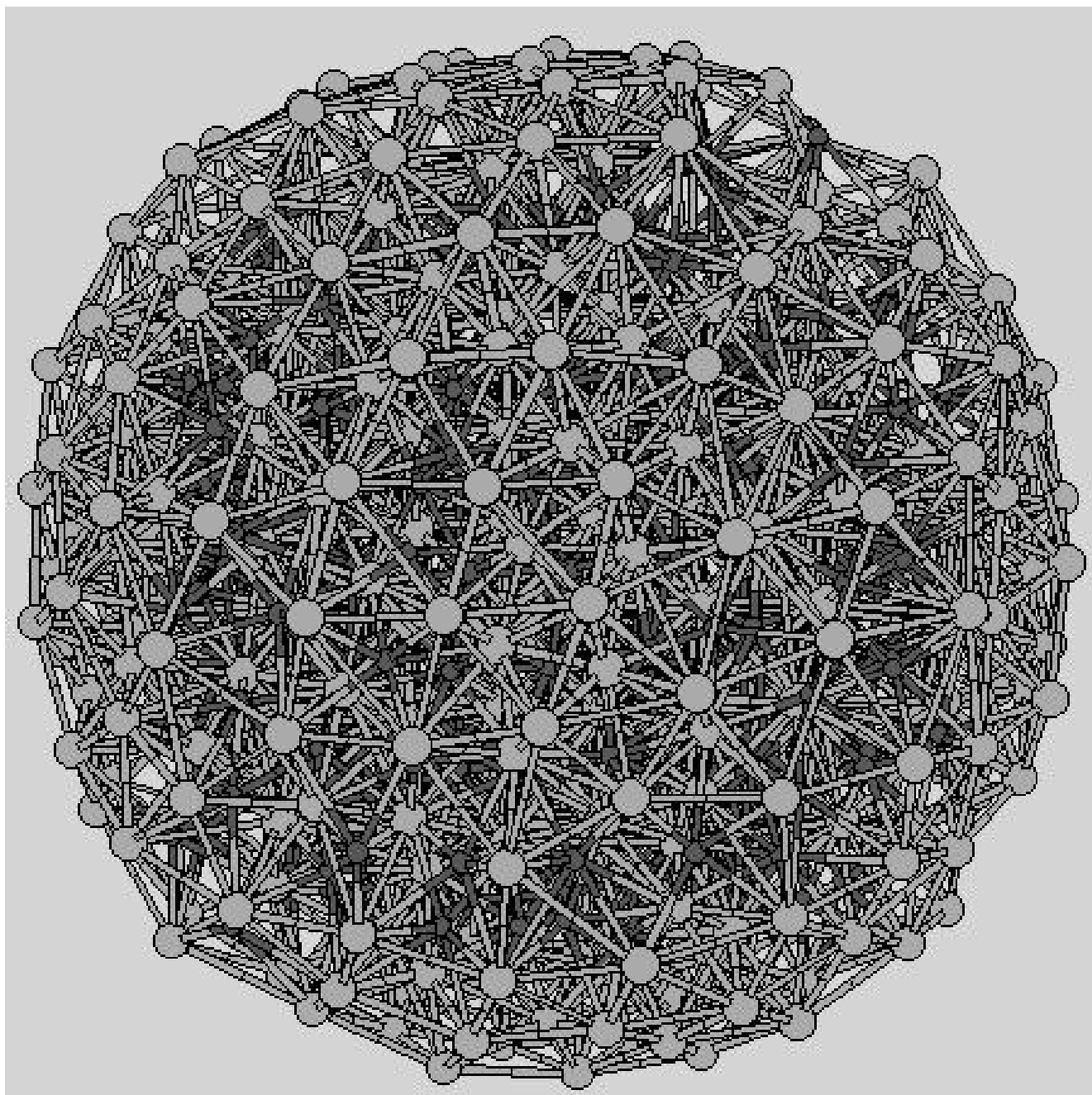
Figure 10: A bcc-core solid of 855-atoms
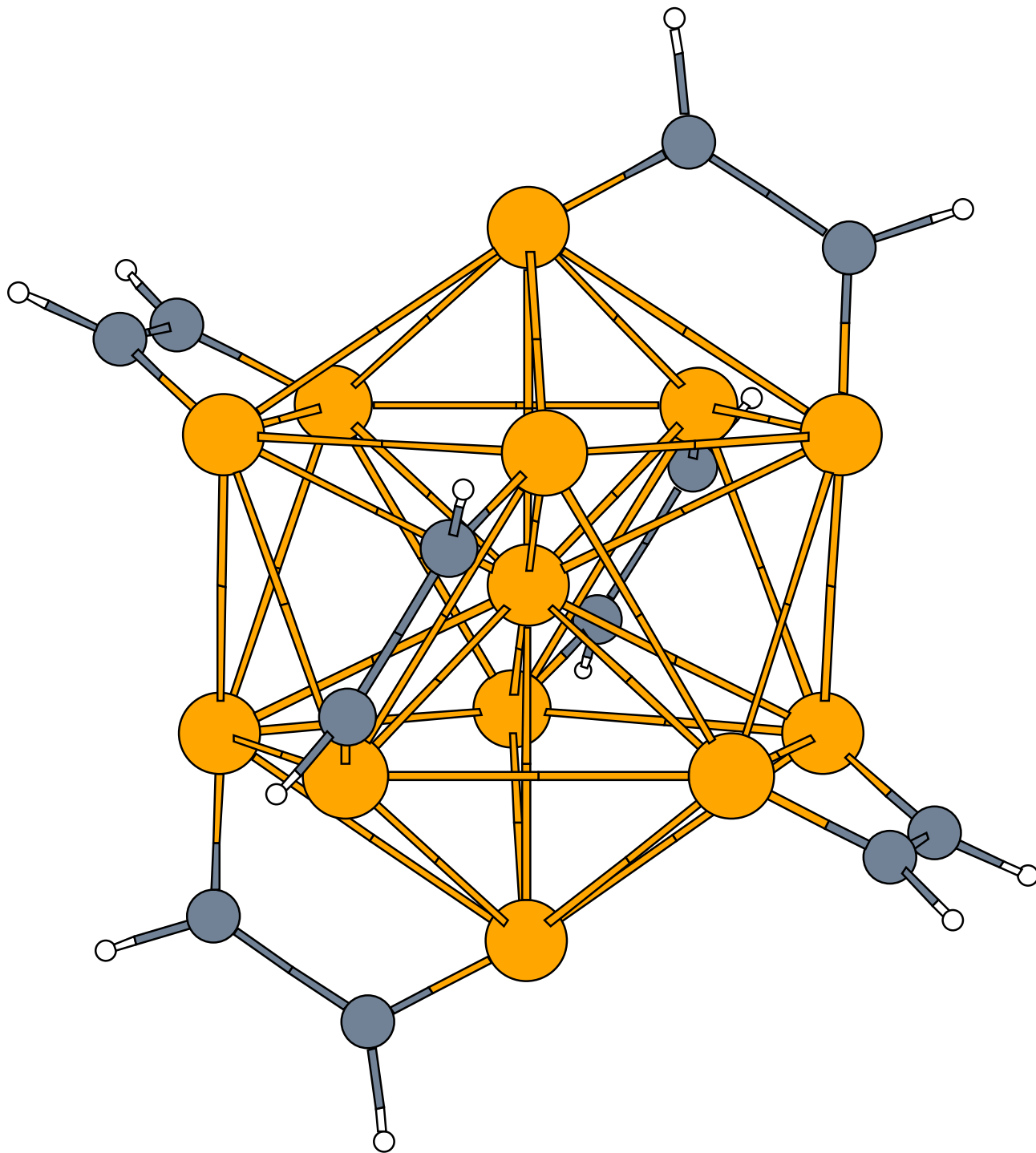
Figure 11: Fe$_{13}$(C$_2$H$_2$)$_6$ cluster
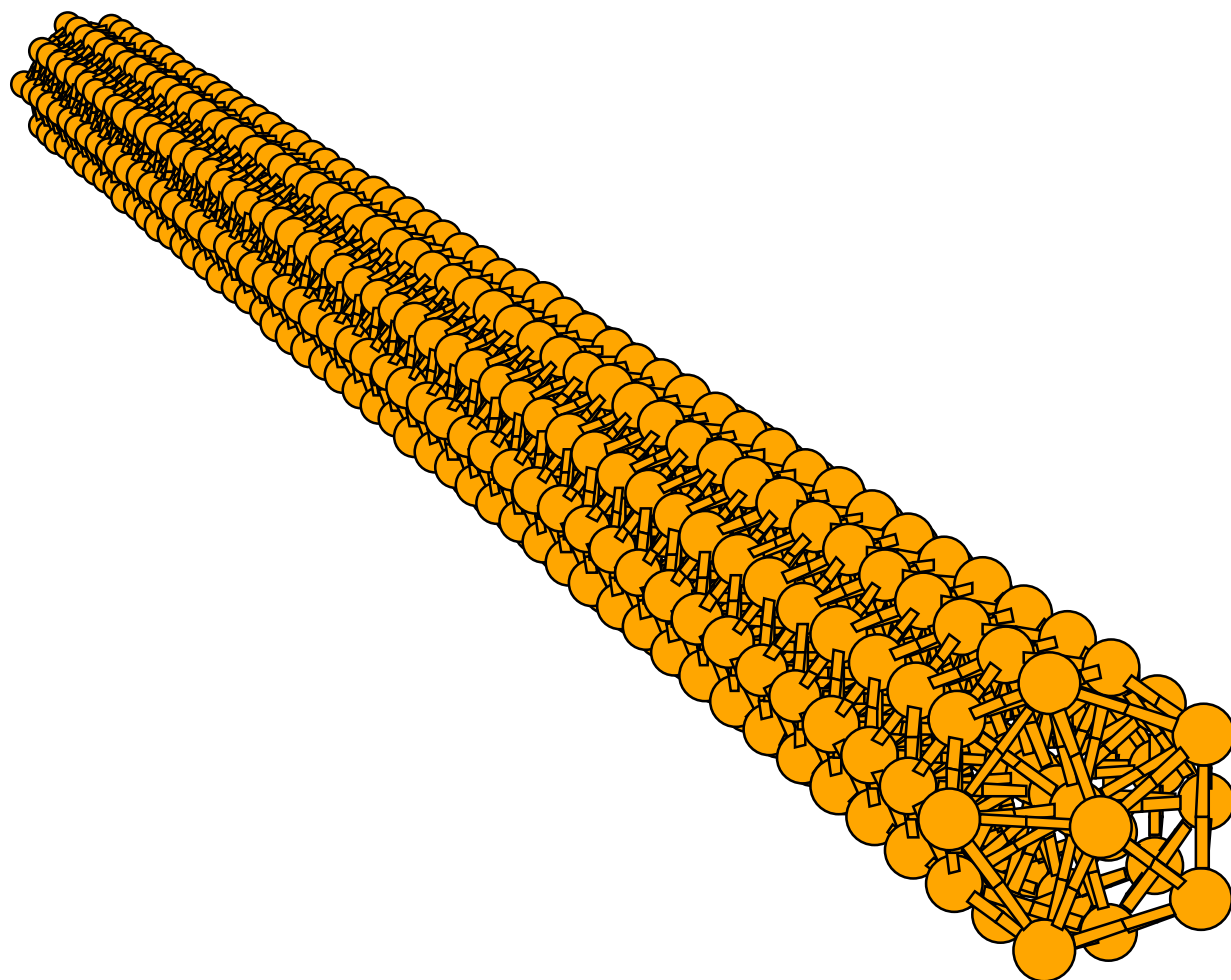
Figure 12: A "popcorn" metallic wire (unstable), single-wall nanotube, made of intertwined icosahedra

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First, we need both Z (atomic number) and N (number of atoms) very lage in order to apply the quasi-classical decsription. Then, we employ a superposition of atomic-like orbitals, localized, and a chemical-bond orbitals (Mullikan), extended; then, we use the kinetic hamiltonian of the valence electrons, their Coulomb attraction to the ionic cores, their Coulomb repulsion, and the Coulomb repulsion between the ionic cores.

$Z \gg 1$, $N \gg 1$, 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

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

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

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

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

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Next, we write down the Hartree-Fock energy functional, the Hartree-Fock equations, and solve them by using the quasi-classical description. To this end we note the "rigidity" character of the exchange energy, the free variational parameter which is the local Fermi vawevector (electron density), the variational equation of equilibrium which is the Thomas-Fermi equation; together with the Poisson equation satisfied by the Hartree self-consistent potential we get the usual 3/2-Thomas-Fermi model, which, however, is valid in the limit of infinite charges (and gives no binding). Applying again the quasi-classical description, we linearize this model, leading to a linear Poisson equation, whose solution is a superposition of screened Coulomb potentials.

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

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

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

Hartree-Fock equation

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

Hartree field

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

Poisson equation

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

Exchange energy

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

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

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Quasi-Classical Description

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

-"rigidity" of the $\varepsilon_{ex}(\Phi)$ 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")

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Linearized Thomas-Fermi theory

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

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

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

$\to$**binding**; $\overline{k}_F$ (q) , variational parameter

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

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

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

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

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

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We are able this way to compute the potential energy, which points out effective inter-atomic potentials, solve for the equilibrium geometric shapes, and, thereafter, add the kinetic energy (linearized) in order to get the full quasiclassical energy; the latter is minimized with respect to the screening wavevector q, thus solving completely the first-stage of the problem.

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

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

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

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

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

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

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

$$E_{ex} \ = \ -\frac{V k_F^4}{4\pi^3} \rightarrow -\frac{\bar{k}_F^3}{4\pi^3}\int d\mathbf{r} \cdot k_F =$$

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

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

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Here, we point out that, within this approximation, the solid looks like a Sommerfeld metal, while the potential energy above points out to a well-known Wigner metal, too.

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

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

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

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

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Now, we may estimate the quantal corrections, indicate the way of computing them, and point out the principle of "inaccuracy", which tells that the maximum accuracy which can be reached with one-electron wavefunctions is $0.17 \cdot 17\% = 3\%$.

Atom
$$\varphi = Ze^{-qr}/r$$

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

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

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

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

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

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

-response, polarizability, diamagnetic susceptibility

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

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-quantal corrections

-spatial structure of the ionic cores

-hetero-atomic clusters

-solids

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