

Metallic cohesion

M. Apostol

Department of Theoretical Physics,
 Institute of Atomic Physics,
 Magurele-Bucharest MG-6,
 POBox MG-35, Romania
 email:apoma@theory.nipne.ro

Abstract

The quasi-classical theory of the slightly inhomogeneous electron liquid is briefly reviewed, for the chemical bond of atomic aggregates like metallic clusters or solids.

1 Introduction: Chemical Bond

A collection of N atoms with atomic numbers Z_i , $i = 1, 2, \dots, N$, may bind together through the Coulomb forces acting between the atomic nuclei and the electrons. The quantal states of such an ensemble are related to the quantal states of the individual atoms. The usual chemical bond is realized by the participation of z_i valence electrons in the upper atomic shells, distributed among various atomic orbitals; part of these electrons do effectively participate in the chemical bond, the remaining being left in the original atomic orbitals. The effective valence z_i^* is only a fraction α of the nominal chemical valence, $z_i^* = \alpha z_i$. The chemical bond is thereby described by a set of $z_0 = \sum_i z_i^*$ electrons moving in a background of ionic cores with charge distributions $\rho_i(\mathbf{R})$, such that

$$\int d\mathbf{R} \cdot \rho_i(\mathbf{R}) = z_i^* ; \quad (1)$$

the ionic charge distributions $\rho_i(\mathbf{R})$ are given by the particle density of the atomic orbitals in the valence shell with "charge" parameters α_{ia} ,

$$\rho_i(\mathbf{R}) = \sum_a \alpha_{ia} |\psi_{ia}(\mathbf{R})|^2 , \quad (2)$$

where a denotes the valence atomic orbitals $\psi_{ia}(\mathbf{R})$, and $\sum_a \alpha_{ia} = z_i^* = \alpha z_i$. The "charge" parameters α_{ia} and the effective valence z_i^* remain undetermined, in principle, within the present theory; they could be obtained by including the dynamics of the electrons left in the valence atomic shells, and they are mainly determined by the overlap and the matrix elements of the hamiltonian between the atomic orbitals and the chemical-bond orbitals; this overlap and the corresponding matrix elements are neglected here, their effects being transferred upon the parameters α_{ia} and z_i^* .

The hamiltonian which describes the chemical bond is therefore given by

$$H = \sum_{\alpha} \mathbf{p}_{\alpha}^2 / 2m - e^2 \sum_{i\alpha} \int d\mathbf{R} \cdot \frac{\rho_i(\mathbf{R})}{|\mathbf{R} - \mathbf{r}_{\alpha}|} +$$

$$\begin{aligned}
& + \frac{1}{2} e^2 \sum_{\alpha \neq \beta} \frac{1}{|\mathbf{r}_\alpha - \mathbf{r}_\beta|} + \\
& + \frac{1}{2} e^2 \sum_{i \neq j} \int d\mathbf{R} d\mathbf{R}' \cdot \frac{\rho_i(\mathbf{R}) \rho_j(\mathbf{R}')}{|\mathbf{R} - \mathbf{R}'|} ,
\end{aligned} \tag{3}$$

where one may recognize, with usual notations, the kinetic energy of the electrons, the Coulomb attraction between the electrons and the ionic cores, the Coulomb repulsion between the electrons and, respectively, the Coulomb repulsion between the ionic cores; the ionic charge distributions are localized around the ionic cores placed at positions \mathbf{R}_i .

2 Hartree-Fock Equations

The quantal states of a large number of electrons may be described in terms of single-particle states; such states lead to a Fermi sea, to quasi-particles, and to a normal Fermi liquid. The Hartree-Fock energy functional for the Hamiltonian (3) reads

$$\begin{aligned}
E = & \sum_{\alpha} \int d\mathbf{r} \cdot \psi_{\alpha}^*(\mathbf{p}^2/2m) \psi_{\alpha} - e^2 \sum_{i\alpha} \int d\mathbf{r} \int d\mathbf{R} \cdot \frac{\rho_i(\mathbf{R})}{|\mathbf{R} - \mathbf{r}|} \psi_{\alpha}^* \psi_{\alpha} + \\
& + \frac{1}{2} e^2 \sum_{\alpha\beta} \int d\mathbf{r} d\mathbf{r}' \cdot \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_{\alpha}^*(\mathbf{r}) \psi_{\alpha}(\mathbf{r}) \psi_{\beta}^*(\mathbf{r}') \psi_{\beta}(\mathbf{r}') - \\
& - \frac{1}{2} e^2 \sum_{\alpha\beta} \int d\mathbf{r} d\mathbf{r}' \cdot \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_{\alpha}^*(\mathbf{r}) \psi_{\beta}(\mathbf{r}) \psi_{\beta}^*(\mathbf{r}') \psi_{\alpha}(\mathbf{r}') + \\
& + \frac{1}{2} e^2 \sum_{i \neq j} \int d\mathbf{R} d\mathbf{R}' \cdot \frac{\rho_i(\mathbf{R}) \rho_j(\mathbf{R}')}{|\mathbf{R} - \mathbf{R}'|} ,
\end{aligned} \tag{4}$$

where the usual Hartree and exchange (Fock, Dirac) contributions to the electron Coulomb repulsion can be seen. It is convenient to introduce the Hartree self-consistent field

$$\varphi = e \sum_i \int d\mathbf{R} \cdot \frac{\rho_i(\mathbf{R})}{|\mathbf{R} - \mathbf{r}|} - e \int d\mathbf{r}' \cdot \frac{1}{|\mathbf{r} - \mathbf{r}'|} n(\mathbf{r}') , \tag{5}$$

where

$$n(\mathbf{r}) = \sum_{\alpha} \psi_{\alpha}^*(\mathbf{r}) \psi_{\alpha}(\mathbf{r}) \tag{6}$$

is the electron density; the Hartree field satisfies Poisson's equation

$$\Delta\varphi = -4\pi e \sum_i \rho_i(\mathbf{r}) + 4\pi e n(\mathbf{r}) ; \tag{7}$$

on the other hand the Hartree-Fock energy functional can be expressed by means of the Hartree field φ , as

$$E = E_{kin} + E_{pot} + E_{ex} , \tag{8}$$

where

$$E_{kin} = \sum_{\alpha} \int d\mathbf{r} \cdot \psi_{\alpha}^*(\mathbf{p}^2/2m) \psi_{\alpha} \tag{9}$$

is the kinetic energy,

$$E_{pot} = -\frac{1}{2}e \int d\mathbf{r} \cdot (\varphi + \varphi_c)n + \frac{1}{2}e \sum_i' \int d\mathbf{R} \cdot \varphi_c \rho_i \quad (10)$$

is the potential energy,

$$\varphi_c = e \sum_i \int d\mathbf{R} \cdot \frac{\rho_i(\mathbf{R})}{|\mathbf{R} - \mathbf{r}|} \quad (11)$$

is the field of the ionic charges, and

$$E_{ex} = -\frac{1}{2}e^2 \sum_{\alpha\beta} \int d\mathbf{r}d\mathbf{r}' \cdot \frac{1}{|\mathbf{r} - \mathbf{r}'|} \psi_\alpha^*(\mathbf{r})\psi_\beta(\mathbf{r})\psi_\beta^*(\mathbf{r}')\psi_\alpha(\mathbf{r}') \quad (12)$$

is the exchange energy (with parallel spins); one may note the Koopmans' factor 1/2 in the energy functional and the exclusion of the ionic self-energy; it is also worth noting that the self-consistent field φ given by (5) is the sum of the field φ_c of the ionic charges and the Coulomb repulsion field of the electrons.

The energy functional (4) leads also to the Hartree-Fock equations

$$\begin{aligned} & (\mathbf{p}^2/2m)\psi_\alpha - e\varphi\psi_\alpha - \\ & -e^2 \sum_\beta \int d\mathbf{r}' \cdot \frac{1}{|\mathbf{r}-\mathbf{r}'|} \psi_\beta^*(\mathbf{r}')\psi_\beta(\mathbf{r}) \cdot \psi_\alpha(\mathbf{r}') = \varepsilon_\alpha\psi_\alpha \quad , \end{aligned} \quad (13)$$

where ε_α denote the energy levels of the Hartree-Fock quasi-particles. The solutions of the (non-linear and self-consistent) Hartree-Fock equations, together with the Hartree-Fock energy functional, solve, in principle, the cohesion problem of the condensed-matter atomic aggregates, and of the chemical bond, as formulated herein, within the general framework of the theory of the normal Fermi liquid for the electron liquid. This solution is provided by the quasi-classical description.[1]·2

3 Quasi-Classical Description

For a large number of electrons ($N \gg 1$) the small oscillations of the extended electron orbitals ψ_α cancel out to a large extent in the electron density (6), so that the electron density varies slowly in space, except for the neighbourhood of the ionic cores; consequently, the solutions of the Hartree-Fock equations (13) are plane waves to the first approximation; it is worth noting that the plane waves are eigenfunctions for the exchange potential in the Hartree-Fock equations. The electron density reads then

$$n(\mathbf{r}) = k_F^3(\mathbf{r})/3\pi^2 \quad , \quad (14)$$

where $k_F(\mathbf{r})$ is the Fermi wavevector, and the energy functional given by (4), or by (8), becomes a functional of the electron density, except for the exchange energy; indeed, the exchange energy is a non-local contribution, and its variations with respect to the local changes in the electron density are vanishing; one may say that the exchange energy exhibits a "rigidity" with respect to the changes in the electron density.[3] The variations of the energy functional with respect to the electron density leads therefore to the vanishing of the (local) chemical potential

$$\hbar^2 k_F^2/2m - e\varphi = 0 \quad , \quad (15)$$

as for a stable isolated aggregate. Making use of (14) and (15) one may solve the Poisson's equation (7) for the self-consistent Hartree field φ , hence compute the energy functional (8), and find out the equilibrium positions \mathbf{R}_i of the ions; thereby, the cohesion problem is finally carried through. This is the quasi-classical description and the Thomas-Fermi scheme. The next-order corrections to this scheme are given by the quantal states of the electrons in the Hartree field φ , according to the Hartree equations

$$-(\hbar^2/2m)\Delta\psi_\alpha - e\varphi\psi_\alpha = \varepsilon_\alpha\psi_\alpha ; \quad (16)$$

at the same time the exchange energy in the Hartree-Fock equations has also to be corrected to the first-order of the perturbation theory. It is worth emphasizing that such higher-order successive iterations of the Thomas-Fermi scheme lead to corrections which may be comparable to the quasi-particle lifetime, and be, therefore, irrelevant. Such corrections involve a short-length scale behaviour of the electrons and ions, and, as such, they do not bring essential contributions to the overall picture. This picture is that of a slightly inhomogeneous electron liquid.[2]

4 Thomas-Fermi Theory

Accordingly, the slow spatial variations require the substitution $k_F^2 \rightarrow \bar{k}_F k_F$ in (15), where \bar{k}_F may be viewed as a variational parameter, the whole spatial variation being transferred upon the new Fermi wavevector k_F ; a similar substitution $k_F^3 \rightarrow \bar{k}_F^2 k_F$ holds for the electron density (14), and it is worth noting that such substitutions are valid over those space regions where \bar{k}_F and k_F are comparable in magnitude; such substitutions are corrected by the quantal effects of the Hartree equations, as discussed above, as due to the abrupt spatial variations of the self-consistent potential and the electron density in the neighbourhood of the ionic cores. A linearized version[1] is thereby obtained for the Thomas-Fermi scheme, which consists in

$$\bar{k}_F k_F / 2 - \varphi = 0 \quad , \quad n = \bar{k}_F^2 k_F / 3\pi^2 = (q^2 / 4\pi) \varphi \quad , \quad (17)$$

according to (14) and (15), where the Thomas-Fermi screening wavevector q has been introduced through

$$q^2 = \frac{8}{3\pi} \bar{k}_F ; \quad (18)$$

it will be taken as the variational parameter; the Bohr radius $a_H = \hbar^2 / me^e = 0.53\text{\AA}$ is used as length unit and the atomic unit $e^2 / a_H = 27.2\text{eV}$ is also used for energy. Poisson's equation (7) reads now

$$\Delta\varphi = -4\pi \sum_i \rho_i(\mathbf{r}) + q^2 \varphi \quad , \quad (19)$$

and its solution provides the self-consistent field φ . It is worth noting that the quasi-classical description and the quasi-classical equilibrium equation (15) are valid for slow spatial variations, requiring thus the linearized Thomas-Fermi scheme; the usual "3/2"-Thomas-Fermi model, where $n \sim \varphi^{3/2}$, would be inappropriate for the slightly inhomogeneous electron liquid; the "3/2"-Thomas-Fermi model holds in the classical limit of the quantal mechanics, which is often called the "quasi-classical approximation".[2],[4]

In order to estimate the effect of the quantal corrections, as arising from those spatial regions of abrupt variations, the variational parameter \bar{k}_F given by (18) (associated with the electron density) may be compared with the average Fermi wavevector

$$k_{Fav} = \frac{1}{z_0} \int d\mathbf{r} \cdot n k_F = \frac{4}{3\pi^2 z_0} \int d\mathbf{r} \cdot \varphi^2 \sim \bar{k}_F = \frac{3\pi}{8} q^2 \quad , \quad (20)$$

where

$$z_0 = \sum_i \int d\mathbf{r} \cdot \rho_i(\mathbf{r}) = \sum_i z_i^* \quad (21)$$

is the total charge; it is worth noting here the electric neutrality of the aggregate, as obtained from Poisson's equation (7), for instance; such a comparison can also be made between the variational parameter q and the average parameter q_{av} , obtained through (18) with \bar{k}_F replaced by k_{Fav} .

5 Energy

The linearized Thomas-Fermi theory requires the kinetic energy $E_{kin} = V\bar{k}_F^5/10\pi^2$ of an electron gas enclosed in the volume V , as given by (9), to be replaced by

$$E_{kin} = \frac{\bar{k}_F^4}{10\pi^2} \int d\mathbf{r} \cdot k_F = \frac{1}{5\pi^2} (3\pi/8)^3 q^6 \int d\mathbf{r} \cdot \varphi ; \quad (22)$$

similarly, the potential energy (10) becomes

$$E_{pot} = -\frac{1}{8\pi} q^2 \int d\mathbf{r} \cdot (\varphi + \varphi_c)\varphi + \frac{1}{2} \sum_i' \int d\mathbf{R} \cdot \varphi_c \rho_i ; \quad (23)$$

the variations of the parameter q are related, through (17), to variations in the electron density; because of the "rigidity" of the exchange energy, such variations imply changes in the quasi-classical energy

$$E_q = E_{kin} + E_{pot} \quad (24)$$

only; the exchange energy is therefore added to the minimum value of the quasi-classical energy E_q in order to get the total energy,

$$E = E_q + E_{ex} ; \quad (25)$$

the well-known exchange energy $E_{ex} = -Vk_F^4/4\pi^3$ of an electron gas is replaced by

$$E_{ex} = -\frac{\bar{k}_F^3}{4\pi^3} \int d\mathbf{r} \cdot k_F = -\frac{9}{128\pi} q^4 \int d\mathbf{r} \cdot \varphi \quad (26)$$

for the slightly inhomogeneous electron liquid, where q is the equilibrium value of the Thomas-Fermi screening wavevector as obtained by minimizing the quasi-classical energy E_q . One can see easily from (22) and (23) that the quasi-classical energy may indeed have a minimum value for a certain screening wavevector q , and the potential energy (23) may also have minima with respect to changes in the ionic positions; therefore, the atomic aggregates are stable, and the solid-state cohesion is obtained, within the present theory; this is the "no-no-binding theorem";[4] the minimization of the energies as discussed here gives both the ground-state of the aggregate and its isomers, *i.e.* locally stable states higher in energy with different ionic positions, *i.e.* with different geometric forms.

Since the atomic energy levels of the electron states participating in the chemical bond vanish within the quasi-classical description the total energy E as given by (25) is in fact the cohesion, or the binding energy. One can see easily that the virial theorem, which requires $E_{kin} = -(1/2)E_{pot}$, is not satisfied within the present theory; this means that both the kinetic energy and the potential energy are not accurate, but the total energy is close to the correct one, due to the variational approach to the linearized Thomas-Fermi theory, as based upon the quasi-classical description.

Therefore, the practical prescription of the present theory consists in solving the linear Poisson's equation (19) for a given distribution of ionic charges, minimizing the quasi-classical energy E_q given by (24) with respect to q , minimizing the potential energy (23) with respect to the ionic positions \mathbf{R}_i (the two operations are in fact intervertible), adding the exchange energy E_{ex} given by (26) in order to get the total (cohesion, binding) energy; estimating the effect of the quantal corrections by comparing the two screening wavevectors according to (20); and correct the results by solving the Hartree equations (16), exchange corrections included; higher-order iterations of this scheme may contribute irrelevant amounts of the order of the quasi-electron lifetime.

6 Metallic Clusters

The α_{ia} -parametrization of the ionic charge distributions $\rho_i(\mathbf{R})$ given by (2) has the spatial symmetry of the density of the valence atomic orbitals; for crystals this parametrization should also be compatible with the crystal symmetry; in general, the directional dependence of the ionic charge distributions $\rho_i(\mathbf{R})$ induces non-central self-consistent potentials φ through Poisson's equation, and, accordingly, non-central inter-atomic potentials through the potential energy E_{pot} . The directional effects are more pronounced for the chemical elements with p -valence orbitals, which give rise to covalent or ionic bonds; metallic ions have usually s , d , and f -valence orbitals, and the directional effects are less pronounced (except for the crystalline symmetry); one may therefore approximate such charge distributions of the metallic ions by point-like charges

$$\rho_i(\mathbf{R}) = z_i^* \delta(\mathbf{R} - \mathbf{R}_i) ; \quad (27)$$

Poisson's equation (19) is then easily solved[5] by

$$\varphi = \sum_i \frac{z_i^*}{|\mathbf{r} - \mathbf{R}_i|} e^{-q|\mathbf{r} - \mathbf{R}_i|} , \quad (28)$$

while the kinetic energy (22) is

$$E_{kin} = (27\pi^2/640)z_0 = Aq^4/4 , \quad (29)$$

the potential energy (23) is

$$\begin{aligned} E_{pot} &= -\frac{q}{4} \left[3 \sum_i z_i^{*2} + \sum_{i \neq j} z_i^* z_j^* \left(1 - \frac{2}{q|\mathbf{R}_i - \mathbf{R}_j|} \right) e^{-q|\mathbf{R}_i - \mathbf{R}_j|} \right] = \\ &= -Bq , \end{aligned} \quad (30)$$

and the exchange energy (26) becomes

$$E_{ex} = -(9/32)q^2 z_0 = -Cq^2 . \quad (31)$$

It is worth noting the inter-atomic potentials

$$\Phi_{ij} = -\frac{q}{2} z_i^* z_j^* \left(1 - \frac{2}{q|\mathbf{R}_i - \mathbf{R}_j|} \right) e^{-q|\mathbf{R}_i - \mathbf{R}_j|} \quad (32)$$

which are repulsive for short distances, attractive for long distances, and have a minimum value for $q|\mathbf{R}_i - \mathbf{R}_j| = 2.73$; they are in fact pseudo-potentials, as they are valid for distances close

to equilibrium; the entire present theory holds in fact for distances close to the equilibrium distances.

The minimization of the potential energy (30) with respect to the ionic positions \mathbf{R}_i involves the minimization with respect to the dimensionless variables $\mathbf{x}_i = q\mathbf{R}_i$; consequently, the coefficient B in the potential energy (30) does not depend on q ; the quasi-classical energy (24) is then given by

$$E_q = Aq^4/4 - Bq ; \quad (33)$$

its minimum value $E_q = -(3/4)Bq$ is obtained for $q = (B/A)^{1/3}$ (and $E_{kin} = -(1/4)E_{pot}$, in contrast to the virial theorem); the inter-atomic distances are therefore obtained from $q|\mathbf{R}_i - \mathbf{R}_j| = |\mathbf{x}_i - \mathbf{x}_j|$, where \mathbf{x}_i are the equilibrium values obtained from the minimization of the potential energy (30). For homo-atomic clusters $z_i^* = z^*$ the geometric forms do not depend on the chemical species. The abundance of such clusters in their ground-states is given by $D = \ln(I_N^2/I_{N+1}I_{N-1}) \sim E_{N+1} + E_{N-1} - 2E_N$, where $E_N = E_q + E_{ex}$ is the ground-state energy of a cluster of N atoms, and I_N is the Boltzmann statistical weight; the abundance spectrum D has a characteristic sawtooth behaviour with the cluster size N , exhibiting sharp peaks at certain magic numbers $N = 6, 11, 13, 15, 19, 23, 26, 29, 34, 45, 53, 57, 61, \dots$; these magic numbers indicate that the corresponding magic clusters are more stable than their neighbours; they correspond to close-packed spatial structures with high symmetry, and are geometric magic numbers; for a reasonable physical range $0 < z^* < 3$ the magic numbers are preserved, while the magic peaks diminish in amplitude on increasing N , as the clusters approach the bulk behaviour; geometric magic forms and magic numbers for homo-atomic metallic clusters are shown in Fig.1 and, respectively, Fig.2. It is worth noting the thermodynamic behaviour of the energy in the limit of large N , according to the definition of coefficients A, B , and C in (29)-(31).

The potential energy E_{pot} given by (30) has many local minima, in general, with respect to the ionic positions; they corresponds to isomers, *i.e.* locally stable geometric forms, higher in energy and less symmetric; such isomers are shown in Fig.3. The isomers are excited at higher temperatures, and, in general, they are produced in experiments; the corresponding abundance spectrum is then given by the free energy, instead of the ground-state energy, and one may speak then of statistical magic numbers, which are distinct of the geometric magic numbers. For the electronic properties of such statistical ensembles slowly-varying potentials obtained by averaging the self-consistent potential φ given by (28) are more appropriate; such potentials read $\varphi = \varphi_0 - \varphi_x x^2 - \varphi_y y^2 - \varphi_z z^2 \dots$, for instance, where $\varphi_{x,y,z}$ are related to the quadrupole moment of the cluster; [6] for instance, $\varphi_0 = 4\pi z^*/a^3 q^2 = (4\pi/c^3)z^*q$, as obtained from (28), where z^* is the average ionic charge, a is the average inter-ionic distance, and $c = aq$ is the average equilibrium value of the dimensionless geometric parameter $q|\mathbf{R}_i - \mathbf{R}_j|$ (one may take, for instance, $c = 2.73$); finite-size effects are therefore included in such electronic potentials, like the quadrupole contributions; the electronic motion in such potentials exhibits electronic shells, and the completion of these electronic shells lead to electronic magic numbers, which is another, distinct set of magic numbers, more appropriate for such smooth electronic potentials; for instance, the magic numbers of a spatial isotropic oscillator are 2, 8, 20,

Making use of the average ionic charge z^* one obtains the equilibrium Thomas-Fermi screening wavevector $q = (B/A)^{1/3} = 0.77z^{*1/3}$ (the position-dependent part of the potential energy vanishes, as expected for a slightly inhomogeneous electron liquid), the quasi-classical energy $E_q = -0.43Nz^{*7/3}$ and the exchange energy $E_{ex} = -0.17Nz^{*5/3}$, so that the total energy is given by

$$E = -0.43Nz^{*7/3} - 0.17Nz^{*5/3} ; \quad (34)$$

for a typical value $z^* = 0.5$ one obtains $E/N \sim -4\text{eV}$, $q \sim 0.6a_H^{-1}$, $a \sim c/q \sim 3.5a_H$, and $\varphi_0 \sim 5\text{eV}$; the average value of the screening wavevector as obtained from (20) is $q_{av} = 0.9z^{*1/3}$; one can see that it compares well with the variational value $q = 0.77z^{*1/3}$, the deviation of $\sim 17\%$ originating in the quantal corrections; the results are therefore accurate up to cca 17%, the inaccuracy affecting the short-length scale behaviour of the aggregate.

7 Atoms and Effective Valence

The quasi-classical description applies to heavy atoms too, *i.e.* to atoms with high atomic numbers Z ($Z \gg 1$);[7] the results are easily derived from (28)-(31) for $N = 1$; the self-consistent potential is $\varphi = Ze^{-qr}/r$, the quasi-classical energy is $E = -11.78Z^{7/3}\text{eV}$ (the exchange energy is $E_{ex} = -4.6Z^{5/3}\text{eV}$), the Thomas-Fermi screening wavevector is $q = 0.77Z^{1/3}$, and the average screening wavevector is $q_{av} = 0.9Z^{1/3}$; the quantal correction to the (Hartree) energy is $\Delta E = -4.56Z^{7/3}\text{eV}$, so that the atomic binding energy is $E = -16.34Z^{7/3}\text{eV}$; it compares well with the empirical binding energy $-16Z^{7/3}\text{eV}$ of the heavy atoms;[4] similar corrections can be done for the exchange energy, which however are not very relevant, as the exchange energy itself is not. The electrons in heavy atoms are mainly concentrated in a sphere of "electronic" radius $R_e \sim 1/q \sim Z^{-1/3}$, which is longer than the radius $R_B \sim 1/Z$ of the first Bohr quantal orbit and shorter than the atomic radius $R \sim 1$ (*i.e.* one a_H), beyond which the quasi-classical description is not valid.

The fraction α of the valence electrons participating in the chemical bond is given by the content of plane waves in the valence atomic orbitals; according to the atomic screening theory[8] of the Thomas-Fermi model this fraction may be estimated as the number N_{out} of outer electrons lying outside of a sphere of radius R to the total number Z of electrons; since the electron density is given by $n = (q^2/4\pi)\varphi$ one obtains

$$\alpha = N_{out}/Z = (1 + qR)e^{-qR} ; \quad (35)$$

for an illustrative purpose one may take $R = 1$ and a mean value $q = 0.84Z^{1/3}$ of the variational $0.77Z^{1/3}$ screening wavevector and the average $0.9Z^{1/3}$ screening wavevector; one obtains $\alpha_{\text{Na}} = 0.44$ for sodium (Na, $Z = 11$, $z = 1$, $z^* = 0.44$), $\alpha_{\text{K}} = 0.34$ for potassium (K, $Z = 19$, $z = 1$, $z^* = 0.34$), $\alpha_{\text{Fe}} = 0.28$ for iron (Fe, $Z = 26$, $z = 2$, $z^* = 0.57$), $\alpha_{\text{Ag}} = 0.19$ for silver (Ag, $Z = 47$, $z = 1$, $z^* = 0.19$), $\alpha_{\text{Ba}} = 0.17$ for barium (Ba, $Z = 56$, $z = 2$, $z^* = 0.34$). It is worth emphasizing that such estimations are only orientative; they do not apply to light atoms, and they are inaccurate for very heavy atoms, as the tail of the outer electrons of the latter is too small. However, such effective valence charges offer a qualitative numerical estimation of the various physical quantities involved in the cohesion of the atomic aggregates. For instance, numerical values of the binding energy per atom are given in Fig.4 for Na, Fe and Ba-clusters *vs* cluster size N .

The fractional occupancy α of the chemical-bond orbitals implies that the ionization potential of an atomic aggregate can be written as

$$I = (1 - \alpha)I_a + \alpha I_b , \quad (36)$$

where I_a is the atomic ionization potential and I_b is the highest occupied level of the electron liquid (chemical potential of the bond orbitals); to the first approximation of the quasi-classical description I_b is vanishing, and the quantal corrections do not bring an appreciable contribution; one may say therefore that the ionization potential of the aggregate is given by

$$I = (1 - \alpha)I_a ; \quad (37)$$

making use of the occupancy factor computed above one obtains[6] $I_{\text{Na}} = 2.88\text{eV}$, $I_{\text{K}} = 2.86\text{eV}$, $I_{\text{Fe}} = 5.67\text{eV}$, $I_{\text{Ag}} = 6.13\text{eV}$, $I_{\text{Ba}} = 4.32\text{eV}$, which compare well with the experimental values 3.5eV (Na), 2.8eV (K), 5.5eV (Ag). For hetero-atomic aggregates an average should be taken over chemical species in (37); similar considerations are also valid for the electron affinity. A similar estimation is also valid for the magnetic moment, and Hund's rule; for instance, an amount of 0.57 spin-paired electrons go to the chemical-bond orbitals for Fe, so that $4 + 1.43$ electrons are left in the d^6 -atomic orbitals; 2×0.43 get now paired, so that 4.57 remain unpaired; one may say that the magnetic moment of Fe-atomic aggregates is 4.57 electron magnetic moments (Bohr magnetons μ_B), to this approximation, $\mu_{\text{Fe}} = 4.57\mu_B$.

8 Metals

The crystalline order brings directional effects which change the ionic interacting part of the potential energy (30); however, the general screening form may be preserved, so that one may use for the potential energy a general representation as the one given by (30); the ionic positions are therefore obtained by minimizing the interacting part of the potential energy, and one may say that the average inter-ionic distance is also given by $a \sim c/q$; averaging out such directional effects one may write

$$E_{\text{pot}} = -\frac{3}{4}Nz^{*2}q + \frac{1}{2} \sum_{i \neq j} \Phi(r_{ij}) = -Bq + q \sum_{i \neq j} F(qr_{ij}) \quad (38)$$

for the potential energy, where r_{ij} are the inter-ionic distances; one may also restrict to the nearest neighbours g , and write

$$\sum_{i \neq j} F(qr_{ij}) = -\frac{1}{4}gNz^{*2}f(qa) \quad ; \quad (39)$$

in (30) $f(x) = (1 - 2/x)e^{-x}$, but in general, it differs from that expression; the interacting contribution to the potential energy is, in general, small in comparison with the "self-energy" $-Bq$; its effects reside mainly in determining the ionic positions; for $c = 2.73$ and $q = 0.77z^{*1/3}$, for instance, the average inter-atomic distances are rather small, in some cases; Madelung sums and the directional effects act in opposite directions, and the directional effects may prevail to some extent in such cases, leading to larger inter-atomic distances. Leaving aside the interacting part in the potential energy one obtains the total energy

$$E = -\frac{3}{4}Bq - Cq^2 \quad , \quad (40)$$

and the screening wavevector $q = 0.77z^{*1/3}$. It is worth noting that the aggregate looks very much in this case like a "Wigner metal", *i.e.* a collection of "quasi-atoms" consisting of electric charges in equilibrium, with a self-energy, and slightly interacting with each other.[9]

The binding energy (40) of such a metal leads to the expression given by (34); for $z_{\text{Fe}}^* = 0.57$ one obtains a reasonable binding energy per atom $E(\text{Fe})/N \sim -5\text{eV}$. The compressibility κ given by $1/\kappa = -V\partial p/\partial V = V\partial^2 |E|/\partial V^2$ can be obtained from (40) by making use of $c = aq$, as for equilibrium;[2] one obtains the sound velocity

$$\begin{aligned} v_s &= 1/\sqrt{\kappa Mn} = \\ &= \left[\frac{1}{A} (0.43z^{*7/3} + 0.68z^{*5/3}) \right]^{1/2} \cdot 1.7 \cdot 10^4 \text{m/s} \quad , \end{aligned} \quad (41)$$

where n is the atom concentration and A is the atomic mass; for Fe ($A = 56$) one gets $v_s \sim 1400\text{m/s}$.

The sound waves do contribute a T^4 -energy (and T^3 -entropy) for low temperatures T ; the heat capacity is therefore given by the T^3 -Debye law, and there is no need to distinguish between the heat capacity at constant volume and the heat capacity at constant pressure, as there is also no need to distinguish between the two compressibilities, at constant temperature and at constant entropy; in addition, Gruneisen's law holds, *i.e.* the ratio of the coefficient of thermal expansion $(1/V)(\partial V/\partial T)_p$ (at constant pressure) to the specific heat is independent of temperature; similar considerations are valid at higher temperatures (typically $\geq 10 - 100\text{K}$), where the heat capacity is constant, according to Dulong-Petit law.

The general form of the quasi-classical energy

$$E_q = Aq^4/4 - Bq + q \sum_{i \neq j} F(qr_{ij}) \quad (42)$$

may be expanded with respect to the variations δq and $\delta \mathbf{R}_i$ around the equilibrium; [2] the δq -variations are related to the changes in the electron density through $q^2 = (8/3\pi)(3\pi^2 n)^{1/3}$ (according to (14) and (18)), while $\delta \mathbf{R}_i$ are changes in the ionic positions; the first variation of the energy vanishes at equilibrium, while the second-order variations give an electron-electron ("renormalized") interaction ($\sim \delta q^2$), an ion-ion interaction ($\sim \delta R_i^\alpha \delta R_j^\beta$), which leads to atomic vibrations (α, β being cartesian labels of polarization), and an electron-phonon interaction ($\sim \delta q \delta R_i^\alpha$); these are elementary excitations associated with the density motion (both electronic and atomic), and vibration spectra of some magic Fe-clusters are shown in Fig.5; they are computed [5] according to the equations of motion $\det(\omega^2 M_i \delta_{ij} - D_{ij}^{\alpha\beta}) = 0$, where M_i denotes the atomic mass and the dynamic matrix $D_{ij}^{\alpha\beta} = \partial^2 E_{pot} / \partial R_i^\alpha \partial R_j^\beta$ is given by (30); typical atomic frequencies are $\sim 10\text{meV}$. In the limit of long wavelengths the "bare" sound velocity has typical values of 10^3m/s ; however, in this limit the electron-ion equilibrium is reached according to the Born-Oppenheimer adiabatic theorem, and the "dressed" sound is the one given by (41); it remains. however, in this limit, an electron-interacting contribution ($\sim \delta q^2$) which brings a small quadratic correction to the plasmon spectrum; within the linearized Thomas-Fermi theory this correction is however uncertain, and it merely indicates the range of validity of the plasmon spectrum; the electron-phonon interaction "renormalizes" therefore the sound waves, while for atomic vibrations the electron-phonon interaction is of the typical form $M z^{*2/3} \int d\mathbf{r} \cdot \delta R \delta n$, where δR is the atomic displacement and δn is the change in the electron density, where $M \sim 0.27\text{eV}$; the electron-phonon interaction vertex brings only small changes of the order of $\sqrt{m/M}$, both to electrons and to atomic vibrations, where m is the electron mass and M denotes here the atom mass; it contributes to transport, by restricting the lifetime of both the phonons and the electrons; and gives also rise to superconducting instabilities; as well as to other electron-ions instabilities, like charge-density waves (Peierls-Frohlich transition) in anisotropic materials (for instance in quasi-one-dimensional materials).

9 Plasmons

The long-wavelength variations in the electron density leads to a vanishing first-order variation of the Hartree-Fock energy functional (4), according to the quasi-classical equilibrium equation (15); [1] [2] the second-order variation gives therefore a potential energy

$$U = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \cdot \frac{e^2}{|\mathbf{r} - \mathbf{r}'|} \delta n(\mathbf{r}) \delta n(\mathbf{r}') ; \quad (43)$$

a displacement field \mathbf{u} generates the change $\delta n = -n \operatorname{div} \mathbf{u}$, and a kinetic hamiltonain

$$T = \frac{1}{2} \int d\mathbf{r} \cdot nm \dot{\mathbf{u}}^2 ; \quad (44)$$

hence, one gets easily the plasma frequency $\omega = (4\pi n^2 e^2 / mn)^{1/2} = (4\pi n e^2 / m)^{1/2}$; actually, the electron density affected by the long-wavelength motion is "renormalized" by the occupancy factor α , so that the substitution $n \rightarrow \alpha n$ is needed in the plasma frequency; one obtains therefore

$$\omega = \sqrt{\alpha} (4\pi n e^2 / m)^{1/2} \quad (45)$$

for the plasma frequency; the occupancy factor α simulates in fact the reduction of the matrix elements of the Coulomb potential for atomic orbitals, in comparison with the plane waves; typical values are $\omega \sim \sqrt{\alpha}(5 - 8)\text{eV}$; the zero-point energy of the plasmons can be estimated as $E_{pl} \sim \omega N(aq)^3 \beta^3$, where $\beta = K/q$ and K is a long-wavelength cut-off; for finite values of this cutoff the zero-point plasmon energy brings a small contribution to the cohesion energy ($\sim \omega/(8 - 10)$); it is worth noting that the inhomogeneities of the electron liquid and the quantal corrections reduce the plasmon lifetime, and restrict the validity of the plasmon spectrum (45) to the long wavelength limit.

10 Electronic Properties

The valence atomic orbitals do contribute plane waves to the chemical-bond orbitals, to the first approximation; the content of plane waves in the valence atomic orbitals are therefore related to the α_{ia} -parameters of the ionic charge distributions; the occupancy of the plane-waves orbitals depend, in general, on these orbitals, and the effective valence electrons are given by the sum total of all these orbital occupancies. The quantal corrections, brought about by the electron motion in the self-consistent field φ , modify slightly the plane-waves orbitals, and the corresponding single-particle energies; they also split the energy levels of the valence atomic orbitals, and this splitting leads to energy bands for crystalline solids; each band consists of N twofold degenerate orbitals, each with a fractional occupancy; they may give electric conductors, or insulators, according to the number of orbitals in the band affected by (fractional) electron filing, along one or another direction in space; the fractional occupancy of the orbitals, though resembling a "strong renormalization" of the electrons caused by their interaction with the ions, and leading to "strongly renormalized" Hartree-Fock quasi-particles, does not show itself except in plasma frequency, ionization potentials, etc, as discussed before. The quasi-particle excitations of the inhomogeneous electron liquid are not affected practically by such a fractional occupancy.

A quasi-particle excitation of the inhomogeneous electron liquid appears through the Born elastic scattering of a plane wave on the self-consistent potential φ . [2] The f -amplitude of the Landau theory of the normal liquid is therefore given by

$$f(\mathbf{k} - \mathbf{k}') = 4\pi e^2 \sum_i \frac{z_i^*}{q^2 + |\mathbf{k} - \mathbf{k}'|^2} e^{i(\mathbf{k} - \mathbf{k}')\mathbf{R}_i} , \quad (46)$$

according to (28) (for parallel spins); one may average out over the ionic positions and get the forward scattering amplitude

$$f(\mathbf{p} - \mathbf{p}') = f \frac{(2\pi\hbar)^3}{V} \delta(\mathbf{p} - \mathbf{p}') , \quad (47)$$

where

$$f = 4\pi N e^2 / q^2 ; \quad (48)$$

the typical integrals in the theory of the normal Fermi liquid involves the variation $\delta n_{\mathbf{p}} = -\delta(\varepsilon - \varepsilon_F)\delta\varepsilon$ of the Fermi distribution at the Fermi surface; in such integrals $\delta(\varepsilon - \varepsilon_F) = 1/\Delta\varepsilon$ for forward scattering, where $\Delta\varepsilon = (p_F/m)(\pi\hbar/a)$, p_F is the Fermi momentum, ε_F is the Fermi level, and a is the average inter-atomic distance. The local Fermi surface is given by $\varepsilon_F = \varphi$, according to the quasi-classical description, where the Fermi energy is $\varepsilon_F = \bar{k}_F k_F / 2 = (3\pi/16)q^2 k_F$; the chemical potential is only a small (quantal) correction, so that it can be neglected; the local Fermi sea is anisotropic; however, in the limit of validity of the quasi-classical description it may be approximated by a spherical Fermi sea given by the average $\varphi = 4\pi z^* / a^3 q^2$; one obtains $k_F = (16/3\pi q^2)\varphi = 64z^*/3a^3 q^4$ (and $\varepsilon_F = \varphi = 4\pi z^* / a^3 q^2$); the variational screening wavevector is $q \simeq 0.77z^{*1/3}$, and $aq \simeq 2.73$ (in general, $aq = c$, where c is a constant; for the present approximation $c \simeq 2.73$).

According to the theory of the normal Fermi liquid one obtains an effective mass

$$m^* = m(1 + 0.39z^{*1/3}) \quad (49)$$

for electrons, which leads to an electronic specific heat $C = V\rho^*\pi^2 T/3$, where $\rho^* = p_F m^* / \pi^2 \hbar^3$ is the renormalized density of states at the Fermi surface (as it is well-known there is no need to distinguish between the two electronic heat capacities, or compressibilities; and the Gruneisen's law holds for electrons); the electronic compressibility (or the thermal expansion coefficient) is not seen experimentally, as the electrons are not decoupled from ions; similarly, the electronic sound velocity $u_e = v_F^0 \sqrt{\alpha/3}$, where v_F^0 is the bare Fermi velocity ($v_F^0 \simeq 3z^{*2/3} \cdot 10^6$ m/s) and α is the orbital occupancy, is immersed in the continuum of electron-hole excitations, and the "electronic sound" does not exist at low temperatures (Landau's damping); the zero-sound also reduces itself to the electron-hole excitations, due to the forward character of the scattering amplitude, and therefore it does not exist either; however, the kinetic equation requires the scattering amplitude at finite momenta, which, in general, differs from f -above at finite energies (the two limits are not intervertible in general), and this leads to plasmons as collective excitations; the quasi-particle (quasi-hole) lifetime τ is given by

$$\gamma = 1/\tau = \frac{\pi}{2\hbar} (4\pi e^2 N z^* / V q^2)^2 (\rho/n)^3 \frac{(\varepsilon - \varepsilon_F)^2 + \pi^2 T^2}{\exp(\mp(\varepsilon - \varepsilon_F)/T) + 1} , \quad (50)$$

where the upper (lower) sign corresponds to quasi-particles (quasi-holes), ρ is the (bare) density of states at the Fermi surface and n is the average electron concentration; finally, the Pauli spin paramagnetic susceptibility is not renormalized, due to two equal and opposite changes in the density of states and the gyro-magnetic factor; it is given by the free susceptibility $\chi = (1/4)g^2 \mu_B^2 \rho$, where g ($\simeq 2$) is the electronic gyro-magnetic factor and μ_B ($= e\hbar/2mc$) is the Bohr magneton (the Zeeman energy $\mu_B H \simeq 0.67$ K for a magnetic field $H = 1$ Ts = 10^4 Gs; 1 eV $\simeq 11.6 \cdot 10^3$ K $\simeq 1.6 \cdot 10^{-19}$ J; $m \simeq 9 \cdot 10^{-31}$ Kg; $\hbar \simeq 10^{-34}$ Js).

11 Polarizability and Diamagnetic Susceptibility

An external electric field \mathbf{E} produces an additional potential $-\mathbf{E}\mathbf{r}$, and a change δn in the equilibrium electron density; since $\int \delta n = 0$, the kinetic energy (22) does not change, while the potential energy (23) gives

$$-\frac{4\pi}{q^2} n \delta n - \frac{1}{2} \varphi_c \delta n + \mathbf{E} n = 0 , \quad (51)$$

and

$$\delta n = \frac{q^2}{4\pi} \frac{\varphi}{\varphi + \varphi_c/2} \mathbf{E}\mathbf{r} \ ; \quad (52)$$

the net change in energy is therefore

$$\delta E = -\frac{q^2}{4\pi} \int d\mathbf{r} \left(\frac{\varphi}{\varphi + \varphi_c/2} \right)^2 (\mathbf{E}\mathbf{r})^2 \ ; \quad (53)$$

hence one can get the electric polarizability.[1],[2] For a uniformly distributed nuclear charge Nz^* in a sphere of radius R , one may use $\varphi = 4\pi z^*/q^2 a^3$ and $\varphi_c = 2\pi z^* R^2/a^3$, where a is the average inter-ionic distance; the change in energy is $\delta E = -[16/15(aq)^2]a^2 R |\mathbf{E}|^2$, and the polarizability $\chi_e = [32/15(aq)^2]a^2 R$; as expected it vanishes for large R .

The electrons in a uniform magnetic field \mathbf{H} have a diamagnetic energy

$$\delta E = -\frac{e^2}{8mc^2} \sum_{\alpha} \overline{(\mathbf{H} \times \mathbf{r}_{\alpha})^2} \ , \quad (54)$$

where c is the light velocity; hence,

$$\delta E = -\frac{e^2 H^2}{12mc^2} \sum_{\alpha} \overline{r_{\alpha}^2} = -\frac{e^2 H^2}{12mc^2} \int d\mathbf{r} \cdot r^2 n \ , \quad (55)$$

and, with a uniform distribution of nuclear charges, one obtains[1],[2] $\delta E = -(\pi e^2/15mc^2)(z^* R^5/a^3) |\mathbf{H}|^2$; the diamagnetic susceptibility is therefore $\chi_d = -(2\pi e^2/15mc^2)(z^* R^5/a^3) \simeq -0.54 \cdot 10^{-4} \cdot (2\pi/15)(z^* R^5/a^3) a_H$.

12 Concluding Remarks

Wavefunctions methods[10] for the chemical bond of large atomic aggregates start with atomic-like orbitals

$$\varphi_s = \sum_{ia} c_{ia}^s \chi_a(\mathbf{r} - \mathbf{R}_i) \ , \quad (56)$$

which are superpositions of individual atomic-like orbitals $\chi_a(\mathbf{r} - \mathbf{R}_i)$ localized at the positions \mathbf{R}_i of the atomic nuclei, and attempt to minimize the Hartree-Fock energy functional

$$\begin{aligned} E_a = & \sum_s (t_s^a - n_s^a) + \frac{1}{2} \sum_{ss'} (d_{ss'}^a - e_{ss'}^a) + \\ & + \frac{1}{2} \sum_{i \neq j} Z_i Z_j / |\mathbf{R}_i - \mathbf{R}_j| \ , \end{aligned} \quad (57)$$

where the matrix elements are the kinetic energy

$$t_s^a = \int d\mathbf{r} \varphi_s^*(\mathbf{p}^2/2) \varphi_s \ , \quad (58)$$

the electron-nuclei attraction

$$n_s^a = \int d\mathbf{r} \sum_i (Z_i / |\mathbf{R}_i - \mathbf{r}|) \varphi_s^* \varphi_s \ , \quad (59)$$

and the direct

$$d_{ss'}^a = \int d\mathbf{r}d\mathbf{r}'(1/|\mathbf{r} - \mathbf{r}'|)\varphi_s^*\varphi_s \cdot \varphi_{s'}^*\varphi_{s'} \quad (60)$$

and exchange

$$e_{ss'}^a = \int d\mathbf{r}d\mathbf{r}'(1/|\mathbf{r} - \mathbf{r}'|)\varphi_s^*(\mathbf{r})\varphi_s(\mathbf{r}') \cdot \varphi_{s'}^*(\mathbf{r}')\varphi_{s'}(\mathbf{r}) \quad (61)$$

interactions; atomic units are used, and a denotes usually the valence atomic orbitals.

Beside the atomic-like orbitals (56) the molecular-like orbitals[11] ψ_s include extended bond-like orbitals Φ_s , such that

$$\psi_s = \alpha_s\varphi_s + \beta_s\Phi_s \quad , \quad \alpha_s^2 + \beta_s^2 = 1 \quad , \quad (62)$$

as for orthonormal sets of wavefunctions; the density-functionals methods[12] for the chemical bond touch upon this point, especially in connection with the Thomas-Fermi model.[13]

The great disparity between the scale-lengths of the localized atomic-like orbitals φ_s and the extended bond-like orbitals Φ_s provides a certain decoupling of the atomic degrees of freedom from the chemical bond degrees of freedom, up to a density-density interaction originating in the direct Coulomb repulsion; the minimization of the Hartree-Fock energy functional for the molecular-like orbitals ψ_s with respect to the β_s -parameters leads to the linear system of equations[14]

$$-A_s + \sum_{s'} D_{ss'}\beta_{s'}^2 = 0 \quad , \quad (63)$$

where

$$A_s = \varepsilon_s^a(HF) - \varepsilon_s^b(HF) + \sum_{s'}(d_{ss'}^b - e_{ss'}^b - \frac{1}{2}d_{ss'}^{ab}) \quad , \quad (64)$$

and the matrix $D_{ss'}$ is given by

$$D_{ss'} = (d_{ss'}^a - e_{ss'}^a) + (d_{ss'}^b - e_{ss'}^b) - d_{ss'}^{ab} \quad ; \quad (65)$$

the b -labelled matrix elements are defined similarly with the atomic-like matrix elements above given by (58)-(61) by using the bond-like orbitals Φ_s instead of the atomic-like orbitals φ_s ; and the Hartree-Fock energies are given by

$$\varepsilon_s^{a,b}(HF) = t_s^{a,b} - n_s^{a,b} + \sum_{s'} d_{ss'}^{a,b} - \sum_{s'} e_{ss'}^{a,b} \quad . \quad (66)$$

Very likely, the matrix $D_{ss'}$ is positive definite, so that A_s must acquire positive values in order to have solutions to (63); the atomic-like orbitals in the upper valence atomic shells may provide such solutions, leading thus to the chemical bond as described by molecular-like orbitals.

Beside the atomic-like energy functional E_a given by (57) one obtains now an additional bond-like energy functional

$$\begin{aligned} E_b = & \sum_s \beta_s^2 t_s^b - \frac{1}{2} \sum_{ss'} \beta_s^2 \beta_{s'}^2 d_{ss'}^{ab} + \frac{1}{2} \sum_{ss'} \beta_s^2 \beta_{s'}^2 d_{ss'}^b - \\ & - \frac{1}{2} \sum_{ss'} \beta_s^2 \beta_{s'}^2 e_{ss'}^b + \frac{1}{2} \sum_{ss'} \beta_s^2 \beta_{s'}^2 (d_{ss'}^a - e_{ss'}^a) \quad , \end{aligned} \quad (67)$$

and an energy

$$\Delta E = - \sum_s \beta_s^2 (A_s + t_s^b) \quad ; \quad (68)$$

the bond-like energy functional E_b indicates the fractional occupancy β_s^2 of the bond-like orbitals, and the hamiltonian

$$\begin{aligned}
 H_b = & \sum_{\alpha} \mathbf{p}_{\alpha}^2/2m - \sum_{\alpha} \int d\mathbf{r}' \cdot \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}_{\alpha}|} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{1}{|\mathbf{r}_{\alpha} - \mathbf{r}_{\beta}|} + \\
 & + \frac{1}{2} \int d\mathbf{r}d\mathbf{r}' \cdot \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}
 \end{aligned} \tag{69}$$

for the bond-like electrons, where

$$\begin{aligned}
 \rho = & \sum_s \beta_s^2 \varphi_s^* \varphi_s = \sum_{ia;jb} \alpha_{ia;jb} \chi_{ia}^* \chi_{jb} = \\
 = & \sum_{ia;jb} \left(\sum_s \beta_s^2 c_{ia}^{s*} c_{jb}^s \right) \chi_{ia}^* \chi_{jb}
 \end{aligned} \tag{70}$$

is the density of positive charge left behind in the atomic-like orbitals by the electrons participating in the chemical bond; the hamiltonian (69) describes the interaction between these electrons and their electronic "holes" in the ionic cores. One can see that H_b given by (69) is in fact the effective hamiltonian given by (3), and the pair-wise distribution ρ given by (70) corresponds to the effective charges

$$z_{ia}^* = \alpha_{ia;ia} = \sum_s \beta_s^2 |c_{ia}^s|^2 \tag{71}$$

and $z_i^* = \sum_a z_{ia}^*$; and an average occupancy β_s^2 equals z_{ia}^* ; neglecting the cross-terms in (70) the density of the ionic cores becomes $\rho = \sum_{ia} \alpha_{ia;ia} |\chi_{ia}|^2$ like in (2); or, for point-like charges, $\rho = \sum_{ia} z_{ia}^* \delta(\mathbf{r} - \mathbf{R}_i) = \sum_i z_i^* \delta(\mathbf{r} - \mathbf{R}_i)$, like in (27).

The atomic-like problem as formulated by the energy functional E_a given by (57) can be solved, in principle, according to the usual practice of the wavefunctions methods; [10] the bond-like hamiltonian H_b given by (69) can be treated by the quasi-classical theory of the slightly inhomogeneous electron liquid; the self-consistent solution to equations (63) is then obtained for the parameters β_s^2 and, implicitly, for the density ρ of the effective charge of the ionic cores; the actual self-consistent solution must also ensure the minimum value of the total energy functional $E_a + E_b + \Delta E$ with respect to the positions of the atomic nuclei. The chemical bond consists therefore of extended bond-like electronic orbitals of fractional occupancy β_s^2 and of localized atomic-like electronic orbitals of fractional occupancy α_s^2 (the atomic-like fractional occupancy may be made to appear explicitly in the atomic-like energy functional E_a); the total electronic energy ensures the equilibrium of the atomic aggregate with respect to the Coulomb repulsion between the atomic nuclei. The contribution of the atomic-like part of the total energy to the binding energy is a quantal correction with respect to the quasi-classical description, so that, to the first approximation it may be neglected; the unrestricted minimization of the bond-like energy functional requires then a unity occupancy $\beta_s^2 = 1$ for the bond-like orbitals, the conservation of the total charge being ensured by the Coulomb interactions in the hamiltonian H_b given by (69); within this approximation, one may say, therefore, that the binding energy and the cohesion of the atomic aggregates are given by the theory of the slightly inhomogeneous electron liquid for the bond-like hamiltonian H_b given by (69); however, while this procedure is satisfactory for the binding energy and the cohesion, the fractional occupancy must be included for the single-electron properties.

Figure Caption

Fig.1 Magic homo-atomic metallic clusters

Fig.2 Ground-state mass-abundance spectrum and geometric magic numbers

Fig.3 Isomers for Fe-clusters ($z^* = 0.57$)

Fig.4 Ground-state energy per atom $E(N)/N$ for Na-clusters ($z^* = 0.44$), Fe-clusters ($z^* = 0.57$) and Ba-clusters ($z^* = 0.34$) plotted *vs* cluster size N

Fig.5 Vibration spectra for some Fe-magic clusters ($z^* = 0.57$)

References

- [1] M. Apostol, J. Theor. Phys. **41** 1 (1999).
- [2] M. Apostol, *Electron Liquid*, apoma, Magurele-Bucharest (2000).
- [3] This "rigidity" of the exchange energy has probably been touched upon for the first time by E. Wigner and F. Seitz, Phys. Rev. **43** 804 (1934); **46** 509 (1934), and J. C. Slater, *The Calculation of Molecular Orbitals*, Wiley, NY (1979).
- [4] See, for instance, the clarifications brought by J. M. C. Scott, Phil. Mag. **43** 859 (1952), and by J. Schwinger, Phys. Rev. **A22** 1827 (1980) and **A24** 2353 (1981), to the asymptotic series of the atomic binding energy provided by the "3/2"-Thomas-Fermi model in the limit $Z \rightarrow \infty$; as well as the "no-binding theorem" of the latter in E. Teller, Revs. Mod. Phys. **34** 627 (1962), E. Lieb and B. Simon, Adv. Math. **23** 22 (1977), L. Spruch, Revs. Mod. Phys. **63** 151 (1991).
- [5] L. C. Cune and M. Apostol, J. Theor. Phys. **49** 1 (2000); **50** 1 (2000).
- [6] L. C. Cune and M. Apostol, J. Theor. Phys. **53** 1 (2000).
- [7] L. C. Cune and M. Apostol, J. Theor. Phys. **45** 1 (1999); **54** 1 (2000).
- [8] J. C. Slater, *Quantum Theory of Atomic Structure*, McGraw-Hill, NY (1960).
- [9] See, for instance, E. Wigner and F. Seitz, *loc cit*, Ref.3, and E. Wigner, Phys. Rev. **46** 1002 (1934); Trans. Faraday Soc. **34** 678 (1938); such qualitative considerations apply in fact to a universal model of solid, as based upon a screened Coulomb interaction.
- [10] See, for instance, J. A. Pople, Revs. Mod. Phys. **71** 1267 (1998).
- [11] R. S. Mullikan, Phys. Rev. **32** 186 (1928).
- [12] P. Hohenberg and W. Kohn, Phys. Rev. **136** B864 (1964); W. Kohn and L. J. Sham, Phys. Rev. **140** A1133 (1965); see also W. Kohn, Revs. Mod. Phys. **71** 1253 (1998).
- [13] See, for instance, the Thomas-Fermi model in the quasi-classical limit in Ref.4.
- [14] M. Apostol, J. Theor. Phys. **55** 1 (2000).

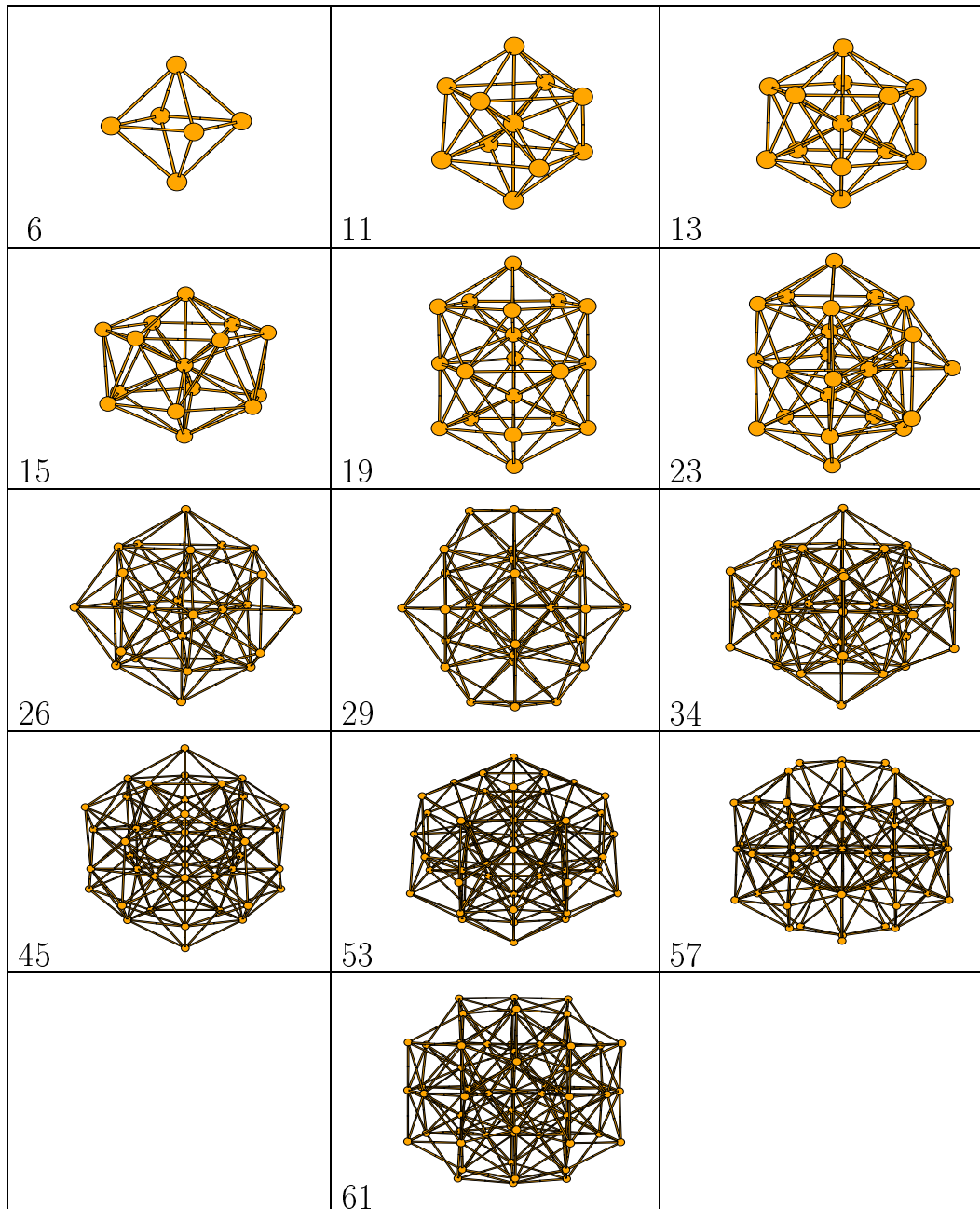


Figure 1: Magic homo-atomic metallic clusters

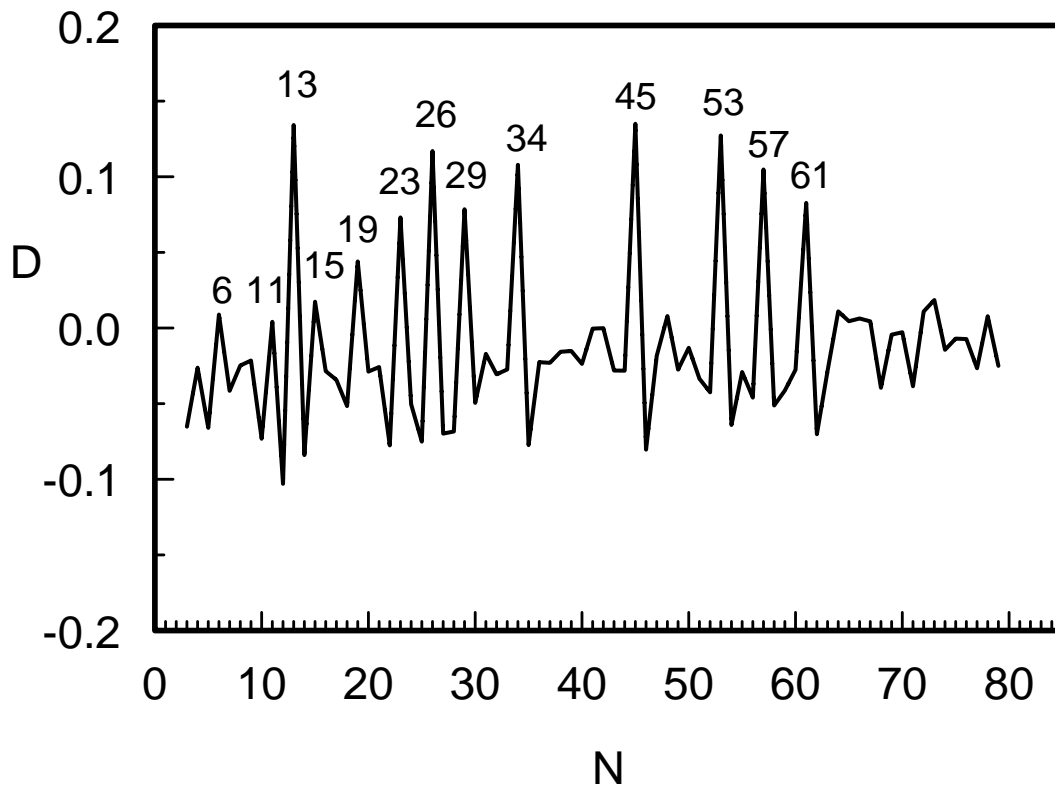


Figure 2: Ground-state mass-abundance spectrum and geometric magic numbers

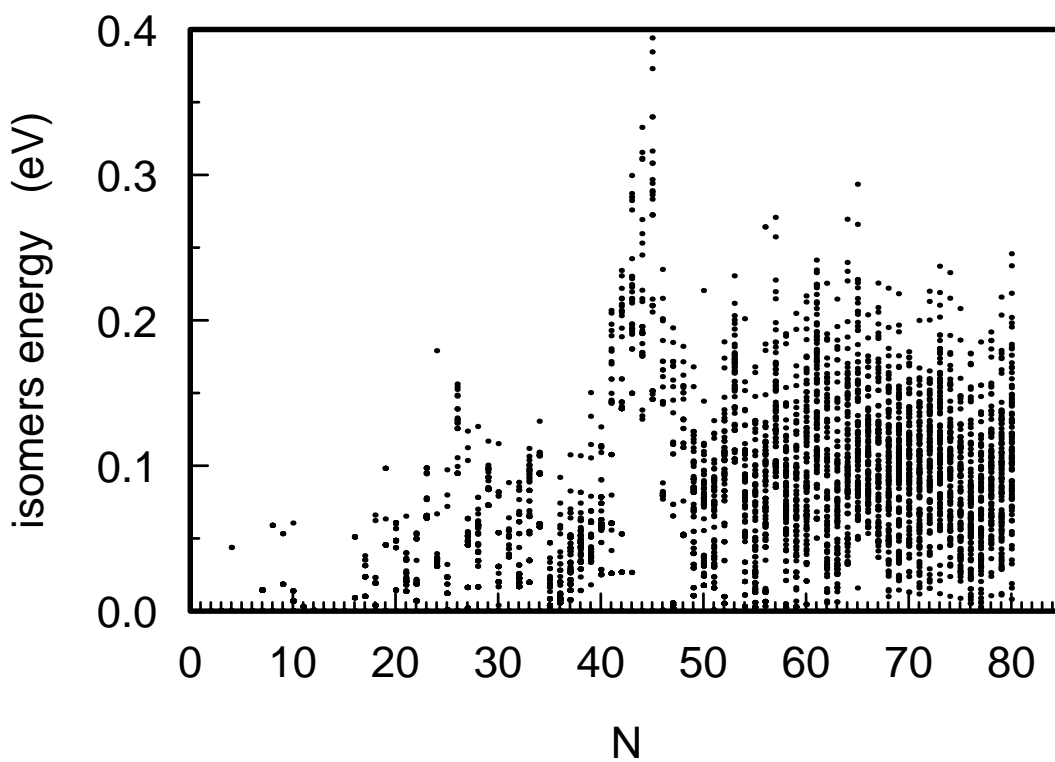


Figure 3: Isomers for Fe-clusters ($z^* = 0.57$)

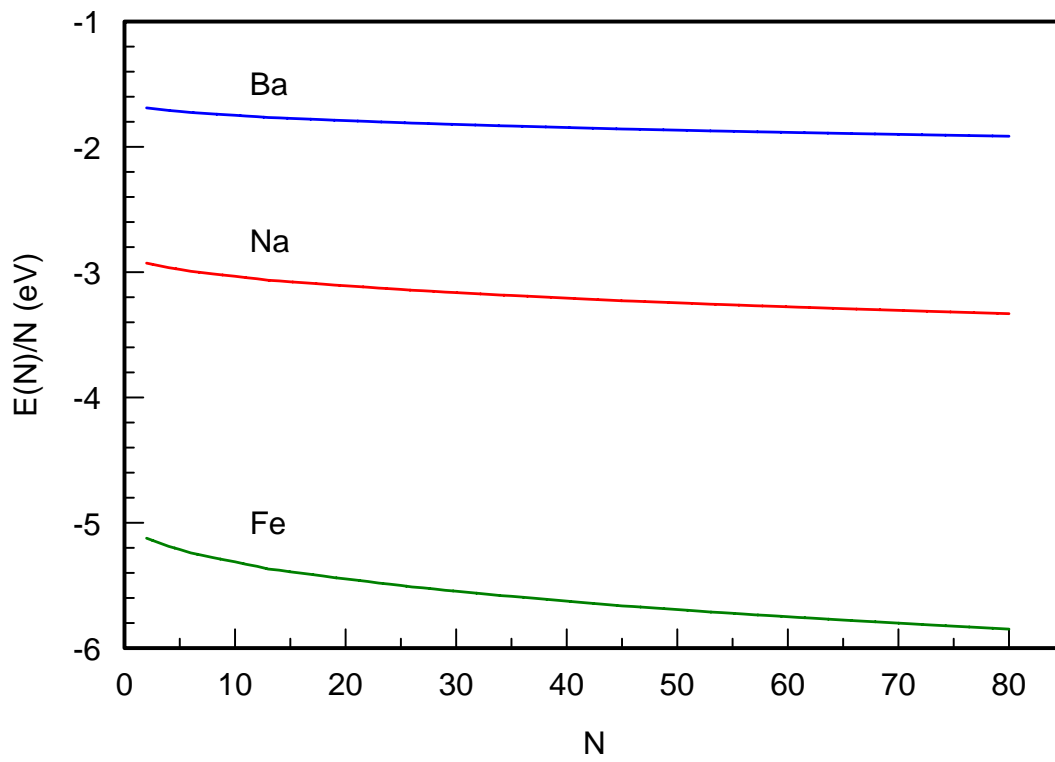


Figure 4: Binding energy per atom $E(N)/N$ for Na-clusters ($z^* = 0.44$), Fe-clusters ($z^* = 0.57$) and Ba-clusters ($z^* = 0.34$) plotted *vs* cluster size N

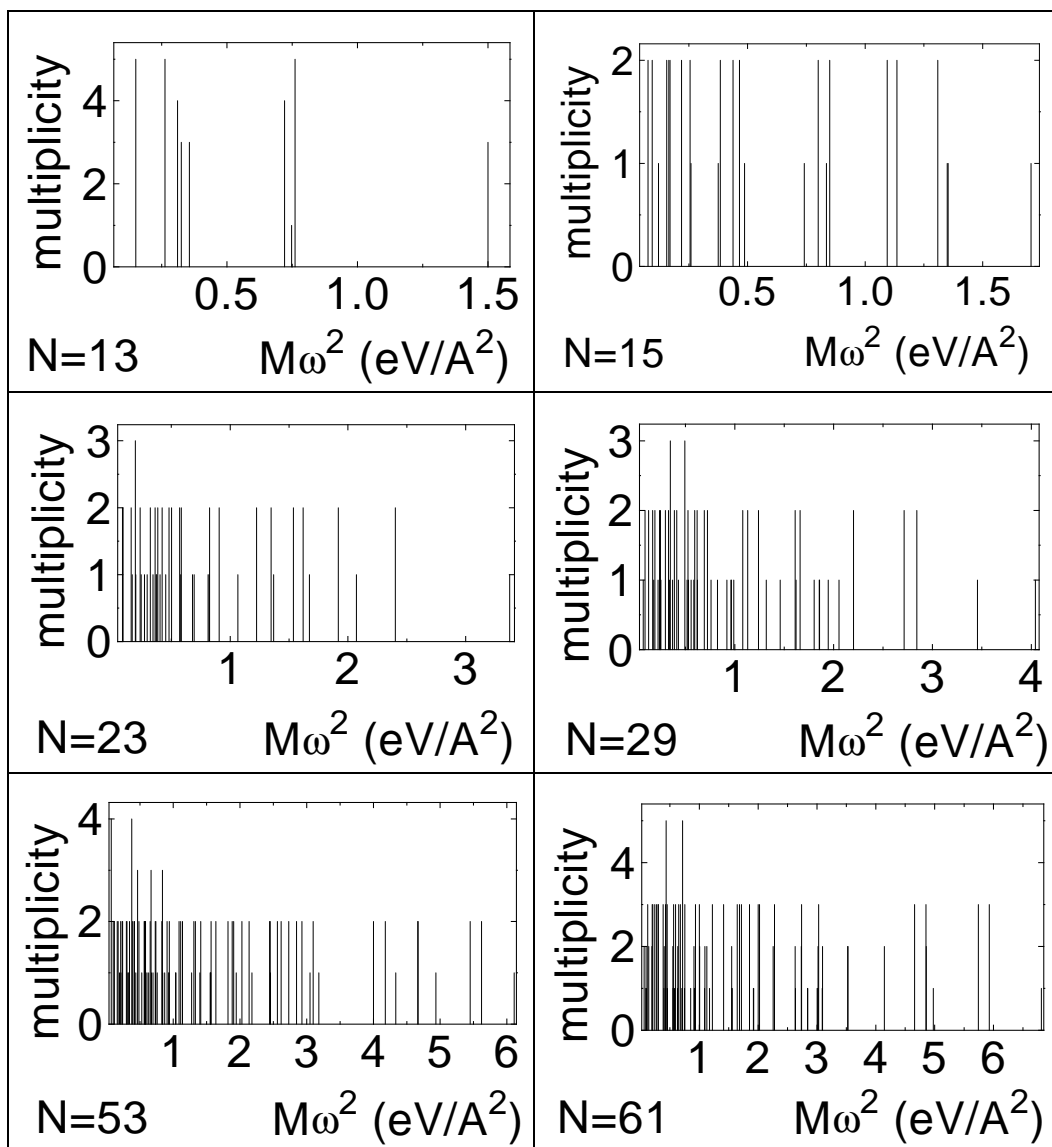


Figure 5: Vibration spectra for some Fe-magic clusters ($z^* = 0.57$)