ATOMIC CLUSTERS

Chemical Bond in Condensed Matter

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Atoms may bind together according to the quantal structure of their single-electron energy shells. Electrons in the valence upper shells participate in the chemical bond, leaving behind a background of positive ions. The hole density of the ionic background is given, in its most general pair-wise form, by

$$\rho(\mathbf{r}) = \sum_{ia;jb} (\sum_s \beta_s^2 c_{ia}^{s*} c_{jb}^s) \chi_{ia}^*(\mathbf{r}) \chi_{jb}(\mathbf{r}) \ , \tag{1}$$

where $\chi_{ia}(\mathbf{r}) = \chi_a(\mathbf{r} - \mathbf{R_i})$ is the a-th atomic-like orbital of the i-th ion placed at $\mathbf{R}_i$, c_{ia}^s are the coefficients of the s-th linear combination of atomic-like orbitals, and β_s is the content of the chemical-bond orbital Φ_s in the molecular-like orbital ψ_s; $\psi_s = \alpha_s \varphi_s + \beta_s \Phi_s$, $\varphi_s = \sum_{ia} c_{ia}^s \chi_{ia}$, $\alpha_s^2 + \beta_s^2 = 1$. Averaging out the β_s^2-coefficient in (1), and in virtue of the orthogonality of the c_{ia}^s-matrix, one gets the ionic density

$$\rho(\mathbf{r}) = \beta^2 \sum_{ia} |\chi_{ia}(\mathbf{r})|^2 \ ; \tag{2}$$

hence, the total number of electronic holes of the ionic background is given by

$$\int d\mathbf{r} \cdot \rho(\mathbf{r}) = \beta^2 \sum_i z_i \ , \tag{3}$$

where z_i is the nominal valence of the i-th atom. One can see that each ion participate in the chemical bond with an effective valence

$$z_i^* = \beta^2 z_i \ , \tag{4}$$

smaller than the nominal valence z_i; and the same is true for each valence atomic-like orbital ia. The general form (1) of the ionic density may also be written as

$$\rho(\mathbf{r}) = \sum_{ia;jb} \alpha_{ia;jb} \chi_{ia}^*(\mathbf{r}) \chi_{jb}(\mathbf{r}) \ , \tag{5}$$

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where $\alpha_{ia;jb} = \sum_s \beta_s^2 c_{ia}^{s*} c_{jb}^s$, and, if the overlap may be neglected, one gets

$$\rho(\mathbf{r}) = \sum_{ia} \alpha_{ia} \left| \chi_{ia}(\mathbf{r}) \right|^2 \quad , \tag{6}$$

where $\alpha_{ia} = \alpha_{ia;ia}$, and the effective charge parameters read now

$$z_{ia}^* = \alpha_{ia} = \sum_s \beta_s^2 \left| c_{ia}^s \right|^2 \quad , \tag{7}$$

and

$$z_i^* = \sum_a z_{ia}^* \ . \tag{8}$$

The chemical-bond orbitals Φ_s are only fractionally occupied by electrons, as well as the atomic-like orbitals φ_s. The electrons spend part of time on atoms, and the remaining part moving in-between the atoms. The coefficients of partial occupancy are β^2, or β_s^2, or the effective valence parameters z_{ia}^* above. The atomic-like orbitals φ_s are localized over atomic-scale lengths, while the chemical-bond orbitals Φ_s extend to the entire atomic aggregate. The single-electron picture requires both reasonably heavy atoms and large atomic aggregates, so that the disparity in the scale-lengths between the atomic-like orbitals and the chemical-bond orbitals be large. This difference allows the hamiltonian of the atomic nuclei and the electrons to be separated into an atomic-like part and a collective, or chemical-bond, part, via the corresponding Hartree-Fock energy functional. The coefficients c_{ia}^s are determined by the usual approach to the linear combination of atomic orbitals (which is the standard ab-initio wavefunctions method[1]), while the coefficients β_s are determined by minimizing the interplay between the atomic and the chemical-bond contributions. The latter provides both solution and self-consistency.

The approach is based on the Hartree-Fock theory and on Mullikan's idea of molecular-like orbitals. The general theory of chemical bond outlined above is given in Ref.[2].

For metals, *i.e.* for s-, d- and f-valence electrons, the ionic background may be approximated by an ensemble of point-like ions; the ionic density is then given by

$$\rho(\mathbf{r}) = \sum_i z_i^* \delta(\mathbf{r} - \mathbf{R}_i) \ . \tag{9}$$

For p-, or sp-elements the directional character of the atomic-like orbitals brings relevant contributions. The theory reviewed below does not depend essentially on the form of the ionic density; the directional character of the ionic cores however requires more extensive numerical computations. The

effective hamiltonian of the chemical bond for point-like (metallic) ions reads

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

$$+\frac{1}{2}e^2 \sum_{\alpha \neq \beta} 1/|\mathbf{r}_{\alpha} - \mathbf{r}_{\beta}| + \frac{1}{2}e^2 \sum_{i \neq j} z_i^* z_j^* / |\mathbf{R}_i - \mathbf{R}_j| \quad, \tag{10}$$

which includes the kinetic energy of the electrons, the electron-ion Coulomb attraction, the electron-electron Coulomb repulsion and the ion-ion Coulomb repulsion; m denotes the electron mass and $-e$ is the electron charge. The problem is to find out the ground-state of the ensemble described by (10), including the stability of the atomic aggregate with respect to the ionic positions, and the lowest excited states, $i.e.$ the cohesion, binding, electronic and ionic properties. Since the ensemble is large, $i.e.$ the number N of ions is much greater than unity, $N \gg 1$, and, accordingly, the corresponding number of (neutralizing) electrons is also large, the Hartree-Fock equations turn out to be the appropriate starting point. The Hartree-Fock energy functional for (10) must be written in terms of the $\beta_s \Phi_s$-wavefunctions. However, the nature of solutions does not depend on the fractional occupancy, so that the Hartree-Fock equations may be written as

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

$$-e^2 \int d\mathbf{r}' \cdot n(\mathbf{r}',\mathbf{r})/ |\mathbf{r} - \mathbf{r}'| \cdot \Phi_s(\mathbf{r}') = \varepsilon \Phi_s \quad, \tag{11}$$

where the electron density is given by

$$n(\mathbf{r}) = \sum_s |\Phi_s(\mathbf{r})|^2 \tag{12}$$

and the two-point electron "density"

$$n(\mathbf{r}, \mathbf{r}') = \sum_s \Phi_s^*(\mathbf{r})\Phi_s(\mathbf{r}') \tag{13}$$

is introduced. The external field of the ions can be seen in (11), as well as both the Hartree and the exchange interactions. Equations (11) can also be written in a more convenient form

$$(\mathbf{p}^2/2m)\Phi_s - e\varphi \cdot \Phi_s + \varepsilon_{ex}(\Phi_s) = \varepsilon \Phi_s \quad, \tag{14}$$

by introducing the Hartree field

$$\varphi = e \sum_i z_i^* / |\mathbf{r} - \mathbf{R}_i| - e \int d\mathbf{r}' \cdot n(\mathbf{r}')/ |\mathbf{r} - \mathbf{r}'| \tag{15}$$

and the exchange energy

$$\begin{aligned}
\varepsilon_{ex}(\Phi_s) &= -e^2 \int d\mathbf{r}' \cdot n(\mathbf{r}',\mathbf{r})/\left|\mathbf{r}-\mathbf{r}'\right| \cdot \Phi_s(\mathbf{r}') = \\
&= -e^2 \int d\mathbf{r}' \cdot 1/\left|\mathbf{r}-\mathbf{r}'\right| \cdot \sum_{s'} \Phi_{s'}^*(\mathbf{r}')\Phi_{s'}(\mathbf{r}) \cdot \Phi_s(\mathbf{r}') \ .
\end{aligned} \tag{16}$$

As usually, the spins are parallel in the exchange energy, and s may equal s'. One may proceeds now to solving the Hartree-Fock equations.

The first remark is that the exchange energy (16) admits plane waves as eigenfunctions for Φ_s. On changing the wavefunctions Φ_s both the exchange energy (16) and the electron density (12) change, and in this sense the exchange energy is a "functional of density". But the exchange energy does not change on changing locally the upper limit of the summation over s' in (16), *i.e.* on changing the "local" electron density, due to the non-local character of the exchange energy; indeed, one can not modify the upper limit of the summation over s' for a given $\mathbf{r}$ without doing the same at $\mathbf{r}'$. In this sense, the exchange energy is not a functional of density, but it remains a functional of "concentration". This "rigidity" property of the exchange energy under local variations of the electron density is the second remark made upon the behaviour of the exchange energy. Since, due to the "rigidity" of the exchange energy, one may change locally the electron density, in a slow manner, such as to preserve the plane waves over as large a spatial extent as possible, without changing the exchange energy; doing so, one can screen off the long tail of the bare Coulomb potential of the electron-ion interaction in the self-consistent Hartree field φ given by (15). The local density of electrons behaves, in this respect, as a free parameter for the exchange energy. Under this circumstance, the self-consistent potential φ is almost rendered to a constant over large spatial regions, such that the Hartree-Fock equations (14) admit indeed plane waves as eigenfunctions, to the first approximation. The self-consistent potential φ is left with abrupt variations over small distances around the ions, whose contributions are treated in the next step. This is the quasi-classical description of the solutions of the Hartree-Fock equations, and the basis of the picture of the slightly inhomogeneous electron liquid for the chemical bond theory.

One may proceed now to give a few more mathematical details about the quasi-classical description of the slightly inhomogeneous electron liquid. For (quasi-) plane waves the kinetic energy, the electron-ion interaction and the electron Hartree interaction in the Hartree-Fock energy functional of the hamiltonian (10) are functionals of density; while the electron exchange interaction stays "rigid" under the variation of the electron density. The vanishing of the first-order variation of the energy functional under varia-

tions of the electron density, as for equilibrium, leads to the quasi-classical equation of motion

$$\hbar^2\mathbf{k}_F^2/2m - e\varphi = 0 \ , \tag{17}$$

where $\mathbf{k}_F = \mathbf{p}_F/\hbar$ is the local Fermi wavevector, $\mathbf{p}_F$ is the corresponding Fermi momentum, and $\hbar$ is Planck's constant; this equation is also the equilibrium equation for a vanishing local chemical potential, as for a neutral atomic aggregate. On the other hand, the Hartree field given by (15) satisfies Poisson's equation

$$\Delta\varphi = -4\pi e \sum_i z_i^* \delta(\mathbf{r} - \mathbf{R}_i) + 4\pi e n \ , \tag{18}$$

where the electron density is given by

$$n = k_F^3/3\pi^2 \ , \tag{19}$$

as for (quasi-) plane waves. Substituting k_F from (17) into (19) one obtains $n \sim \varphi^{3/2}$ and the 3/2-Thomas-Fermi model for the self-consistent field φ. However, both the quasi-classical equation of motion (17) and the electron density (19) are not valid anymore in the vicinity of the ionic cores where the variations of the field φ are large; consequently, using them in this context of large errors in the ionic boundary conditions would introduce large errors in the overall behaviour of the self-consistent potential φ over large distances. The 3/2-Thomas-Fermi model is valid in the asymptotic limit of infinite charges, where the electrons are localized on the ionic cores; this is the "quasi-classical approximation", which, however, leads to the "no-binding theorem" for such hypothetical atomic aggregates, as expected. On the contrary, since the self-consistent potential φ and the electron density vary slowly over large distances, according to the quasi-classical description, one must linearize both the Fermi energy $\hbar^2 k_F^2/2m \rightarrow \hbar^2\overline{k}_F k_F/2m$ in (17) and the electron density $n = k_F^3/3\pi^2 \rightarrow \overline{k}_F^2 k_F/3\pi^2$ in (19), where the parameter $\overline{k}_F$, to be determined variationally, is constant in space, and the entire spatial dependence is transferred upon the new Fermi wavevector k_F. This linearized Thomas-Fermi theory corresponds to the quasi-classical description of the slightly inhomogeneous electron liquid, where the ionic effective charges z_i^* are small, the number N of ions is large, and the cohesion is realized over large distances in comparison with the small regions around the ionic cores where one encounters abrupt variations; giving thereby a statute of quantal corrections to the contributions brought about by these abrupt variations over short-scale lengths. In this respect the theory is close to Schwinger's remarks upon the chemical bond.[3] The theory applies also to heavy individual atoms, where, quantal corrections included, it reproduces the empirical binding energy $\sim -16Z^{7/3}$eV, where $Z \gg 1$ is the

(finite) atomic number.[4] Making use of the linearization procedure given above the electron density can be written as $n = (q^2/4\pi)\varphi$, where q is the Thomas-Fermi screening wavevector given by $q^2 = (8/3\pi)\overline{k}_F$, and Poisson's equation (18) becomes a linear equation,

$$\Delta\varphi = -4\pi \sum_i z_i^* \delta(\mathbf{r} - \mathbf{R}_i) + q^2\varphi \; ; \tag{20}$$

whose solution

$$\varphi = \sum_i \frac{z_i^*}{|\mathbf{r} - \mathbf{R}_i|} e^{-q|\mathbf{r} - \mathbf{R}_i|} \tag{21}$$

is a superposition of screened Coulomb potentials, as expected. Bohr radius $a_H = \hbar^2/me^2 = 0.53$Å and the atomic unit $e^2/a_H = 27.2$eV are used for lengths and, respectively, for energy. The Thomas-Fermi screening wavevector is determined variationally, as discussed above.

The "potential" energy, *i.e.* the sum of the electron-ion attraction, the Hartree electron-electron repulsion and the ion-ion repulsion, is given by

$$
\begin{aligned}
E_{pot} &= \int d\mathbf{r} \cdot \left(-\varphi n + \frac{1}{2}\varphi_e n\right) + \frac{1}{2}\int d\mathbf{r} \cdot \varphi_{ion}\rho = \\[2mm]
&= -\frac{1}{2}\int d\mathbf{r} \cdot (\varphi + \varphi_{ion})n + \frac{1}{2}\int d\mathbf{r} \cdot \varphi_{ion}\rho = \\[2mm]
&= -\frac{q^2}{8\pi}\int d\mathbf{r} \cdot (\varphi + \varphi_{ion})\varphi + \frac{1}{2}\int d\mathbf{r} \cdot \varphi_{ion}\rho \; ,
\end{aligned}
\tag{22}
$$

according to the Hartree-Fock energy functional for the hamiltonian (10), where φ_e is the electron contribution to the self-consistent field φ,

$$\varphi_{ion} = \sum_i z_i^* / |\mathbf{r} - \mathbf{R}_i| \tag{23}$$

is the ionic contribution to the self-consistent φ, $\varphi = \varphi_e + \varphi_{ion}$, and ρ is the ionic density given by (9); it is worth noting the Koopmans' 1/2-factor in the potential energy above. Using the potential given by (21) one obtains

$$E_{pot} = -\frac{q}{4}\left[3 \sum_i z_i^{*2} + \sum_{i \neq j} z_i^* z_j^* (1 - 2/qr_{ij})e^{-qr_{ij}}\right] \; , \tag{24}$$

where $r_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ is the inter-atomic distance. The above equation tells that ionic cores have a "self-energy" corresponding to the first term in (24), and interact slightly through effective potentials[5]

$$\Phi_{ij} = -\frac{1}{2}q z_i^* z_j^* (1 - 2/qr_{ij})e^{-qr_{ij}} \; ; \tag{25}$$

this resembles closely Wigner's "metal" picture. The minimum values of the potential energy (24) with respect to the ionic positions $\mathbf{R}_i$, or, equivalently, with respect to the dimensionless position parameters $\mathbf{x}_i = q\mathbf{R}_i$, give the equilibrium geometric forms of the atomic aggregate; they include both the ground-state form and the isomers. It is easy to see that the equilibrium average inter-atomic distance is $a \simeq r_{ij} \simeq c/q$, where $c \simeq 2.73$. Ground-state magic numbers $N = 6, 11, 13, 15, 19, 23, 26, 29, 34, 45, 53, 57, 61$, etc, and magic geometric forms have been obtained thereby for homo-atomic metallic clusters, which are independent of the effective charge $z^* = z_i^*$, $i.e.$ independent of the nature of the chemical species (for point-like ions).[5] The corresponding ground-state value of the potential energy can be written as $E_{pot} = -Bq$, where the effective atomic interaction contributes little to the ciefficient B, in comparison with the atomic "self-energy" contribution. With a few possible exceptions, the isomers are very close in energy to the ground-state.

According to the quasi-classical description of the inhomogeneous electron liquid the kinetic energy of the electrons reads

$$
\begin{aligned}
E_{kin} &= V k_F^5/10\pi^2 \rightarrow \frac{\overline{k}_F^4}{10\pi^2} \int d\mathbf{r} \cdot k_F = \\
&= \frac{1}{5\pi^2}(3\pi/8)^3 q^6 \int d\mathbf{r} \cdot \varphi = \frac{27\pi^2}{640} z_o q^4 = A q^4/4 ~,
\end{aligned}
\tag{26}
$$

where V is the volume the electrons and ions are confined to, $z_0 = \sum_i z_i^*$ is the total charge, and the coefficient A is defined by (26). The Thomas-Fermi screening wavevector q is obtained by minimizing the quasi-classical energy

$$
E_q = E_{kin} + E_{pot} = A q^4/4 - Bq ~;
\tag{27}
$$

one obtains

$$
q = (B/A)^{1/3} \simeq 0.77 z^{*1/3} ~,
\tag{28}
$$

where z^* is the average effective charge $\overline{z_i^*}$; the effective atomic interaction contributes little to this variational value of the equilibrium screening wavevector. Making use of this q-value one gets the average inter-atomic distance $a \simeq 2.73/q \simeq 3.55 z^{*-1/3}$; the equilibrium quasi-classical energy is $E_q \simeq -0.43 N z^{*7/3}$; the average self-consistent potential given by (21) is $\varphi_0 = \overline{\varphi} = 4\pi z^*/a^3 q^2 = (4\pi/c^3) z^* q \simeq 0.48 z^{*4/3}$.

The total energy is given by the quasi-classical energy E_q plus the exchange energy E_{ex}. The latter reads

$$
E_{ex} = -V k_F^4/4\pi^3 \rightarrow -\frac{1}{4\pi^3} \overline{k}_F^3 \int d\mathbf{r} \cdot k_F =
$$

$$(29)$$

$$= -\frac{1}{2\pi^3}(3\pi/8)^2 q^4 \int d\mathbf{r} \cdot \varphi = -\frac{9}{32}q^2 z_0 \ ,$$

or $E_{ex} = -0.17 N z^{*5/3}$. Therefore, the total energy is given by

$$E = E_q + E_{ex} \simeq -N(0.43 z^{*7/3} + 0.17 z^{*5/3}) \ . \qquad (30)$$

Since the chemical potential of the independent atoms vanishes in the quasi-classical description the total energy given above is the binding energy E_b of the atomic aggregate, $E_b = E$. The direct (Hartree) contribution $-0.43 z^{*4/3}$ to the global (thermodynamic) chemical potential $\partial E/\partial(N z^*) = -0.43 z^{*4/3}$ $-0.17 z^{*2/3}$ compares well with the average self-consistent potential energy $-\varphi_0$ given above.

The quantal effects originate in the abrupt variations near the ionic cores. They are included by solving the Hartree contribution to (14), $i.e.$ Schrodinger's equation

$$(\mathbf{p}^2/2m)\Phi_s - e\varphi \cdot \Phi_s = \varepsilon\Phi_s \qquad (31)$$

with the self-consistent potential φ given by (21), and treating the corresponding exchange contribution to the first-order of the perturbation theory; the latter is indeed a perturbation as a consequence of the off-diagonal character of the exchange energy (16) with respect to the electron states; this is the third remark made upon the exchange energy. The correction statute of the quantal effects is established by estimating the average k_{Fav} of the Fermi wavevector

$$k_{Fav} = \frac{1}{z_0} \int d\mathbf{r} \cdot k_F n \ , \qquad (32)$$

and comparing it with the variational Fermi wavevector $\overline{k}_F = (3\pi/8)q^2$ obtained above. Equation (32) leads to

$$k_{Fav} = \frac{16}{3\pi z_0} \int dr \cdot r^2 \varphi^2 \ , \qquad (33)$$

and $q_{av} \simeq 0.9 z^{*1/3}$. Comparing it with the variational screening wavevector $q \simeq 0.77 z^{*1/3}$ given by (28), one may estimate the contribution of the quantal effects of $\sim 17\%$ to all the relevant quantities. Since the symmetry of φ is the same with the quasi-classical symmetry of the aggregates the latter is preserved by such quantal corrections. The quantal effects however correct the Fermi level (which is the chemical potential and may be taken as the ionization potential), and give the structure of the lowest-energy spectrum

of the electronic excitations (which are relevant for the spectroscopic properties; the lowest unoccupied level being taken as the electron affinity); the long-wavelength behaviour of the self-consistent potential (21) may be relevant for statistical ensembles of atomic aggregates, or for their liquid state, allowing for deformation, finite-size, and electronic-shell effects; statistical magic numbers and electronic magic numbers are obtained this way.

Extended quantal structure of the ionic cores, and the corresponding fractional occupancy of the electronic orbitals fall in the class of quantal corrections, due to their short-scale lengths nature. However, though quantitatively small, they may bring qualitative changes in the structure symmetry of the aggregates, especially when constraints like translational symmetry of bulk solids are involved. The effects of the fractional occupancy act in opposite directions in the chemical-bond orbitals part and the atomic-like orbitals part of the energy functional; consequently, within the limits discussed herein, the fractional occpancy may be neglected ($\beta^2 = 1$) in global quantities like those related to cohesion, binding, structure, etc. However, in specific electronic quantities the fractional occupancy is relevant. One example is the ionization potential of such an atomic aggregate, which can be written as $I = (1 - \beta^2)I_a + \beta^2 I_b$, where β^2 is the fractional occupancy, I_a is the atomic ionization potential and I_b is the ionization potential of the slightly inhomogeneous electron liquid; in the quasi-classical description the latter vanishes. One may say that the electronic states in an atomic aggregate are "strongly renormalized" through the fractional occupancy by the atomic interaction. Similarly, the fractional occupancy affects the plasma frequency; the latter is obtained as the second-order variation of the collective energy functional of the hamiltonian (10) with respect to the electron density (the first-order variation vanishes, for equilibrium).

The self-consistent nature of the Hartree potential φ leads to a quasi-classical quasi-particles picture for the slightly inhomogeneous electron liquid. The f-function of the normal Fermi liquid is given by Born scattering amplitude

$$f(\mathbf{k} - \mathbf{k}') = 4\pi e^2 \sum_i \frac{z_i^*}{q^2 + |\mathbf{k} - \mathbf{k}'|^2} e^{i(\mathbf{k} - \mathbf{k}')\mathbf{R}_i} \tag{34}$$

for parallel spins, and its main contribution is the forward scattering amplitude

$$f(\mathbf{p} - \mathbf{p}') = (4\pi e^2 N z^*/q^2)\frac{(2\pi\hbar)^3}{V}\delta(\mathbf{p} - \mathbf{p}') \; ; \tag{35}$$

the variation of the Fermi distribution at the Fermi surface implies $\delta(\varepsilon - \varepsilon_F) = 1/\Delta\varepsilon = (m/p_F)(a/\pi\hbar)$, where ε_F is the Fermi level and a denotes

the average inter-atomic distance. One obtains the effective mass

$$m^* = m(1 + 0.39z^{*1/3}) \tag{36}$$

for the quasi-classical electronic quasi-particles, no zero-sound and no renormalization of the Pauli spin paramagnetism. The quasi-particles (quasi-holes) lifetime $\tau = 1/\gamma$ is given by

$$\gamma = \frac{\pi}{2\hbar}(4\pi e^2 N z^*/V q^2)^2 (\rho/n)^3 \frac{(\varepsilon - \varepsilon_F)^2 + \pi^2 T^2}{\exp(\mp(\varepsilon - \varepsilon_F)/T) + 1} \ , \tag{37}$$

where $\rho = m p_F/\pi^2 \hbar^3$ denotes here the density of states, n is the electron concentration and T denotes the temperature; it can also be written as

$$\gamma \simeq (\varepsilon - \varepsilon_F)^2/\varepsilon_F \ , \tag{38}$$

since $\varepsilon_F \simeq \varphi_0$ given above. The relative uncertainty in the $(\varepsilon - \varepsilon_F)$-energy is $(\varepsilon - \varepsilon_F)/\varepsilon_F$.

The second-order variations of the quasi-classical energy E_q with respect to both the electron density (or, equivalently, the screening wavevector q, since $q^2 = (8/3\pi)(3\pi^2 n)^{1/3}$) and the atomic positions leads to the vibration spectrum of the aggregate (phonons), to electron-phonon interaction, and to plasmon renormalization (which, however, brings irrelevant contributions). In the long-wavelength limit the electron-phonon interaction is renormalized to zero, according to the adiabatic Born-Oppenheimer theorem, and the aggregate exhibits the adiabatic sound with typical velocities

$$v_s = [(0.43z^{*7/3} + 0.68z^{*5/3})/A]^{1/2} m/s \ , \tag{39}$$

where A is the atomic mass. The short-wavelength electron-phonon interaction involves the product of the electron density variation by the local atomic displacement times a $M \sim 10^{-2} z^{*2/3}(0.27z^{*2/3}\text{eV})$-factor. The thermodynamics, transport, spectroscopic and various response properties of the atomic aggregate are given by its elementary excitations like phonons, quasi-classical electronic quasi-particles, plasmons, etc. In particular the static electric polarizability is computed by the first-order variation of the potential energy to an external electric field, and the diamagnetic susceptibility is also obtained by making use of the known electron density.

An estimation of the effective charge z^* is provided by the atomic screening theory for heavy metallic atoms. As remarked before, the Thomas-Fermi theory applies to this case,[4] and it leads to a self-consistent potential $\varphi = Ze^{-qr}/r$, a quasi-classical energy $-11.78Z^{7/3}\text{eV}$ (the exchange energy is $-4.6Z^{5/3}\text{eV}$), where the variational 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 quasi-classical energy is $-4.56Z^{7/3}$eV, so that the total energy is $\simeq -16Z^{7/3}$eV, in agreement with the empirical binding energy. The number of electrons lying outside a sphere of radius R is given by

$$N_{out} = \int_{r>R} d\mathbf{r} \cdot n = Z(1 + qR)e^{-qR} \ , \tag{40}$$

where $n = (q^2/4\pi)\varphi$, and the ratio N_{out}/Z may be taken as an estimate for the fractional occupancy, in virtue of the fact that the latter represents the content of plane waves in the molecular-like (atomic-like) orbitals. For typical $R = 1$ values and a mean screening wavevector $q = (0.77 + 0.9)Z^{1/3}/2 = 0.84Z^{1/3}$ one obtains

$$z^* = z(1 + 0.84Z^{1/3})e^{-0.84Z^{1/3}} \ ; \tag{41}$$

$z^* = 0.57$, for instance, for iron Fe $(Z = 26, z = 2)$. Two electrons out of the six d-electrons of the isolated Fe atom pair up according to Hund's rule to give a $4\mu_B$-magnetic momentum, where μ_B is Bohr's magneton; in atomic aggregates 0.57 electrons participate in the chemical bond, and the remaining 0.43 pair up, leading to $4.57\mu_B$ a magnetic momentum.

It is worth nothing that there is a natural limitation for the convergence of the iterative self-consistency scheme of computation, brought about by the single-electron picture. Indeed, the quantal corrections bring a contribution $\delta\varepsilon \sim \delta\varphi$, to the first order, and contribute $\sim (\delta\varphi)^2$ to the next-order; the latter, however, is comparable with the lifetime effects, according to (38). According to the estimations given before this implies a limitation as large as $0.17 \cdot 17\% = 3\%$.

Another final remark may be made upon the so-called virial theorem, which is satisfied by the average kinetic and potential energies, within a complete scheme of computation procedure.

In conclusion, one might note that the atomic aggregation proceeds by quantal delocalization, Fermi statistics, and Coulomb potential, as the essential, basic ingredients of the theory presented above.

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