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Study of the Interactions in Fermionic Systems

- Metallic Clusters -

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PhD Thesis
(Summary)

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Magurele-Bucharest
2004

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KEY-WORDS: nanoscience, nanostructures, atomic clusters, metallic clusters, homo-atomic clusters, quasi-classical description, Thomas-Fermi model, Hartree-Fock equations, inter-atomic potentials, multi-particles interactions, binding energy, abundance spectra, magic numbers, ionization potential, surfaces, clusters deposited on surfaces, interfaces.

SUMMARY

1. Introduction. The main result of this investigation consists in obtaining the cohesion of the atomic clusters, either free or deposited on solid substrates. The cohesion of metallic structures is a direct consequence of the partial delocalization of the valence electrons and their screened Coulomb interaction with the ionic cores. It is shown that the quasi-classical description of these delocalized charges allows the determination of the self-consistent potential of the electrons. This potential is a superposition of screened Coulomb potentials, and exhibits a weak spatial dependence in the inter-ionic regions, where the electrons move almost (quasi-) freely. By estimating all the energy contributions, *viz* the kinetic energy, electron-electron interaction, electron-ion interaction and ion-ion interaction, the quasi-classical energy functional is determined. It exhibits a dependence on the atomic poositions and a variational parameter related to the mean electron density. By such an estimation, the effective inter-atomic potentials acting in these nanostructures are determined. They are highly repulsive at small distance, weakly attractive at long distance, and exhibit a negative minimal value in the region of the inter-atomic distances where the metallic binding occurs. The expression of these inter-atomic potentials is

$$\Phi(\mathbf{R}_i-\mathbf{R}_J)=-\frac{1}{2}qz_i^*z_j^*\left(1-\frac{2}{q\left|\mathbf{R}_i-\mathbf{R}_J\right|}\right)e^{-q\left|\mathbf{R}_i-\mathbf{R}_J\right|}\quad ,$$

where $\mathbf{R}_i$ and $\mathbf{R}_j$ are the positions of the atoms i and, respectively, j , $z_i^*$and $z_j^*$are the effective valence charges of these atoms, and q is the screening wavevector determined from the minimization of the quasi-classical energy of the ensemble of N atoms.

The quasi-classical energy functional is derived within the approximation of the point-like ionic cores, each ion having an effective valence charge. In principle, these valence effective charges are input parameters for the present method. For getting numerical values for the binding energies and inter-atomic distances the effective valence charges are estimated by making use of the theory of the atomic screening. For this reason, the numerical results are only valid for heavy atoms, *i.e.* atoms with large atomic numbers Z . In addition, because of the quasi-classical description, the results are affected by errors for clusters consisting of small number of atoms.

2. Atomic binding energy. For consistency, the quasi-classical decription is applied to the atomic cohesion of the heavy atoms, so that their empirical binding energy is reproduced highly satisfactorily, in a more direct manner than the usual procedure which involves successive corrections to the Thomas-Fermi result. In addition, effective charges are produced by the present quasi-classical description for these atoms.

3. Cohesion of the atomic clusters. The method is applied to the homo-atomic metallic clusters consisting of up to 160 Fe, Ba or Na atoms. The approximation of the point-like ionic cores simplifies considerably the computations. The first step in applying the method is the minimization of the potential energy, $\sum_{i<j}\Phi(\mathbf{R}_i - \mathbf{R}_J)$, with respect to the reduced ionic positions $\mathbf{x}_i = q\mathbf{R}_i$. Since for homo-atomic clusters the energy dependence on $\mathbf{x}_i$ implies the atomic nature only through a multiplicative factor z^{*2}, the geometric forms obtained by this minimization are general, the effect of the atomic species being present only in the inter-atomic distances, binding energies and vibration spectra. This universality is a consequence of the point-like approximation for the ionic cores, so it must be viewed as a prediction only for those atoms classes where this approximation holds.

Minimization of the potential energy is performed by the gradient method. Originally, the atoms are distributed randomly in a volume, close in magnitude to the expected cluster volume. The optimization of this volume is reached by repeated runs of the minimization computing program, or directly from the inter-atomic potential Φ. One can see that Φ reaches its minimum value for $x_0 \simeq 2.73$, so one expects the equilibrium inter-atomic distances to be close to this value. Therefore, the original volume wherein the atoms are distributed randomly is of the order of Nx_0^3. For the random positions of the atoms one computes the force acting on each atom, and, iteratively, displaces the atoms along these forces, by steps sufficiently small as to get a decrease of the potential energy every step, untill equilibrium is reached (in the present numerical computations all forces are smaller than $10^{-4}\mathrm{eV/\AA}$ at equilibrium). The equilibrium positions determined this way may correspond to the ground state or to isomers, *i.e.* to clusters with the same number N of atoms, but having different shapes and higher energies. In order to differentiate the ground state from isomers, the minimization program is run a few hundreds times for each atomic aggregate (for each number N of atoms), in order to get as close as possible to a statistical ensemble as large as possible. In addition, in order to distinguish the local minima from the saddle points the vibration spectrum is computed within the harmonic-oscillator approximation. Finally, the quasi-classical energy E_q is computed, it is thereafter minimized, the screening wavevector thus determined, and the exchange energy E_{ex} added. The later is computed by using the equilibrium value of the screening wavevector q. Finally, the total equilibrium energy E is thereby obtained. The lowest value of the energy is associated to the ground-state energy, while higher energy values are attributed to isomers. The binding energy determined this way exhibits small irregularities with respect to the atomic size N, which explains the higher stability of some clusters in comparison with their neighbours in size (clusters with one more or one less atom). In order to get such variations the so-called abundance, or mass, spectrum is computed, given by $D = E(N+1) + E(N-1) - 2E(N)$, where $E(N)$ is the ground-state energy of a cluster consisting of N atoms. On such abundance spectra magic numbers (local maxima) are identified, some obtained previously, both experimentally and theoretically, the latter by using model inter-atomic potentials. Having obtained the equilibrium reduced atomic coordinates $\mathbf{x}_i$ by minimizing the potential energy, and the screening wavevector q by minimizing the quasi-classical energy, the equlibrium inter-atomic distances $R_{ij} = x_{ij}/q$ are obtained; on the average, their values are of the order of $2-3\mathrm{\AA}$.

Usually, the clusters ground-state structures possess a higher symmetry in comparison with their isomers. It is worth noting that the homo-atomic clusters structures agree satisfactorily with structures obtained by other methods, like the density-functional method. A high peak in abundance spectrum indicates a highly symmetric ground state and a higher isomers energy (there is usually a gap in the energy distribution of the isomers in this case, with respect to the ground state). For instance, the most abundant clusters are those with an icosahedral symmetry, they consisting of superposed atomic shells, with the upper-shell atoms placed in the lower-shell faces centres. In addition, special situations are investigated, like one- and two-dimensional clusters, interaction of two clusters, or clusters of a very large size (up to 1000 atoms).

The binding energies of the ground states obtained by the present method are in good agreement with those obtained by other methods, where results are availbale, as, for instance, density-functional computations for Fe cluster (iron, $Z = 26$, $z = 2$, $z^* = 0.57$) with $N = 13$ ($E(N)/N \simeq -5.2$eV); similarly, the inter-atomic distances, of the order of 2Å are close in value to those reported in other works. Similar results are obtained for other metallic clusters, for instance, the ground-state energy per atom for Na clusters (sodium, $Z = 11,\ z = 1,\ z^* = 0.44$) is, on the average, $E(N)/N \simeq -3$eV, and, similarly, $E(N)/N \simeq -2$eV for Ba clusters (barium, $Z = 56,\ z = 2,\ z^* = 0.34$). These numerical estimates are in good qualitative agreement with other numerical results obtained within different theoretical models. In this respect, it is worth noting the immense amount of work in atomic clusters, making use of *ab-initio* wavefunction method, molecular dynamics, density functional or jellium models. The present method offers the advantage of obtaining qualitative and quantitative results by using relatively low computational resources; in addition, it offers an adequate starting point for getting more refined results. One may also note here that the structures, magic numbers and binding energies, as obtained recently by using a theoretical method based on an embedded-atom potential for Pd (palladium) clusters of up to $N = 20$ atoms are very close to the values obtained by the present method ($z^*_{Pd} = 0.40$, cohesion energy per atom $\simeq -2.5$eV for $N = 20$).

4. One-particle properties. Taking into account the slow varying part only of the self-consistent potential within this approach, the Clemenger-Nilson potential is derived, a potential which is usually relevant for the electronic properties of the atomic clusters. The one-particle picture of the Hartre-Fock quasi-particles is thereby obtained. The main contribution to the ionization potential of the atomic clusters consisting of a large number of atoms is also derived.

5. The cluster $Fe_{13}(C_2H_2)_6$. The method is extended to metallic clusters which contain a small number of non-metallic inclusions, covalent or ionic inclusions. This way, the study of the cluster $Fe_{13}(C_2H_2)_6$, recently synthesized experimentally, is made possible. Possible structures are obtained, inter-atomic distances, vibration spectra and the metallic contribution to the binding energy, the results being in a satisfactory agreement with the experimental ones. A special point here is the distinction between the ground state and an isomeric state, very close in energy.

6. Effective potentials in nanostructures. Another result is the general form of the effective inter-atomic potentials obtained for a non-point-like charge distribution of the ionic cores. Such results represent a first step toward studying the directional chemical bonds, a situation where the spatial distribution of the ionic-core charges plays an important part, the point-like approximation not holding anymore. For this general case the multi-particle character is highlighted for the general interaction in nanostructures, and the particular way these interactions are included within the present method.

7. Metallic clusters deposited on surfaces. Another application of the method is the study of the solid surfaces and clusters deposited on solid surfaces. Within the continuum approximation for the solid substrate the potential of a semi-infinite solid is obtained, as well as the description of the surface-charge double layer. This potential, corresponding to a free surface, is in perfect agreement with the experimental data related to the work function of solids. The interaction potential of atoms and solid surfaces is also derived within the present method, leading to the investigation of the cohesion of metallic clusters deposited on solid substrates. Similarly as for free clusters, geometric forms, inter-atomic distances, binding energies, abundance spectra and geometric magic numbers are derived for ground states and isomers of metallic clusters deposited on surfaces. Typically, there is a competition between the two, horizontal and vertical, growth directions for these clusters. For small clusters the ground states structures are two-dimensional, consisting of one layer deposited along the solid substrate, while for larger clusters the growth proceeds along the two directions, giving rise to multi-layer structures. Mono-layer structures for large clusters only exist as isomers. An interesting result is getting structures with part of their atoms underneath the surface, inside the solid substrate, suggesting incipient forms of interfaces and contacts. These structures may also be viewed as incipient quantum dots, of a very small size. All these results are encouraging for employing the present theory and method to more complex situations, particularly for nanostructured interfaces, or nano-aggregates displaying other dynamical or geometrical particularities.

8. Conclusions. At this stage of development, the present theory and method may find various relevant applications, for instance, to hetero-atomic clusters, *i.e.* clusters consisting of several atomic species, with various dynamic or geometric constraints. Such an instance is provided by clusters under the action of an external force. The jumps in mechanical tension, observed experimentally in this case along nanostructured wires, is explained within the present theory.

In addition, there are a few directions the present theory and method can be extended to. For instance, one expects that giving up the ionic-cores point-like approximation gives more refined results regarding the inter-atomic distances and binding energies. On the other side, taking into account the charge-density variations on small distances (of the order of Bohr radius) cannot be done without estimating the quantum corrections brought about by the abrupt variations of the self-consistent potential within such regions. A more realistic picture is thereby obtained for the quasiparticles properties.

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