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Research Project on Chemical Bond and Matter Aggregation

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1 The State of Research in the Field

Quantal Mechanics and the entire modern physics were born out from the attempt to understand the behaviour of the atoms. Since the very beginning the chemical bond and the way the atoms bind together were central points, and the quantal physics would have been evolved into a quantal theory of chemistry, had the course been another; in fact, it is actually a quantal theory of the structure of matter.

Atoms consist of electrons and atomic nuclei, and they bind together by the Coulomb forces acting between these constituents (relativistic effects may be left aside). But the classical atoms are unstable, and the electrons need to be quantally delocalized and individually distributed among the quantal states, according to the Pauli exclusion principle and the Fermi statistics, in order to get consistent atoms and matter. The quantal theory of the electrons moving in the attractive Coulomb field of the atomic nuclei and interacting with one another by repulsive Coulomb forces has been a matter of permanent investigation; the perseverance in this direction led, among others, to what is commonly known as the theory of the many-body physics.

The first attempt to describe the chemical bond is due to Heitler and London¹ who introduced what later becomes the superposition of atomic orbitals. According to this theory the binding electrons assume quantal states which are linear combinations of atomic orbitals. The hydrogen molecule was thereby described as having a binding energy $E = 3.14\text{eV}$ and an inter-nuclei separation $d = 0.87\text{\AA}$ in qualitative agreement with the experimental $E = 4.75\text{eV}$ and $d = 0.74\text{\AA}$. The theory has been developed along such lines after the War, and culminated recently with half of a Nobel prize in Chemistry awarded to J. A. Pople in 1998.² The investigations carried on currently within the framework of this theory are able to describe the chemical bond of a reasonable number of atoms, of the order of ten, by a large amount of numerical calculations (the theory was in fact pushed on to a further impetus by the modern computers). Various sets of atomic-like orbitals are used as basis functions, a reason for which the theory is also called the wavefunctions method.

¹W. Heitler and F. London, *Z. Phys.* **44** 455 (1927)

²J. A. Pople, *Revs. Mod. Phys.* **71** 1267 (1999)

Almost at the same time with Heitler and London's theory the attention has been drawn to the molecular-like orbitals, beside the atomic-like ones, by Mullikan.³ According to this theory the binding electrons occupy also quantal states which are specific to the extended chemical bond, which are bond-like orbitals, as distinct from the atomic-like orbitals. Indeed, as long as the electrons are close to the atoms they may occupy atomic-like orbitals, but over the rather large inter-atomic distances (a few angstroms as compared with the atomic-like distances of cca half an angstrom) they are described by a different set of quantal states, namely by bond-like orbitals. The molecular-like orbitals are touched upon by the density-functionals methods, for which the second half of the 1998 Nobel prize for Chemistry has been awarded to W. Kohn.⁴ The density-functionals methods are developed in this context in connection with the Thomas-Fermi model of the quasi-classical limit, and, unfortunately, the latter predicts no chemical binding, as expected in the classical limit. Quantal-states computations are currently performed with various ansatzen for the density-functionals, and atomic aggregates are described thereby, of similar sizes as the ones obtained by means of the wavefunctions method (or a bit larger perhaps, by the aid of powerful computers).

Both methods (the wavefunctions method and density-functionals method) are based on the first principles, so that they may usually be called ab-initio methods. In addition, various other theoretical approaches have been developed for atomic aggregates like molecules, atomic clusters, solids,⁵ which are based on model-dependent parameters. The present project aims at developing an original method of treating the atomic aggregates, starting from the basic principles.

2 New and Original Research

New and original results have recently been obtained; they have been published in a series of scientific articles, mostly in J. Theor. Phys. 1999-2000, and in two books.⁶ These results may be listed as follows:

1. A clear-cut separation between the atomic-like orbitals and bond-like orbitals has been obtained in the Hartree-Fock energy functional, which provides the extent of the bond-like orbitals in the chemical bond, and the extent to which the latter is in fact realized; a fractional occupancy has thereby derived for the chemical-bond orbitals, which reflects the electron share between the atomic-like orbitals and the bond-like orbitals; a "strongly renormalized" and "strongly correlated" ensemble of electrons participating in the chemical bond has therefore been described, corresponding to the interaction between these electrons and the ionic cores.

2. "Effective" ionic cores of positive charges have been derived in this way, consisting of the electronic holes left behind in the atomic orbitals of the valence upper shells by the electrons participating in the chemical bond; the chemical-bond electrons move therefore in a background of such positively-charged ionic cores; the corresponding charge density is given by the atomic orbitals and a set of parameters which can, in principle, be obtained from the interplay between the atomic-like orbitals and the bond-like orbitals, according to the ab-initio theory listed at #1

³R. S. Mullikan, Phys. Rev. **32** 186 (1928)

⁴P. 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 (1999).

⁵For recent reviews see W. A. de Heer, Revs. Mod. Phys. **65** 611 (1993) and M. Brack, *ibid*, 611

⁶M. Apostol, *The Electron Liquid*, apoma, Magurele-Bucharest (2000); L. C. Cune and M. Apostol, *Metallic Binding*, apoma, Magurele-Bucharest (2000)

above; for practical reasons however these parameters may be taken as undetermined effective-charge input parameters.

3. It has been shown that the Hartree-Fock equations and energy functional for ensembles of many interacting electrons admit a quasi-classical description through a self-consistent field which varies slowly over characteristic scale-lengths; this applies both to atoms of high atomic numbers and to extended chemical bonds. The quasi-classical description requires the linearization of the Thomas-Fermi theory, leading thereby to a linear Thomas-Fermi model which binds the atoms (it was perhaps suggested for the first time by Schwinger⁷), while allowing for quantal effects of the self-consistent field as next-order corrections. The theory of a slightly inhomogeneous electron liquid has thereby been obtained, which is the basis of the theoretical treatments of various chemical bonds. The linearization of the Thomas-Fermi theory simplifies appreciably the amount of computations, opening prospects for practical approaches to large atomic aggregates.

4. The theory has been applied to atoms of high atomic numbers Z , reproducing in an excellent agreement the empirical binding energy ($\sim 16Z^{7/3}$ eV), as well as other minor corrections. The atomic screening theory has been applied in this context to get effective-charge parameters for point-like models of ionic cores, as those employed for metallic clusters.

5. Metallic clusters have been studied within the theory of the slightly inhomogeneous electron liquid, and binding energies, geometric forms, inter-ionic distances, vibration spectra, ionization potentials, electric polarizability and diamagnetic susceptibility, etc have been obtained, both for ground-states and for isomers. It has been shown that the metallic binding is realized by small values of effective charges, as corresponding to the valence upper atomic shells; the total energy derived within this theory is in fact the binding energy, as the atomic levels participating in the chemical bond have a vanishing energy within the quasi-classical description; the exchange energy contributes as an invariable quantity, this "rigidity" character being specific to the non-local (quasi-) plane waves of the single-electron states in the quasi-classical description; the quantal corrections turn out to amount to cca 17% of the quasi-classical results of the linearized Thomas-Fermi theory, involving inaccuracies over a short-scale length only. Effective inter-atomic (pseudo-) potentials have been derived within this theory, as based on Coulomb screened potentials, and magic forms have been obtained for the ground-states of the homo-atomic metallic clusters, corresponding to a high local stability (as revealed by the abundance spectra) and to a high symmetry; 13 magic numbers (6, 11, 13, 15, 19, 23, 26, 29, 34, 45, 53, 57, 61) have been obtained for cluster sizes up to 80 atoms, which are geometric magic numbers, i.e. magic numbers corresponding to the ground-states, and which do not depend on the chemical species; the corresponding magic forms may be considered as the kernels of the condensed matter, due to their high stability, symmetry and simplicity. Beside the geometric magic numbers, statistical magic numbers have been introduced, corresponding to thermal occupancy of statistical ensembles of atomic clusters (isomers including), and the relationship of both the geometric and the statistical magic numbers to the electronic magic numbers has been described; the electronic magic numbers correspond to complete filling up of various energy shells of the self-consistent potential. The quantal properties of the self-consistent potential have been employed in deriving the ionization potentials of the clusters, and various response functions like the electric polarizability and the diamagnetic susceptibility.

6. The theory has been extended to bulk metals, where the point-like approximation for the ionic cores is less appropriate for the crystalline symmetry, and its consequences for the classical theory of a normal Fermi liquid have been investigated for the slightly inhomogeneous electron

⁷J. Schwinger, Phys. Rev. **A24** 2353 (1981)

liquid. It has been shown that the electrons acquire a heavier effective mass, that the electronic specific heat is correspondingly renormalized, that the paramagnetic spin susceptibility is left unchanged, that the zero-sound does not exist, but, in turn, the plasmons are renormalized by the fractional occupancy; the quasi-classical quasiparticles have therefore introduced, and their lifetime computed; the electron-phonon interaction has been derived, its strength estimated, and its renormalizing properties in the long wavelength limit have been described; the sound velocity and compressibility have been obtained in good agreement with experimental data, and an entire picture of a quasi-universal metal has thereby been formulated, which resembles, and confirms practically, the picture of a Wigner metal; it may be viewed as consisting of a sort of renormalized ionic cores, or metallic quasi-atoms, involving both positive and negative charges in equilibrium, with a self-energy of their own, and slightly interacting with each other by effective potentials. One may say that the present theory of a slightly inhomogeneous electron liquid confirms and extends the Wigner theory of metals.⁸

3 Objectives

The project aims at further developing the theory of the slightly inhomogeneous electron liquid for various types of chemical bonds in large molecules, atomic clusters, solids and other atomic aggregates, both isolated or subjected to various physical and chemical contexts. Specifically, the following objectives may be formulated:

1. The description of heavy atoms by means of a superposition of screened Coulomb potentials, as suggested by the linearized Thomas-Fermi theory, with the aim of obtaining the atomic shells, the properties of the open atomic shells (magnetic properties included), the ionization potentials and the electron affinities, the lowest excited electronic states, the quasi-classical Rydberg states, the spectroscopic properties, the response to electric, magnetic, and optic fields, etc; in particular, the Table of the Chemical Elements is envisaged, with its shell-inversions, s, d, f-metallic-like elements and p-elements, alkali, earth-alkali, transition (or rare-earth, lanthanides and actinides) elements, halogens, s-p-amphibolic elements and noble gases; the full atomic characterization of oxygen, carbon, silicon, germanium, gallium, arsenic, aluminium; copper, silver and palladium is pursued.

2. One-dimensional and quasi-one-dimensional solids treated within the theory of the slightly inhomogeneous electron liquid, with due observance of the restricted transversal geometry; aiming at typical one-dimensional-like instabilities, like Peierls distortion, Frohlich charge- and spin-density waves, the role of the electron-phonon interaction.

3. A similar treatment for two-dimensional extended sheets of atomic aggregates, with particular attention to the relevancy of the results for the quantal Hall effect (both integer and fractional), and various other electronic properties.

4. Hetero-atomic metallic clusters and metallic clusters doped with various inclusions, like oxygen and magnetic inclusions, by using model charge densities for the dopant ionic cores; the saturation of the oxidization degree is pursued, as well as the oxide-metal phase segregation; the magnetic properties of the clusters as brought about by the magnetic inclusions are also envisaged, in particular the Kondo effect.

⁸E. Wigner and F. Seitz, *Phys. Rev.* **43** 804 (1934); **46** 509 (1934); E. Wigner, *Phys. Rev.* **46** 1002 (1934); *Trans. Faraday Soc.* **34** 678 (1938)

5. Building up clusters deposited on surfaces, at interfaces, under various geometric constraints, quantal dots, wells and gratings, the commensurability-incommensurability effects of the atomic substrates and environments.

6. Tensile force and breaking down of atomic chains.

7. Finite-size effects in clusters of various geometries and dimensionality, surface effects in the atomic and electronic behaviour.

8. Solid-liquid transition by cluster surface fluctuations.

9. Extension of the charge densities of the ionic cores to p-orbitals, and s-p-hybridization orbitals, including thereby the local directional character of such chemical bonds, with the specific aim of getting fullerenes and carbon nanotubes, for instance, as by-products; chemical binding for Si, Ge, Ga, As and H-, O-, C-bonds.

10. Band-energy computations for electrons in solids, by means of the self-consistent potential of the theory of the slightly inhomogeneous electron liquid.