Digest Journal of Nanomaterials and Biostructures Vol. 2, No. 2, June 2007, p. 252 - 255

BUILDING THE MATTER: MOLECULES AND CHEMICAL BOND

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The general principles of building up molecules and matter are briely outlined. A former version is in J. Theor. Phys. **43** 25 (1999).

(Received June 28, 2007; accepted June 30, 2007)

Keywords: Chemical bond, Molecules, Clusters

Atoms may bind together into molecules, atomic clusters, solids; and, more slightly, they may form real gases and condense into liquids, both classical and quantal; matter aggregates over a large scale, from “soft” matter, like liquid crystals and polymers, up to the nuclear “starr” matter. In binding up the atoms into atomic, or molecular, aggregates the main principles of the atomic theory remain valid: in particular, the non-relativist approximation, the self-consistent (“mean”) field and the single-particle states of the electrons, the quasi-classical description. In addition, the electrons motion is largely decoupled from the nuclei, or ions, motion, as a consequence of the great mass disproportion between these two entities; this is known as the adiabatic, or Born-Oppenheimer approximation [1].

The energies of the electron states, to which the Coulumb repulsion between the nuclei is added, are called molecular, or electron, terms, and they depend on the inter-nuclei separation; these terms may cross each other, for some shapes and sizes of the atomic aggregates, especially for a high symmetry, where the electrons states are degenerate; a strong coupling there exists in this case, however, between electrons and nuclei, and the aggregate changes, in general, its shape and size, such as to remove this degeneracy, and to reestablish the adiabatic behaviour; this is known as the Jahn-Teller effect [2]. Another strong coupling may also appear locally between electrons and ions, whose positions get polarized, by Coulumb forces, and distorted; the local ensemble of electron and its ions surrounding is called a polaron, [3] and it may have a mobility, slower or faster; otherwise, the adiabatic approximation holds. In classifying the electron terms the symmetries of the atomic aggregate are helpful, to a great extent, as, for instance, for the diatomic molecule, either homo- or heteronuclear [4].

There are two main methods for computing the electron terms [5], and thereby the binding energy and the equilibrium, of an atomic aggregate; these methods are in fact intimately related, and their general principle is the linear superposition of atomic orbitals (LCAO), spin included, of a sui-generis form; such a superposition is called a molecular orbital (MO). In the first treatment a set of atomic orbitals is assigned to each atom, usually with parameters which are determined variationally; these may be individual atomic orbitals, or linear combinations of them, in which case the orbitals, are said to be hybridized; then we have a number of electrons to distribute over these orbitals, form up the corresponding Slater determinants, and superpose them linearly; get the Schrodinger equation in the matriceal form between the determinants, and solve it for the spectrum of the electron single-particle states of the atomic aggregate; and finally, one may vary the solution with respect to the parameters; the method is fairly carried out through for the hydrogen molecule, and it is known, basically, as the Heitler-London method [6]; obviously, it is the Hartree-Fock method for single-particle wavefunctions whose form is pre-determined to a certain extent; the ground-state of the hydrogen molecule is obtained as a singlet state, *i.e.* with antiparallel spins and a symmetric spatial orbital for the two electrons.

In the second treatment one starts with molecular orbitals [7], usually with variational parameters, properly antisymmetrized, and solve the corresponding Hartee or Hartree-Fock equations for them; for this reason, the method, which is usually called the molecular orbitals method, is also referred to as the self-consistent ("mean") field method; as a matter of fact, various approximations are made in applying this method, most of them related to the self-consistency, though usually touching less upon the quasi-classical description. Binding up the atomic aggregates shows that a rather small number of electron charges are involved in the process, and usually the high-energy electron states of the atomic constituents; thus, the valence concept in the chemical bond gets meaning [8]. Moreover, the spatial distribution of the binding electrons charge varies from the localization on some ions, through an almost equal sharing in-between, up to a more or less uniform distribution in space; the chemical bonds are thus conventionally described as ionic, covalent or, respectively, metallic; the superposition of wavefunctions between spatially distinct structures, which is sometimes called the resonance- (or resonating) – valence bond, is the underlying concept in all these developments; it originates in Heisenberg's exchange integrals [9].

Studies in atomic, or molecular, aggregates led naturally to the dissociation phenomenon too [10], as well as to the nature of the inter-atomic, or inter-molecular, potentials [11]. Basically, the atoms repel each other at short distances due to the Coulumb repulsion between their nuclei, and attract each other at longer distances by the Coulumb attraction between electrons and nuclei; at very long distances they attract each other by van der Waals forces ($\sim -1/r^6$), as an average [12]; in between there exists a minimum value, or more, which are relevant for matter stability, in its various forms; slight inter-atomic forces act in real gases and liquids, while stronger interactions appear in clusters and solids.

Semi-empirical inter-atomic, or inter-molecular, potentials are usually employed for the cohesion of matter, like for solids, for instance; solids may bind up weakly by van der Waals forces, like molecular solids; or stronger by ionic, or covalent bonds; and in a more particular manner as metals; indeed, in contrast with the ionic or covalent bonds which ar more directional, simple, alkali metals develop a more or less uniform distribution of electrons charge, as for a jellium model [13], while in more complex compounds, involving transition elements for instance, the localized charges of the open atomic shells may come into play. For crystalline solids the molecular orbitals acquire a particular form, due to the translation symmetry, and they become "crystal" orbitals, or Bloch wavefunctions [14]; the crystal (quasi-) momentum labels them, while orthogonal quasi-atomic "crystal" orbital have also been devised [15]; in a " crystal" orbital an atomic orbital is periodically superposed with the same orbital placed at all the other atomic positions in a crystal, and the interaction between neighbouring atoms (usually the nearest-neighbours) splits that atomic orbital into an energy band of dense electron levels, each for the two spin orientations of the electron (this is known as the "tight-binding approxiamtion"); such an energy band, thereore, accommodates up to 2 electrons at most per unit cell in the crystal, according to the translation symmetry; each atomic orbital (or linear combination of atomic orbitals in the unit cell) generates such an energy band, and the bands are separated by energy gaps, reminiscent of the energy separation in the atomic states; usually, a few bands are constructed this way, corresponding to the "valence" states, including the lowest excited states, in the constituting atoms; the energy bands may intersect each other, such that the filling of the bands with electrons varies, it may be partial or total; the electrons in a filled band do not transport charge, while those in an open band do; thus, some solids are insulators, while others conduct the electric current, and there exists a great variety of crystalline solids classified as conductors, insulators, semiconductors, semimetals, etc.

This is, basically, the theory of the energy bands in crystalline solids, and the determination of the energy bands, and the starting atomic orbitals, is a matter of approximation; for instance, especially for metals, the Schrodinger equation is solved in a "cell" assigned to each structural unit (and called the Wigner-Seitz cell), and care is taken to satisfy the boundary conditions at the frontiers [16]. As metioned above, the electron energy structure of the complex compounds, involving transition elements, exhibits peculiarities in constructing the energy bands, due to the atomic orbitals of the open atomic shells; and a direct spatial picture of the electron states in the lattice may often be more convenient; such a picture is embodied, for instance, in the so-called Hubbard model, as well as in various other versions of this model [17]. Particularly interesting are such models with "localized" electrons for the magnetic properties of the solids, like ferromagnetism, or various other "electronic" transitions. Likewise, particularly interesting with respect to their crystalline and electronic structures are the low-dimensional solids, like the layered structures and the quasi-one-dimensional materials; charge- and spin-density waves developed in these low-dimensional solids, associated with structural transitions and peculiar electron excitations [18]. The electron energy bands hold in crystalline solids, while in amorphous solids (which are not at equilibrium, in principle) the electrons are localized, their energy levels are locally valid, and these levels may be quasi-statistical distributed; while the electrons may "hop" slowly from place to place [19]; solids, or various other atomic aggregates, with a broken translational symmetry, but with various other local symmetries, more or less extended, like quasi-crystals, or fractals, have their own particularities as regarding the electronic structure.

Apart from the ground-state, which implies the atomic and electronic structures, the great variety of phenomena in solids are associated with the great variety of excited states and elementary excitations, corresponding to various forms of motion of the various degrees of freedom [20]; first, for instance, there are the vibrations of the ions, called phonons, then the excitons, associated with electron-hole pairs across an energy gap, the electron quasi-particles and plasmons of the electron density oscillations, the magnouns of the magnetic momenta, etc.; such elementary excitations may transport charge, heat, energy or mass; and they interact with one another, according to their dynamics, leading to various other phenomena, like for instance, the superconductivity, as arising from electron-phonon coupling; or participate in various, structural, electronic, magnetic, etc., phase transitions; and they also respond to various external fields, like electric, magnetic, or electromagnetic fields; leading, for instance, to various electric, magnetic or optical properties, or to various phenomena of magnetic resonance, etc.; and solids may have defects, or imperfections, whose occurrence, dynamics and properties form a subject apart.

Most of the basic concepts of solids were adapted for molecules, and atomic aggregates, especially those concerning the electron structure; an exception is perhaps the rational spectrum of excitations, which is specific to the molecules; however, the "crystal" electron orbital is often employed for molecules of high symmetry, like the benzene molecule, for instance [2]; energy bands are obtained this way (with due care for the resonating carbon-hydrogen double valence), often within a nearest-neighbours approximation, and electron "conducting" (ring, aromatic) or "insulating" (open chains, aliphatic) forms of such molecules are obtained; such an application of the molecular orbitals is often called Huckel's method, or approximation; spin correlations may also be discussed in such a case, via Heisenberg's exchange integrals, for instance.

In general, a quasi-classical description is appropriate for large "pieces" of matter, like atomic, or molecular, aggregates, and even solids, made up of heavy atoms; both for their stability and equilibrium and for the lowest excited states of the electrons; for instance, the self-consistent field originating in every nuclei may be used fist to solve for the corresponding atomic orbitals in the quasi-classical description (quasi-plane waves, actually), by using the Bohr- Sommerfeld quantization rules; their superposition for a molecular orbital may thereafter be emplyed in the tight-binding approximation for getting the corresponding electron energy band; for identical atoms this is a Huckel- or Bloch-type computation in fact; fixing up the chemical potential by treating similarly the cation problem, also within the quasi-classical description, or by estimating the filling of the band through comparison with the quasi-classical approximation, may serve as a more accurate identification of the lowest energy electron states of the aggregate; as well as molecular orbitals may be devised within the quasi-classical description for a thorough electron motion over the whole metallic aggregate.

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