

COMPUTATIONAL INORGANIC CHEMISTRY

Carlo Mealli

Istituto di Chimica dei Composti Organometallici, ICCOM-CNR, Florence, Italy

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Summary

The principles of Molecular Mechanics (MM), Quantum Mechanics (QM) and their combination (QM/MM hybrids) are outlined with emphasis on their applications. In particular, the methods to obtain quantitative computational results and the interpretational tools are illustrated for transition metal compounds. The wavefunctions, derived from semiempirical, *ab-initio* or DFT methods contain in their phases significant chemical information and allow establishing bonding/antibonding relations between atoms. Methods based on the measurable electron density and known as Quantum Theory of Atoms in Molecules (QTAIM) do not contain this information but are useful to detect and quantify the strength of chemical bonds. Rather than focusing on the mathematical aspects, the chapter outlines general strategies for planning a computational project in chemistry. Techniques are illustrated for locating stationary points (minima and saddle points or transition states) on the potential energy surface (PES). The latter permits the study of molecular interconversions (isomerism, fluxionality phenomena, etc.) and chemical reactions. Following the optimization of a model, important physical-chemical properties can be computed, such as charge distributions, bond orders, spectroscopic behavior (IR, NMR and other spectroscopic techniques), implications for the electrochemistry, magnetism, non-linear optics, and more.

Much attention is devoted to the qualitative aspects of the MO architectures and their symmetry properties. The tools of perturbation theory are illustrated to analyze molecules in terms of fragment orbitals (FMOs) and to derive powerful concepts such as those based on electron counting rules and *isolobal analogy*. The latter are useful guidelines for the analysis of high level computations and help tracing back the electronic origin of chemical phenomena also in the case of complex inorganic compounds. Finally, the computational approaches to extended systems (solids and surfaces), Molecular Dynamics, and other modern techniques are also illustrated.

1. General Considerations

The growth of computational chemistry has been accompanied by a plethora of manuals, books and other publications illustrating principles, methods and applications. The textbooks, recommended in the bibliography, illustrate mathematical details and technical aspects. This presentation is aimed to outline a general philosophy for tackling problems of theoretical inorganic chemistry. A key idea is that the numbers generated by the calculations cannot be accepted without criticism but translated in chemical facts in order to receive validation and make useful predictions.

The virtuous combination of methodology and computer technology has given rise to the modern *Computational Chemistry*, whose definition is not completely unambiguous. Often, a computational chemist is considered a specialist in computer-related tasks, such as writing algorithms or presenting numerical results in a graphic form. However, he must have deep knowledge of both the experimental and theoretical facts in order to provide new significant contributions to chemistry.

Molecular modeling has become an essential laboratory instrument. For instance, the structure of newly synthesized molecules can be *ab-initio* determined for a comparison with the experimental data (*e.g.*, X-ray crystallography, NMR spectroscopy or other techniques). Moreover, experimentally undetectable species, which are formed during a chemical reaction (*e.g.*, metastable intermediates or transition states), can be computationally characterized with the same degree of reliability as those in the ground state.

Computational tools should be equally applicable to different areas of chemistry. In fact, the atomic elements form small or large (macro) molecules, polymers, solid state compounds, etc. by following the same fundamental laws of physics, so that a general theory should be able to explain the formation of all bonds and other type of interatomic interactions in different contexts. In practice, some difficulties are still encountered with heavier elements and transition metals, due to their complex electronic structure and the variable electron occupation of the d orbitals. Thus, computational inorganic chemistry, at variance with the organic counterpart, contains a larger degree of approximation and specific actions must be often taken to overcome these problems.

1.1. The Fundamental Relation between Structure and Energy

The first goal of any theoretical calculation is to determine the optimal molecular structure associated with minimum energy. From this combined information most of the chemical and physical properties can be derived.

As a matter of fact, any structural variation affects energy so that, given a chemical formula with N atoms (*i.e.*, $3N$ spatial coordinates), an hypersurface of the potential energy (**PES**) with dimension $3N-6$ can be constructed (the deduction of six variables is due to the $3+3$ global translations and rotations about the main x,y,z axes). Although there are computational algorithms to construct such a hypersurface, a full graphic representation is impossible. Only particular sections can be visualized, which at most depend on two geometric parameters, usually selected for their chemical significance (see Figure 1). Normally, these are interatomic distances, bond or torsion angles, *i.e.* internal coordinates, which are definitely more intuitive to chemists than other type of coordinates such as, for instance, the Cartesian ones (see Section 3.1.).

The minima on the PES correspond to stable structures, while the saddle points (characterized by a downward curvature for a single direction and upward curvature for all the other directions) represent the transition states (TS). These also define the lowest energy barrier connecting two minima, which correspond to different isomers if the system under investigation is unimolecular. Thus, the PES defines isomerization pathways. Otherwise, if the system undergoes molecular association or dissociation, the PES permits charting reaction mechanisms in which reactants, intermediates and products are involved. In this case, the coordinates, plotted *vs.* the energy, are actual reaction coordinates. It will be shown that for a correct identification of the stationary points on the PES, it is necessary to examine the vibrational properties (see Section 3.3.).

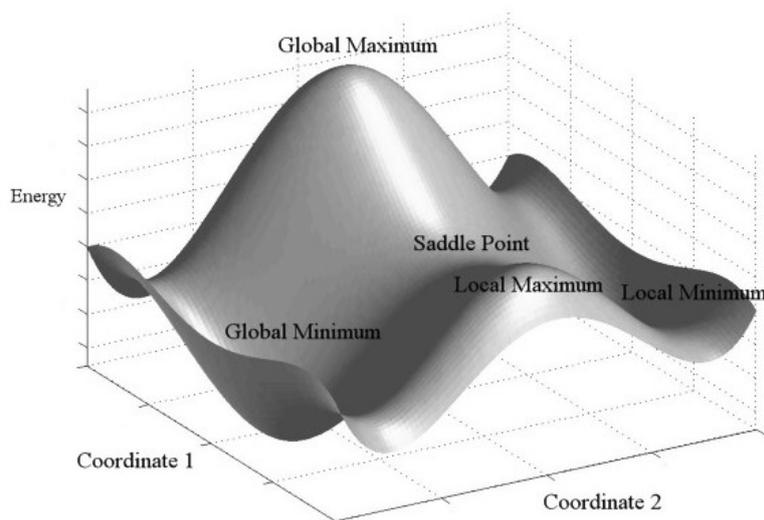


Figure 1. An example of Potential Energy Surface (PES).

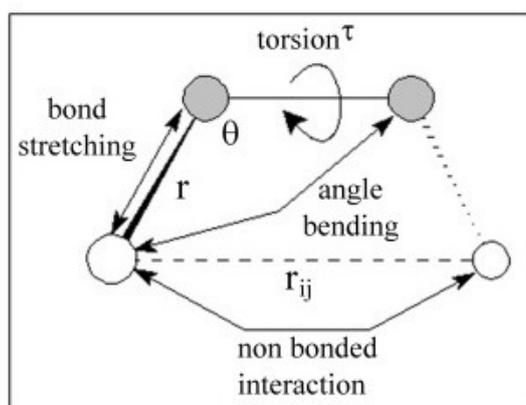
In general, the PES establishes a direct correlation between structures and energies. Additional calculations of various chemical-physical properties at the stationary points can provide an overall picture of the *Structure-Properties Relationship*, which is of fundamental importance in chemistry.

2. Basic Computational Tools

The basic methods of computational chemistry are either based on classical mechanics, (the molecules seen as series of atoms held together by bonds similar to springs, hence the definition of Molecular Mechanics, **MM**), Quantum Mechanics (**QM**) or a mixture of the two (**QM/MM**).

2.1. The Molecular Mechanics Approach

The MM method allows optimizing the molecular geometry by minimizing the steric energy, hence determining the best conformation(s). The great advantage is the capability of dealing also with big molecules in relatively short computing times. The method requires the definition of a Force Field (**FF**), which does not involve any knowledge of the wavefunctions or the distribution of the electrons. In fact, the total energy of the system is given by the sum of different contributions, the first three of which, called valence terms, are relative to bond stretching, angle bending and bond torsion, respectively. Additional terms are relative to non-bonding interactions of both the van der Waals and electrostatic types. These aspects are sketched in Figure 2 together with an analytical formula for the energy. Accordingly, several parameters need to be introduced relative to the force constants and the equilibrium geometry.



$$E = \sum_{\text{bonds}} k_b (r - r_{eq})^2 + \sum_{\text{angles}} k_\theta (\theta - \theta_{eq})^2 + \sum_{\text{torsions}} V [1 + \cos(n\tau - \phi)] + \sum_i \sum_j \frac{-A_{ij}}{r_{ij}^6} + \frac{B_{ij}}{r_{ij}^{12}} + \sum_i \sum_j \frac{q_i q_j}{r_{ij}}$$

Figure 2. A sketch of the various contributions to the MM energy and a typical analytic expression of the Force Field used to calculate the energy.

For instance, the first two valence terms require the definition of the constants k_b and k_θ , which control the stiffness of the bond and angle springs. Additionally, the equilibrium distance and angle (r_{eq} and θ_{eq}) are determined from the available experimental data for a certain class of compounds. The torsional energy is evaluated as a simple periodic function in which the parameters V , n and ϕ control amplitude, periodicity and phase of the entire curve, respectively. In the van der Waals interaction term, the non-bonded interactions are expressed by a Lennard-Jones potential, the parameters A_{ij} and B_{ij} being relative to stickiness of the attraction between the atoms i

and j (separated by the r_{ij} distance) and their relative hardness, respectively. The potential includes an attractive contribution due to the dispersion ($\propto 1/r_{ij}^6$) and a repulsive one due to the exchange repulsion ($\propto 1/r_{ij}^{12}$). Finally, the electrostatic term is modeled by using a Coulombic potential. This depends on the atomic charges q_i , which are commonly derived from QM calculations not being measurable quantities

The FF's may differ for the energy expression and the derivation of the constants, which are strictly dependent on the nature of the atoms. Thus, a given set of parameters cannot be adopted to study different chemical species. For instance, the parameters for sp^3 and sp^2 carbon atoms are different and not interchangeable.

The energies derived from MM calculations are meaningful only to compare different conformations for similar classes of molecules. With appropriate energy minimization algorithms, which evaluate the gradient of the energy (first derivative) with respect to the atomic coordinates, the optimal molecular conformations are found on the PES (see Figure 1). The same procedure also applies to the QM approach (see 2.2.), but with a conceptual distinction. In fact, QM is based on the Born-Oppenheimer approximation for which the electrons move much faster than the nuclei so that the motion of the latter is neglected. Conversely, in the MM method the nuclear positions change with respect to an electron distribution of reference. Thus systems, where bond making/bond breaking effects occur (especially in correspondence of transition states), are not adequately treated by the MM techniques.

2.1.1. Applications of the MM Method and Problems with Transition Metal Complexes

The MM method provides a relatively good evaluation of the enthalpies of formation of the molecule from the single atoms and also the normal modes of vibration can be calculated.

Most FF's have been developed to deal with organic molecules. In this area, the great advantage of the MM approach is the capability of modeling enormous molecules such as proteins and segments of the DNA within a reasonable amount of time. The most popular FF's are the MM2 and MM3, GROMOS, AMBER and CHARMM (for biological molecules), OPLS (for liquids), etc.

Concerning transition metal complexes, a major force is associated with the binding of the metal to the ligands. Thus, the best molecular conformation does not depend only on the non-bonding interactions between the organic parts of the molecules but is largely imposed by the bonding capabilities of the metal center. These may greatly differ even for the same metal atom depending on its size, electron population and surrounding environment, so that the generation of standard and transferable parameters is very difficult to make. Nonetheless, there have been important applications of the MM methodology to metal complexes. In particular, the work of Peter Comba and Angelo Sironi (for metal carbonyl compounds) needs special mention. Another complication

concerns organometallic species, where the bonding to the metal occurs through the π system of the ligand (*e.g.*, cyclopentadienyl complexes).

Specific FF's to deal with inorganic elements are SHAPES, VALBOND and MOMECC. In the latter, the metal-ligand interactions consist of a bond stretch term only. The coordination sphere is maintained by non-bonded interactions between ligands.

2.2 Foundations of the Quantum Mechanical Approach

The QM methods are based on the development of wavefunctions which appear in the Schrödinger equation: $\hat{H}\Psi = E\Psi$. In the latter, \hat{H} is the Hamiltonian operator, Ψ is the total wavefunction, which depends on the position of all nuclei and electrons, and E is the system's energy. The exact solution of the equation is possible only for one electron systems, while a myriad collection of methods has been developed for approximating the solution for multiple electron systems. The main approximations are the time independency of the wavefunctions and the Born-Oppenheimer (**BO**) separation of the nuclear and electronic motions. Computationally, the latter is very advantageous because it allows treating only the electrons, which adapt instantaneously (adiabatically) to the positions or field of the nuclei.

2.2.1 The Hartree-Fock Method

In the BO approximation, the typical Hamiltonian \hat{H} consists of three terms: one for the kinetic energy of the electrons, one for the attraction between the nuclei and the electrons and the third for the repulsion between electrons (consult classic textbooks for the analytic expressions of all the terms). It is worth mentioning that in approximated approaches, such as the Extended Hückel (**EHMO**) or other semiempirical methods (*e.g.* **CNDO**, **MNDO**, **AM1**, **PM3**, **Fenske-Hall**), some of the terms are either neglected or parameterized from the experimental data. In contrast, the *ab-initio* methods only use the fundamental constants of the universe such as the speed of light, the masses and charges of the nuclei and electrons, the Planck's constant. Today, the semiempirical methods are much less adopted because the efficiency of modern computers no longer provides an economical justification of their usage with respect to the *ab-initio* and the DFT approaches. However, the **EHMO** method maintains some interest, especially in the approach to transition metal compounds, for providing a quick overview of the qualitative MO architecture, including the often decisive effect of the symmetry on chemical bonding (see Section 6).

The solution of the QM equation in terms of eigenfunction (Ψ) and the eigenvalue (E) allows to derive additional properties of the individual molecule. This is done by taking the expectation value of the operator for the required property (denoted with angled brackets $\langle \rangle$). For example, the operator can be that of the molecular dipole moment or the energy itself. In the latter case, the expectation value is given by the expression:

$$\langle E \rangle = \int \Psi^* \hat{H} \Psi d\mathbf{v}.$$

Normally, a wavefunction is expressed as a linear combination of atomic orbitals ($\Psi = \sum_i c_i \varphi_i$ (please change Ψ in ψ_j) in the LCAO approach). If the wavefunction is approximate, also the energy is approximate and is always higher than the actual energy of the system. This is the foundation of the *variational principle*, which allows minimizing the energy through the variation of the c_i (italics not bold) coefficients. For a closed-shell system (*i.e.*, the one where a set of low energy MOs are well separated and doubly occupied), the minimization of the coefficients is normally done by operating on the elements of the so called one-electron density matrix: $\mathbf{P}_{rs} = 2 \sum_i c_{ri} c_{si}$. In the latter, the summation is over the doubly occupied MOs only. The procedure implies the definition and solution of the *secular determinant*: $|\mathbf{H}_{ij} - \mathbf{eS}_{ij}| = 0$, where $\mathbf{S}_{ij} = \int \varphi_i \varphi_j \mathbf{d}\mathbf{v}$ (overlap integral between two atomic orbitals) and $\mathbf{H}_{ij} = \int \varphi_i \hat{\mathbf{H}} \varphi_j \mathbf{d}\mathbf{v}$ (phisubi and phisubj use math font italics not bold) (Coulomb integral). The procedure is iterative and applies to QM calculations at the various levels of approximation. In practice, the wavefunction (Ψ), which define the ground state (GS) of the system, is systematically improved by judging their quality from its associated energy E_0 : the lower, the better.

2.2.2 Basis Sets

One way to improve the overall quality of the results is to choose mathematical expressions for the φ_i functions which best shape the space in which a given electron is allowed to move, *i.e.* the choice of the *basis set*. This is generally done by using a combination of Gaussian functions (primitives). The larger is the number of primitives and the more articulated is their convolution, the better is the basis set. This requires significant work of optimization of the coefficients with which the primitives sum up together. Such a procedure is called *contraction*. The most popular QM packages offer the possibility of using predefined basis sets. A single example of the latter (with symbol 6-31++G*) provides information on the mathematical generation of the various atomic orbitals. Thus, the core orbitals are derived from a single contraction of six primitives and the valence shell orbitals from two contractions, one with three primitives and the other with one primitive. The symbols ++ indicate that diffusion functions are added to increase the flexibility of the orbital far from the nucleus. In this manner, one peripheral electron is less tight to the remaining electron density and can account for weak interactions such as the intermolecular ones. Finally, the sign * indicates the presence of polarization functions. These functions provide additional mathematical flexibility, which accounts for peculiar structural features. For instance, without the polarization function in the nitrogen basis set, the structure of ammonia would be optimized as trigonal planar. If we assume that the 2p orbitals, which are involved in N-H bonds, are polarized by additional d orbitals, as shown in Figure 3, the correct geometry is reproduced. Analogous flexibility is attained by polarizing hydrogen s orbitals with p orbitals, and transition metal di orbitals with f orbitals.

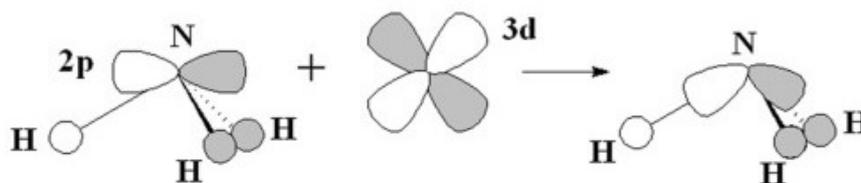


Figure 3. Polarization of the nitrogen 2p orbital induced by the higher 3d orbital as a stabilizing factor of the pyramidal geometry.

The basic *ab-initio* method is the Hartree-Fock method (**HF**), in which the inter-electronic interaction is computed in the central field approximation. This is done by integrating the Coulombic repulsion term and by estimating how each electron moves in the net field of all the others. The method allows breaking the many electron QM equation into many simpler one-electron equations and deriving single electron wavefunctions. For a given basis set, the procedure starts with an initial guess of the orbital coefficients c_i (usually from an EHMO calculation) necessary to evaluate energy and a new set of coefficients which are used to calculate a new set and so on. The procedure, which is called Self Consistent Field (**SCF**), converges when the energy and the coefficients are unchanged from one iteration to the next.

For closed shell systems (singlet ground state), the same orbital can be used for α and β spins. This is called a restricted HF method (**RHF**). For open shell systems, there are two possible approaches. The first is the use of completely separate sets of orbitals for the α and β spins (unrestricted HF method or **UHF**) although, in this manner, the paired electrons do not have the same spatial distribution. The disadvantage is that the wavefunctions are no longer eigenfunctions of the total spin operator S^2 . In general, the *spin contamination* error is insignificant for organic molecules but it can be important for transition metal compounds and can affect the geometry and other molecular properties. To avoid the problem, the electrons are forced to occupy pairwise the same orbitals (restricted open shell HF method, **ROHF**).

2.2.3 Methods of the Electron Correlation

Since single electron-electron interactions are not exhaustively treated by the HF method, the probability of finding an electron at some location is determined only by the distance to the nucleus and not the distance to the other electrons. This is not physically true and the quality of the structure as well as the molecular properties may be affected. As a matter of fact, the HF approach determines only single-determinant wavefunctions, whereas a better solution requires a multi-determinant approach. In fact, spin orbitals, which are empty (*virtual*) according to the single-determinant HF solution, can be temporarily populated by the electrons of the lower levels. Each new electron configuration corresponds to a different determinant and the corresponding wavefunctions mix into the basic HF wavefunctions with a weight to be determined. A full Configuration Interaction (**CI**) involves all the possible substitutions by which the occupied spin orbitals are replaced by the *virtual* ones. The procedure affords accurate results but it is hardly applicable even to small molecules.

More affordable electron correlation methods are based on the Møller-Plesset perturbation theory (namely, **MP_n** methods with n being the order at which the perturbation is truncated). Qualitatively, the MP approach adds higher excitation to the HF picture as a non-iterative correction (in the physical-mathematical area, the theory is known as multi-body perturbation theory).

The simplest, yet expensive, **MP2** method has been often adopted for accurate calculations of transition metal compounds, although for the first row elements it usually gives underestimated distances. Nowadays, the DFT approach is definitely preferred. Other methods for treating the correlations are the Multi Configurational Self Consistent Field (**MCSCF**), the Coupled Cluster Theory (**CC**), the Configuration Interaction Single, Double and Triple excitation (**CIS**, **CISD** and **CSDT**, respectively), the Complete Active Space SCF (**CASSCF**).

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Bibliography

Autschbach J. (2004). *The calculation of NMR Parameters in Transition Metal Complexes*, in Structure and Bonding, Vol. 112. [An overview presenting the computational approaches to nuclear shielding and spin-spin coupling constants of transition metal complexes].

Bader R. F. W. (1994). *Atoms in Molecules. A Quantum Theory*. Clarendon Press, Oxford. [The fundamental book illustrating the foundations of the AIM theory].

Bader R. F. W. (2003). *Int. J. Quantum Chem.* 94, 173. [The response of Bader to the criticism of Frenking (2003) to the AIM theory]

Baratta, W., Mealli, C., Herdtweck, E., Ienco, A., Mason, S. A., Rigo, P. (2004) *Journal of the American Chemical Society*, 126, 5549. [Author's article illustrating how to tackle a problem of fluxionality in solution with a DFT approach. Also, it contains an exhaustive analysis of the stereochemistry of the *agostic* interactions].

Bickelhaupt E. M. and Baerends E. J.(2000). In *Reviews in Computational Chemistry*, Vol. 15, 1. Lipkowitz, K.B. and Boyd D.B., Ed's. John Wiley & Sons, Inc. [A complete review of the Energy Partitioning method adopted in the ADF package].

Clark T. (1985). *A Handbook of Computational Chemistry*, John Wiley & Sons, New York. [A book which illustrate many practical aspects of computational chemistry]

Clark T. and Koch R. (1999) *The Chemist's Electronic Book of Orbitals*. Springer-Verlag Berlin Heidelberg. [A book with an accompanying CD, which introduces the reader into the basic qualitative molecular orbital theory also through interactively worked out examples].

Comba P. and Hambley T.W. (1995). *Molecular Modeling of Inorganic Compounds*, VCH Verlagsgesellschaft mbH, Weinheim. [An overview of the MM approach to explore conformations and coordination modes of transition metal complexes].

Cotton F.A. (1990). *Chemical Applications of Group Theory*, John Wiley & Sons, New York. [A fundamental book for understanding the principles of symmetry commonly applied in computational chemistry].

Cramer C.J. (2005) *Essentials of Computational Chemistry. Second Edition*, John Wiley & Sons, Chichester, UK. [The book carefully leads the reader thorough the theoretical background of computational chemistry]

Curreli, S., Deplano, P., Faulmann, C., Ienco, A., Mealli, C., Mercuri, M. L., Pilia, L., Pintus, G., Serpe, A., Trogu, E. F. (2004). *Inorganic Chemistry* 43, 5069. [Author's article reporting a test case study of second-order NLO properties in a series of metal complexes through a quantitative and qualitative MO approach].

Fabrizi de Biani, F., Ienco, A., Laschi, F., Leoni, P., Marchetti, F., Marchetti, L., Mealli, C., Zanello, P. (2005). *Journal of the American Chemical Society*, 127, 3076. [Author's article illustrating several structure/properties/reactivity relationships in a hexanuclear metal cluster. In particular, the theoretical methods help to understand the electrochemical behavior in solution].

Flemmig, B., Wolczanski P. T. and Hoffmann R. (2005). *Journal of the American Chemical Society*, 127, 1278. [An example of how computational chemistry can be exploited to make chemical prediction on yet unknown species such as ozone's coordination compounds].

Foresman J. B. and Frisch Æ (1996). *Exploring Chemistry with Electronic Structure Methods*. Gaussian Inc., Pittsburgh, USA. [A primer book in Quantum Chemistry providing many specific examples and exercises. Although aimed to exploit the usage of the Gaussian commercial package, the book has a wide utility].

Frenking G. (2003). *Angewandte Chemie, International Edition* 42, 143. [A critical review of the Gillespie-Popelier book of 2001, which addresses the relative powers of the MO and AIM methods].

Frenking G., Wichmann K., Fröhlich N., Grobe J., Golla W. Le Van D., Krebs B., Läge M. (2002). *Organometallics*, 21, 2921. [An illustrative paper for the quantitative evaluation of Bond Dissociation Energies in organometallic species through the energy partitioning method implemented in the ADF package].

Fueno T. Editor (1999). *The transition State*. Gordon and Breach Science Publisher, Amsterdam. [A collection of monographs on the best strategies for studying chemical reactions though the identification of transitions states].

Gillespie R. J. and Popelier, P. L. A. (2001) *Chemical Bonding and Molecular Geometry. From Lewis to Electron Densities*. Oxford University Press, New York. [Amongst other topics, the book contains a rather simple illustration of the AIM theory and its applications. The book has been subject to some criticism relative to potentiality of the AIM method vs. that of the MO theory (see Frenking, 2003)]

Hehre W.J., Radom L., Schleyer P.v.R. and Pople, J.A. (1986). *Ab Initio Molecular Orbital Theory*, John Wiley & Sons, New York. [A most classic textbook on the *Ab initio* methods].

Hoffmann R. (1982) *Building bridges between inorganic and organic chemistry: Nobel lecture. Angewandte Chemie, International Edition* 21, 711. [A classical paper which illustrates how basic MO concepts simplify the understanding of complicate transition metal species by establishing their links with organic molecules].

Hoffmann R. (1988) *Solids and Surfaces, A Chemist's View of Bonding in Extended Structures*. Wiley-VCH Inc. [An Illustration of the basic concepts for tackling the problem of the electronic structure in solid state compounds and chemisorption on surfaces]

Jensen F. (1999). *Introduction to Computational Chemistry*. John Wiley & Sons, Chichester, UK. [A comprehensive textbook on the principles of the most important computational methods].

Koch W. and Holthausen M. C. (2001). *A Chemist's Guide to Density Functional Theory*. Second Edition. Wiley-VCH Verlag GmbH [A presentation of the DFT basic principles and an exhaustive analysis of the successes and failures of the density functionals in use].

Lipkowitz, K.B. and Boyd D.B., Eds (1990-2003) *Reviews in Computational Chemistry*, John Wiley & Sons, Inc. [A most exhaustive collection of reviews, tutorials, advances, and information related to the wide field of Computational Chemistry. In particular, an appendix to Volume 17 (2001) contains a most complete compilation of all the books published on the subject of Computational Chemistry].

Macchi P., Sironi A. (2003) *Coordination Chemistry Reviews* 238-239, 383. [An extensive review article on the applications of the AIM theory to metal carbonyl complexes]

Mingos S. M. P. and Wales D. J. (1990). *Introduction to Cluster Chemistry*. Prentice-Hall International Editions. [A introduction to transition metal cluster chemistry with the illustration of the basic electron counting rules and their MO underpinnings]

Phillips, A. D., Ienco, A., Reinhold, J., Böttcher, H.-C., Mealli, C. (2006). *Chemistry an European Journal* xxx . [Author's article reporting the case study of metal-metal bond protonation, analyzed through an extended integration of MO and AIM methods]

Popelier P.L.A. (2000). *Atoms in Molecules. An Introduction*. Pearson Education, Harlow. [A primer for topological study of the electron density.]

Rogers D.W. (2003) *Computational Chemistry Using the PC*. John Wiley & Sons, Inc. [A comprehensive book with the description of the mathematical algorithms and many practical exercises to perform MM and QM calculations on a PC]

Rauk A. (2001). *Orbital Interaction Theory of Organic Chemistry*. John Wiley & Sons, Inc. [A book which describing the basic orbital interactions in organic chemistry with useful extensions to organometallics]

Ruiz, E., Cano, J., Alvarez S., Caneschi A., Gatteschi D. (2003). *Journal of the American Chemical Society*, 125, 6791. [An article illustrating how the modern DFT approach can successfully deal with complex problems of magnetism in polymetallic species].

Young D. (2001). *Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems*, John Wiley & Sons, New York. [An overview of the computational method in a conversational style].

Wells, A. F. (1984). *Structural Inorganic Chemistry*. Oxford University Press, Oxford. [A fundamental textbook for solid state chemistry].

Woodward R.B. and Hoffmann R. (1970) *The Conservation of Orbital Symmetry*, Verlag Chemie and Academic Press, Weinheim and New York. [This classic book describes the principles of how symmetry can control the mechanism of chemical reactions]

Zonnevylle M. C., Hoffmann, R., Mealli C., Bianchini C. (1987). *Gazzetta Chimica Italiana*, 117. [A worked example of band structure analysis for a monodimensional transition metal polymer]

Biographical Sketch

Carlo Mealli. Born in 1946, he received the Degree in Chemistry from the Università di Firenze in 1969, by mastering in X-ray crystallography. After postdoctoral work at the University of Washington (Seattle, USA) with Prof. E.C. Lingafelter, he joined the staff of the CNR Institute of Florence directed by Prof. L. Sacconi. Since then, he made his career in CNR and, in 1991, he reached the position of Research Director, which he presently holds in the "Istituto di Chimica dei Composti Organometallici" (ICCOM, Firenze). He has spent several periods, as a visiting scientist, in famous laboratories around the world, among which that of Prof. J.A. Ibers (1974, Northwestern University, USA) and that of the Nobel Laureate Prof. R. Hoffmann (1980, Cornell University, USA). His research interest is about the relations between the 3D structure and the chemical aspects (including reactivity) of transition metal compounds through computational analysis. He is the author of about 200 publications in the field of inorganic/organometallic chemistry.