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GLOSSARY OF TERMS USED IN THEORETICAL ORGANIC CHEMISTRY

(IUPAC Recommendations 1999)

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Glossary of terms used in theoretical organic chemistry (IUPAC Recommendations 1999)

Abstract: The glossary contains definitions and explanatory notes for more than 450 terms used in the context of multidisciplinary research and publications related to applications of modern theoretical concepts, computational and graph-theoretical methods to investigation into structure, reactivity, spectroscopic and other physical and physicochemical properties of organic, organometallic and metal coordination compounds. The aim of the glossary is to provide guidance on terminology used in theoretical organic chemistry and to contribute to the elimination of inconsistencies and ambiguities in the meanings of terms in the area.

GENERAL REMARKS

Recent years have seen a deep penetration of the language, concepts and methods of quantum chemistry, statistical mechanics and graph theory into the conceptual system of organic chemistry and cognate fields. The terminology of modern quantum chemistry interlaces with that of classical electronic and resonance theories, and the use of new technical terms, methodologies and acronyms proliferated. This process necessitates examination of the terms used in theoretical organic chemistry for meaning, utility and consistence. Although theoretical organic chemistry cannot be separated from theoretical chemistry itself, it constitutes a significant part of the latter representing the domain of physical organic chemistry associated with theoretical modeling of reaction mechanisms, computational studies of structural, thermodynamic, spectroscopic and other physical properties of organic compounds, and has grown tremendously. A need has, therefore, been recognized for providing an organic chemist, who uses in the research modern methodologies or is interested in their comprehension, with the relevant operational definitions or explanations of frequently employed notions and concepts. For this purpose, concise introductory descriptions and leading references (to original sources, important reviews or monographs) are given for a number of important terms.

The Glossary may be considered as a supplement to the comprehensive compendium [38] of terminology traditionally established in physical organic chemistry. Therefore, the styles of the presentation of the material in both Glossaries are basically similar. The general criteria adopted for inclusion of a term into the Glossary were: (a) its wide use in the literature; (b) uncertainty or ambiguity in its current use. There is almost no overlap in included terms between the two Glossaries. This Glossary is supplemented by a list of most frequently encountered (about 200) acronyms used in the literature on theoretical organic chemistry (appendix). This list is intentionally much shorter than that of the parallel project 'Acronyms used in Theoretical Chemistry' [*Pure Appl. Chem.* **68**(2), 387–456 (1996)] developed by the Physical Chemistry Division which includes a giant number (about 2500) of specific acronyms and abbreviations, e.g. those of numerous program packages, and covers areas of application far beyond those of primary interests of organic and physical organic chemists.

The Commission considers it necessary to emphasize that the primary objective of the Glossary is to serve as an update and consistent reference to terminology used in theoretical organic chemistry and cognate fields. There is no intention to impose any restrictions or rules on the use of the recommended terminology.

The Commission and the Working Party gratefully acknowledge important contributions of many scientists who helped by proposing or defining certain terms as well as providing useful criticisms and advice. The following names are to be mentioned: A. Dneprovskii, E. Eliel, E. Halevi, R. Hoffmann, A. Katritzky, A. Levin, I. Stankevich, R. Thummel, M. Yanez.

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ARRANGEMENT

The arrangement is alphabetical. Italicized words in the body of a definition, as well as those given at the end, point to relevant cross-references. No distinction is made between singular and plural in cross-referencing. Capitalized names indicate references which are either those where the term was originally defined or pertinent review articles or monographs where it is used.

FUNDAMENTAL PHYSICAL CONSTANTS USED IN THE GLOSSARY*

Atomic mass constant (unified atomic mass unit) $m_u = 1u = 1.6605402(10) \times 10^{-27}$ kg

Bohr radius $a_0 = 4\pi\epsilon_0(h/2\pi)^2/m_e e^2 = 5.29177249(24) \times 10^{-11}$ m

Electron rest mass $m_e = 9.1093877(54) \times 10^{-31}$ kg

Elementary charge $e = 1.60217733(49) \times 10^{-19}$ C

Energy in hartrees $E_h = (h/2\pi)^2/m_e a_0^2 = 4.3597482(26) \times 10^{-18}$ J

Permittivity of vacuum $\epsilon_0 = 8.854187816 \times 10^{-12}$ F m^{-1}

Speed of light in vacuum $c_0 = 299792458$ m s^{-1} (defined)

Plank constant $h = 6.6260755(40) \times 10^{-34}$ J s

Boltzmann constant $k = 1.380658(12) \times 10^{-23}$ J K^{-1}

Avogadro constant $N_A = 6.0221367(36) \times 10^{-23}$ mol^{-1}

***Ab initio* quantum mechanical methods** (synonymous with *nonempirical quantum mechanical methods*)—Methods of quantum mechanical calculations independent of any experiment other than the determination of fundamental observables. The methods are based on the use of the full Schrödinger equation to treat all the electrons of a chemical system. In practice, approximations are necessary to restrict the complexity of the electronic *wavefunction* and to make its calculation possible. In this way methods of *density functional theory* are usually considered as *ab initio* quantum mechanical methods.

Absolute electronegativity—The property of a chemical system derived from *density functional theory* defined as

$$\chi = -\mu = -(\partial E/\partial N)_\nu \cong (I + A)/2$$

where μ is the *electronic chemical potential*, ν is the potential due to the nuclei, and N is the number of electrons, I and A are respectively the *ionization potential* and *electron affinity* of the chemical system in its ground state (in contrast to a similar relationship for the Mulliken *electronegativity* where I and A refer to the valence state). The 'absolute' part of the term comes from the relationship to the electronic chemical potential, μ. The absolute scale is essentially a measure of the chemical reactivity of a free atom, molecule, radical or ion, whereas the Pauling scale of *electronegativity* has no meaning with regard to molecules or ions. The scales are, therefore, comparable only for atoms and radicals where these are roughly parallel. Absolute electronegativity serves as a measure of bond polarity. For the species composed of two entities X and Y, the difference $\chi_X - \chi_Y$ is positive when $X - Y$ has the polarity $X^- - Y^+$ [1,2].

Absolute hardness—The resistance of the *electronic chemical potential*, μ of a chemical system to a change in the number of electrons as measured by the curvature of the plot of energy E versus number of electrons.

$$\eta = (1/2)(\partial\mu/\partial N)_\nu = (1/2)(\partial^2 E/\partial N^2)_\nu \cong (1/2)(I - A)$$

where I and A are respectively ground state *ionization potential* and *electron affinity*, and ν is the potential

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**I Mills, T. Cvitas, K. Homann, N. Kallay, K. Kuchitsu. *Quantities, Units and Symbols in Physical Chemistry—The Green Book*. 2nd edn, Blackwell Science (1993).*

due to the nuclei. In *molecular orbital theory*, the absolute hardness is measured by the energy gap between the *lowest unoccupied* and *highest occupied molecular orbitals*.

$$\eta = (\epsilon_{LUMO} - \epsilon_{HOMO})/2$$

A high value of the absolute hardness is, thus, an indication of high stability and low reactivity. *Absolute softness* is defined as the reciprocal of the hardness [1,2].

Absolute softness—The reciprocal of *absolute hardness*: $\sigma = 1/\eta$.

Active space—Set of active orbitals in the formalism of *Multiconfigurational SCF method*, see also *Complete active space*.

Adiabatic approximation—see *Born–Oppenheimer approximation*.

Adiabatic electron affinity—see *Electron affinity*.

Adiabatic ionization potential—see *Ionization potential*.

Adiabatic reaction—Within the *Born–Oppenheimer approximation*, a reaction that occurs on a single *potential energy surface*.

Adjacency matrix of a graph—the matrix which consists of entries $a_{ij} = 1$ for adjacent vertices, and $a_{ij} = a_{ii} = 0$ otherwise. The matrix is isomorphic to the bonds drawn in simple molecular representation.

Aggregate—An assembly of molecules stabilized by noncovalent interactions (hydrophobic interactions, π–π interactions, *ionic* and *hydrogen bonds*). In contrast to stable molecules, aggregates are equilibrated mixtures of several associates corresponding to certain thermodynamic minima [3].

Agostic interaction—The manner of interaction (termed according to the Greek 'to hold or clasp to oneself as a shield') of a coordinatively unsaturated metal center with a bond of a ligand. This results in an attraction between the metal and the bond and thus often in structural distortions of the whole complex. Initially described for a C–H–Metal bond interaction where M is a transition metal complex, it has been commonly used to describe M...YZ interaction. It is thought to be determining in the activation of a bond, notably (C–H [4].

Alternancy symmetry—A topological property of the *molecular graphs* of *alternant hydrocarbons* which allows the carbon atoms to be divided into two subsets in such a way that no two atoms of the same subset are adjacent. A consequence of this property is the symmetrical arrangement of the energy levels of *bonding* and *antibonding* Hückel MOs relative to the level of *nonbonding orbital* (energy level of the p AO of a carbon atom).

Alternant hydrocarbon—A conjugated hydrocarbon whose molecule does not contain odd-membered rings, so that it is possible to divide the carbon atoms into two sets, 'starred' atoms and 'unstarred' atoms in such a way that no two atoms of the same set are linked by a bond.
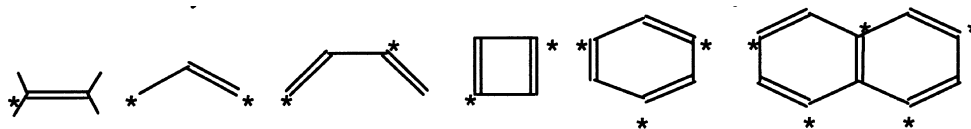
If the total number of starred and unstarred atoms in an alternant hydrocarbon is even, it is assigned to the even alternant hydrocarbon type. If this number is odd, the hydrocarbon belongs to the type of odd alternant hydrocarbons. The *molecular orbitals* and energy levels of alternant hydrocarbons are perfectly paired (see *Perfect pairing*).

Angular Overlap Model (AOM)—A method of description of transition metal–ligand interactions and main-group element stereochemistry, whose basic assumption is in that the strength of a bond formed using *atomic orbitals* on two atoms is related to the magnitude of overlap of the two orbitals. The interactions between the central-atom and ligand orbitals are usually divided into the σ-, π- and δ-types and parametric equations of the type

$$\epsilon_{\text{stab},\sigma} = F^2 e_\sigma - (F^2)^2 f_\sigma$$

$$\epsilon_{\text{destab},\sigma} = -[F^2 e_\sigma - (F^2)^2 f_\sigma]$$

are used, where F is angle-dependent contribution to the *overlap integral* S_{ab} between the two interacting orbitals, whereas parameters e_σ and f_σ are proportional to S^2 and S^4 respectively and depend on the identity of atoms A and B as well the A–B distance. Similar equations are derived for the π- and δ-type interactions. Neither orbital mixing nor nuclear repulsions are accounted for by the model. Its advantage is in that for simple systems a molecular orbital diagram is easily constructed on the basis of two-orbital interactions and clearly reveals trends in orbital energies on distortion [5,6].

Antiaromaticity (antithetical to *aromaticity*)—Those cyclic molecules for which cyclic electron delocalization provides for the reduction (in some cases loss) of thermodynamic stability compared to acyclic structural analogues are classified as antiaromatic species. In contrast to aromatic compounds, antiaromatic ones are prone to reactions causing changes in their structural type, and display tendency to alternation of bond lengths and fluxional behavior (see *fluxional molecules*) both in solution and in the solid. Antiaromatic molecules possess negative (or very low positive) values of *resonance energy* and a small energy gap between their *highest occupied* and *lowest unoccupied molecular orbitals*. In antiaromatic molecules, an external magnetic field induces a paramagnetic electron current. Whereas benzene represents the prototypical aromatic compound, cyclobuta-1,3-diene exemplifies the compound with most clearly defined antiaromatic properties [7,8].

Antibonding molecular orbital—The *molecular orbital* whose occupation by electrons decreases the total bonding (as usual, increases the total energy) of a molecule. In general, the energy level of an antibonding MO lies higher than the average of the valence *atomic orbitals* of the atoms constituting the molecule.

Antisymmetry principle (synonymous with the *Pauli exclusion principle*)—The postulate that electrons must be described by *wavefunctions* which are antisymmetric with respect to interchange of the coordinates (including spin) of a pair of electrons. A corollary of the principle is the *Pauli exclusion principle*. All particles with half-integral spin (fermions) are described by antisymmetry wavefunctions, and all particles with zero or integral spin (bosons) are described by symmetric wavefunctions.

Apicophilicity—In trigonal bipyramidal structures with a five-coordinate central atom, the stabilization achieved through a ligand changing its position from equatorial to apical (axial). The apicophilicity of an atom or a group is evaluated by either the energy difference between the stereoisomers (permutational isomers) containing the ligand in apical and equatorial positions or the energy barrier to *permutational isomerization* (see also *Berry pseudorotation*). In general, the greater the electronegativity and the stronger the π-electron-withdrawing properties of a ligand (as for Cl, F, CN), the higher is its apicophilicity. The notion of apicophilicity has been extended to four-coordinate bisphenoidal and three-coordinate T-shaped structures, which can be viewed as trigonal bipyramidal species where respectively one or two vertices are occupied by phantom ligands (lone electron pairs) [9,10].

Aromaticity—The concept of spatial and electronic structure of cyclic molecular systems displaying the effects of cyclic electron delocalization which provide for their enhanced thermodynamic stability (relative to acyclic structural analogues) and tendency to retain the structural type in the course of chemical transformations. A quantitative assessment of the degree of aromaticity is given by the value of the *resonance energy*. It may also be evaluated by the energies of relevant *isodesmic* and *homodesmotic reactions*. Along with energetic criteria of aromaticity, important and complementary are also a structural

criterion (the lesser the alternation of bond lengths in the rings, the greater is the aromaticity of the molecule) and a magnetic criterion (existence of the diamagnetic ring current induced in a conjugated cyclic molecule by an external magnetic field and manifested by an exaltation and anisotropy of magnetic susceptibility). Although originally introduced for characterization of peculiar properties of cyclic conjugated hydrocarbons and their ions, the concept of aromaticity has been extended to their homoderivatives (see *homoaromaticity*), conjugated heterocyclic compounds (heteroaromaticity), saturated cyclic compounds (σ-aromaticity) as well as to three-dimensional organic and organometallic compounds (three-dimensional aromaticity). A common feature of the electronic structure inherent in all aromatic molecules is the close nature of their valence electron shells, i.e. double electron occupation of all bonding MOs with all *antibonding* and delocalized *nonbonding MOs* unfilled. The notion of aromaticity is applied also to *transition states* [8,11,12].

See also *Electron counting rules, Hückel rule*.

Atom-atom polarizability—A quantity used in *perturbation* HMO *theory* as a measure of the change in electron density, q, of atom s caused by a change in the *electronegativity* (or *coulomb integral*), α_r, of atom r:

$$\pi_{SI} = \partial q_S / \partial \alpha_r$$

Atom-bond polarizability—A quantity used in *perturbation* HMO *theory* as a measure of the change in electron density, q, of atom m caused by a change in the resonance integral, β, of bond rs:

$$\pi_{m,rs} = \partial q_m / \partial \beta_{rs}$$

Atomic basin—Within the *topological electron distribution theory*, the region of three-dimensional space defined by the gradient paths of the charge density which terminate at each nucleus in a molecule. The atomic basin is an unambiguous definition of an atom in a molecule.

Atomic charge—The charge attributed to an atom A within a molecule defined as $\zeta = Z_A - q_A$ where Z_A is the atomic number of A and q_A is the electron density assigned to A. The method of calculation of q_A depends on the choice of the scheme of partitioning electron density. In the framework of the *Mulliken population analysis* q_A is associated with the so-called gross atomic population: $q_A = \Sigma_\mu^A q_\mu$ where q_μ is a gross population for an orbital μ in the basis set employed defined according to

$$q_\mu = P_{\mu\mu} + \sum_{\nu \neq \mu} P_{\mu\nu} S_{\mu\nu}$$

where $P_{\mu\nu}$ and $S_{\mu\nu}$ are the elements of density matrix and overlap matrix respectively (see *overlap integral*). In the *Hückel molecular orbital theory* (where $S_{\mu\nu} = \delta_{\mu\nu}$), $q_\mu = n_\mu P_{\mu\mu}$, where n_μ is the number of electrons in the MO μ [13].

Atomic orbital—see *Orbital*.

Atomic units—The units designed to simplify the form of the fundamental equations of quantum mechanics by eliminating from them fundamental constants. The atomic unit of length is the Bohr radius, $a_o = h^2/4\pi^2 me^2 = 5.29177249 \times 10^{-11}$ m (0.529177249 Å). Energy is measured in hartrees, where 1 hartree $= e^2/a_o = 4.3597482 \times 10^{-18}$ J. Masses are specified in terms of atomic mass unit, amu $= 1.6605402 \times 10^{-27}$ kg and of the electron mass units, $m_e = 0.910953 \times 10^{-30}$ kg. The advantage of atomic units is that if all calculations are directly expressed in such units, the results do not vary with any revision of the numerical values of the fundamental constants [14].

Atomization energy—synonymous with *Heat of atomization*.

Atoms in molecules (AIM), theory of—A quantum chemical method based on the assumption that the *wavefunction* of a molecule can be expressed as a linear combination

$$\Psi_i = \Sigma c_i \Psi_i$$

where Ψ_i are the antisymmetrized products of wavefunctions $\Psi_{\alpha i}^{A}$, $\Psi_{\beta i}^{B}$ ... of atoms A, B ... in *electronic states* α_i, β_i, ... [15,16].

See also *Topological electron distribution theory*.

Aufbau principle—A rule for building up the electronic configuration of atoms and molecules. It states that a maximum of two electrons are put into orbitals in the order of increasing orbital energy: the lowest-energy orbitals are filled before electrons are placed in higher-energy orbitals.

See also *Pauli exclusion principle* and *Hund's rule*.

Automerization (synonymous with *degenerate rearrangement, permutational isomerization, topomerization*)—A molecular rearrangement in which the reactant is transformed to the product which differs from reactant only in the permutation of identical atoms. Automerizations may be detectable by the methods which allow one to distinguish individual atoms within a molecule: by isotopic labelling and by dynamic nuclear magnetic resonance technique. An example of an automerization reaction is the photochemical rearrangement of benzene via tricyclo $[3.1.0.0^{2,6}]$hex-3-ene (benzvalene) [17–20].
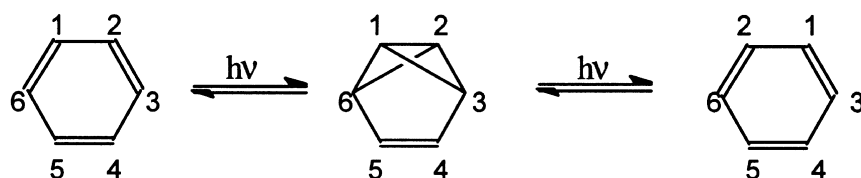
Avoided crossing—Within the *Born–Oppenheimer approximation*, when two *electronic states* change their energy order as the molecular geometry is continuously changed along a *reaction path*, their energies may become equal at some points (surface crossing) or only come relatively close (the surface crossing is said to be avoided). If the electronic states are of the same symmetry, the surface crossing is always avoided in diatomics and usually avoided in polyatomics [21].

See also *Noncrossing rule*.

Back donation (also known as the Dewar–Chatt–Duncanson model)—A description of the bonding of π-conjugated ligands to a transition metal which involves a synergic process with donation of electrons from the filled π-orbital or lone electron pair *orbital* of the ligand into an empty orbital of the metal (donor-acceptor bond), together with release (back donation) of electrons from an nd orbital of the metal (which is of π-symmetry with respect to the metal-ligand axis) into the empty π^*-antibonding orbital of the ligand.

Band orbital—see *Crystal orbital*.

Basis function—A one-electron function used in the expansion of the *molecular orbital* function. Basis functions are commonly represented by *atomic orbitals* (see also *Slater-type orbital* or *Gaussian-type orbital*) centered on each atom of the molecule.

Basis set—In quantum chemistry, a set of *basis functions* employed for the representation *molecular orbitals*. One may distinguish the *minimal basis set* (includes one basis function for each SCF occupied atomic *orbital* with distinct principal and angular momentum quantum members); *split valence basis set* (includes two or more sizes of basis function for each valence orbital); *double zeta DZ) basis set* (a split valence basis set that includes exactly twice as many functions as the minimal basis set); *extended basis set* (the set larger than the double zeta basis set); *polarized basis set* (incorporates basis functions of higher angular quantum number beyond what is required by the atom in its electronic *ground state*; allows orbitals to change not only a size, but also a shape); basis set with *diffuse functions and others* [13,22–24].

Basis set superposition error (BSSE)—An artifactual increase in calculated stability of the supersystem

(the system formed by noncovalent interaction between two or more *molecular entities*, e.g. *hydrogen bond* system) resulting from the *basis set* of the supersystem being larger than for the component subsystems. The BSSE arises from a lowering of the quantum mechanical energy when the *electron density* of each subsystem spreads into the basis functions provided by the other subsystems [22].

Bent's rule—In a molecule, smaller bond angles are formed between electronegative ligands since the central atom, to which the ligands are attached, tends to direct bonding *hybrid orbitals* of greater p character towards its more electronegative substituents [25].

Berry pseudorotation—A mechanism for the interconversion of trigonal bipyramid structures (**1a** and **1b**) through an intermediate (or *transition state*) tetragonal pyramid structure **2**. It may be visualized as two synchronized bending motions by which a pair of apical ligands (1 and 2) exchange their positions with a pair of equatorial ones (3 and 4), whereas one equatorial ligand (5) described as 'pivotal' remains unchanged. This process results in an apparent rotation (pseudorotation) of the actual trigonal bipyramid structure.
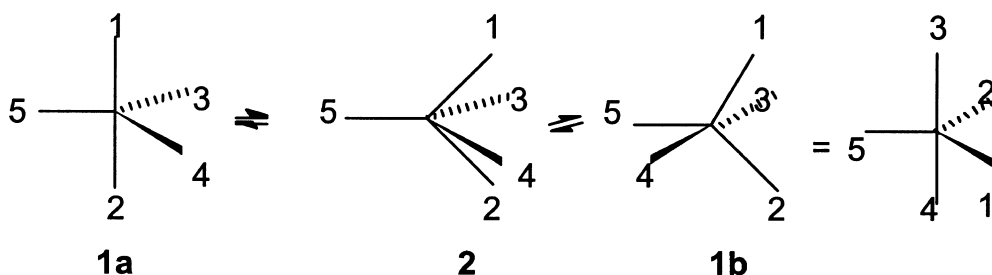
For the majority of five-coordinate main-group and transition metal compounds the energy difference between the trigonal bipyramid (**1**) and tetragonal pyramid (**2**) structures is sufficiently low, so that Berry pseudorotation represents a widespread mechanism of *stereochemical nonrigidity*. The same type of intramolecular rearrangement is characteristic also of four-coordinate bisphenoidal structures, a lone pair always playing the role of the pivotal phantom-ligand [26,27].

See also *Pseudorotation*.

Bethe lattices—The infinite connected *graphs* (a graph is connected if each pair of its points is joined by a path) not containing cycles, all vertices of which are equivalent and have equal numbers (n) of neighbours. Although Bethe lattices with arbitrary n cannot be realized in three-dimensional space, this model is useful in the electronic theory of disordered systems.

Bifurcation—Branching of the *minimum energy reaction path* into two different paths at a certain point (bifurcation point) on the *potential energy surface*.

Binding energy—The difference between the *total energy* of a molecular system and the sum of the energies of its isolated π- and σ-bonds. The value of binding energy depends upon the geometrical arrangement of the isolated subunits (molecules). According to another definition, the term to be substracted from the total energy is the sum of the energies of the separate atoms in the corresponding valence states, which compose the molecule [28].

Biradical—An even-electron molecular entity with two (in some cases delocalized) radical centers which act almost independently of each other. The lowest-energy triplet state of a biradical lies below or at most only a little above its lowest singlet state. The states of those biradicals whose radical centers interact particularly weakly are described in terms of a pair of local doublets [29,30].

Biradicaloid—A *biradical* displaying a strong coupling between the radical centers.

Bloch orbital—see *Crystal orbital*.

Bohr magneton—The magnitude of the standard magnetic moment (the negative first derivative of the energy with respect to the magnetic field) for an electron:

$$\mu_B = eh/4\pi m_e c = 0.927408 \times 10^{-23} \, J \, T^{-1} (0.927408 \times 10^{-20} \, erg \, G^{-1})$$

Bond critical point (synonymous with *bond point*)—Within the *topological electron distribution theory*, a $(3, -1)$ critical point (the point of the gradient field of the electron density within a given nuclear configuration in which $\nabla\rho\,(\mathbf{r},q) = 0$) which is a local maximum in two directions and is a local minimum in the third, i.e. a *saddle point* in three dimensions. A bond critical point appears between every pair of neighbouring bonded atoms, its position on the *bond path* reflecting the polarity of a bond. The location of the bond critical point of bond A–B is shifted toward A and thus, assigns a larger volume of the electronic density to B if B is more electronegative than A [15].

Bond ellipticity—Within *topological electron distribution theory*, the quantity, ϵ, which gives a measure of the deviation of the charge distribution from cylindrical symmetry and thus is correlated with the amount of π-character of a bond

$$\epsilon = \lambda_1/\lambda_2 - 1$$

where λ_1 and λ_2 are the principal curvatures of the *electron density function* at the *bond point* [15].

Bond energy—The energy required to break a given type of bond between atoms in certain valence states. An averaged bond energy is commonly derived by dissecting the *heat of atomization* of a molecule into contributions of individual bonds. For molecules with localized bonds, the heats of atomization (formation) are usually well approximated by the sum of pertinent averaged bond energies [31].

Bond length—The distance between atomic centers involved in a *chemical bond*. The notion of bond length is defined differently in various experimental methods of determination of molecular geometry; this leads to small (usually 0.02–0.02 Å) differences in bond lengths obtained by different techniques. For example, in gas-phase electron diffraction experiments, the bond length is the interatomic distance averaged over all occupied vibrational states at a given temperature. In an X-ray crystal structural method, the bond length is associated with the distance between the centroids of electron densities around the nuclei. In gas-phase microwave spectroscopy, the bond length is an effective interatomic distance derived from measurements on a number of isotopic molecules, etc. A number of empirical relationships between bond lengths and *bond orders* in polyatomic molecules were suggested, see, for example, *fractional bond number* (*the Pauling's bond order*).

Bond orbital—A *localized molecular orbital* related to a certain σ-, π-, or δ-bond.

Bond order—The electron population in the region between atoms A and B of a molecular entity at the expense of *electron density* in the immediate vicinity of the individual atomic centers. Different schemes of partitioning electron density give rise to different definitions of bond orders. In the framework of the *Mulliken population analysis*, bond order is associated with the total overlap population

$$q_{AB} = 2 \sum_{\mu}^{A} \sum_{\nu}^{B} P_{\mu\nu} S_{\mu\nu}$$

where $P_{\mu\nu}$ and $S_{\mu\nu}$ are respectively the elements of the *density matrix* and overlap matrix (see *overlap integral*). A large positive value of bond order signifies strong bonding between the atoms of the molecular entity, whereas negative values of q_{AB} imply that electrons are displaced away from the interatomic region and point to an antibonding interaction. In *valence bond theory*, bond order is given by a weighted average of the formal bond orders (i.e. by the number of electron pairs in a given Lewis structure) between the atoms in the resonance structures (see *Resonance hybrid*).

Bond path—Within the *topological electron distribution theory*, the line resulting from the addition of two gradient paths of the *electron density function* emanating from the *bond critical point* located between each two neighbouring atomic basins. A bond path can be associated with all types of interatomic interactions, including *hydrogen bonds* and interactions in *van der Waals systems* [15].

Bond point—see *Bond critical point*.

Bond resonance energy (BRE)—A quantity that represents the contribution of a given π-bond in a molecule to the *topological resonance energy*, π-Bonds with large negative BREs are presumed to be antiaromatic (see *antiaromaticity*) in nature. The greater is the number of such π-bonds in a molecule, the more the molecule becomes reactive and less thermodynamically stable [32].

Bond-atom polarizability—A quantity used in *perturbation* HMO *theory* as a measure of the change in *bond order*, p, between the centers r and s caused by a change in *electronegativity* or *coulomb integral* of atom m:

$$\pi_{rs,m} = \partial p_{rs}/\partial \alpha_m$$

Bond-bond polarizability—A quantity used in *perturbation* HMO *theory* as a measure of the change in *bond order*, p, between the centers r and s caused by a change in the *resonance integral*, β, between the centers m and n:

$$\pi_{rs,mn} = \partial p_{rs}/\partial \beta_{mn}$$

Bond-dissociation energy (BDE)—For a diatomic molecule, the maximum vibrational energy that a molecule can have prior to its decomposition into the ground *electronic states* of the constituent atoms (spectroscopic bond-dissociation energy, D_e). The D_e value is related to the chemical dissociation energy: $D_0 = D_e - E_{vib}(0)$, where $E_{vib}(0)$ is *zero-point vibrational energy*. This definition is usually extended to the dissociation of polyatomic molecules into certain molecular fragments through *homolytic* or *heterolytic bond cleavages* [33,34].

Bond-separation reactions—A class of *isodesmic reactions* of considerable importance for the quantitative characterization of the interaction between neighboring bonds. All formal bonds between heavy (non-hydrogen) atoms are separated into the simplest reference (two-heavy atom) molecules containing these same kind linkages. The set of the molecules involving H, C, N consists of ethane, ethene, ethyne, methylamine, methanimine, hydrogen cyanide, hydrazine and diazene. Stoichiometric balance is achieved by the addition of one heavy atom hydrides (for the H, C, N compounds—methane and ammonia) to the left-hand side of the reaction scheme. A unique bond-separation reactions may be drawn for any molecule with a classical valence structure. The positive bond-separation energy characterizes stabilization of such a structure with respect to the corresponding isolated bonds and the opposite is true for negative values of bond-separation energies. Thus, the bond-separation reactions (1) and (2) reproduce correspondingly the destabilization energy (*strain energy*) of cyclopropane and stabilization energy (due to the *aromaticity*) of benzene.

$$c\text{-}(CH_2)_3 + 3CH_4 \rightarrow 3CH_3-CH_3 \tag{1}$$

$\Delta H_{exp} = -22.1\,\text{kcal/mol}\,(-92.5\,\text{kJ/mol});\ \Delta H_{calc}(6\text{-}31G^*) = -26.2\,\text{kcal/mol}\,(-110.9\,\text{kJ/mol})$

$$C_6H_6 + 6CH_4 \rightarrow 3CH_3-CH_3 + 3CH_2 = CH_2 \tag{2}$$

$\Delta H_{exp} = 64.1\,\text{kcal/mol}\,(268.2\,\text{kJ/mol});\ \Delta H_{calc}(MP2/6\text{-}31G^*) = 67.2\,\text{kcal/mol}\,(281.2\,\text{kJ/mol})$ [13].

Bond-stretch isomers—A concept introduced to distinguish molecules (still hypothetical) which differ only in the length of one or several bonds and correspond to minima on the same *potential energy surface*. A typical example is given by tricyclo[2.2.2.0^{1,4}] octane ([2.2.2]propellane) in which stretching of the central C–C bond provides for crossing of the *electronic states* of the same symmetry.
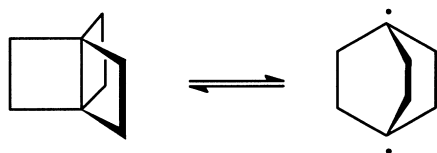
By contrast, in experimentally observed *spin-state isomers* changes in bond length are associated with changes in spin state [35,36].

Bonding molecular orbital—A *molecular orbital* whose occupation by electrons increases the total bonding (usually, lowers the total energy) of a molecule. Generally, the energy level of a bonding MO lies lower than the average of the valence orbitals of the atoms constituting the molecule.

Born–Oppenheimer (BO) approximation—Representation of the complete *wavefunction* as a product of an electronic and a nuclear part

$$\Psi(r, R) = \Psi_e(r, R)\Psi_N(R)$$

where the two wavefunctions may be determined separately by solving two different Schroedinger equations. The validity of the Born–Oppenheimer approximation is founded on the fact that the ratio of electronic to nuclear mass ($m/M \cong 5 \times 10^{-4}$) is sufficiently small and the nuclei, as compared to the rapidly moving electrons, appear to be fixed. The approximation breaks down near a point where two *electronic states* acquire the same energy (see *Jahn–Teller effect*). The BO approximation is often considered as being synonymous with the *adiabatic approximation*. More precisely, the latter term denotes the case when Ψ_e diagonalize the electronic *Hamiltonian*. Thus, the adiabatic approximation is an application of the BO approximation.

Brillouin theorem—The theorem that states that there is no nonvanishing *configuration interaction* matrix elements between the *ground-state* determinantal *wavefunction* and those determinants resulting from the excitation of one electron to an empty orbital of the initial SCF calculation.

Brillouin zone (usually used as short for the first Brillouin zone)—The set of all values of the *wave vector* which generate non-equivalent *crystal orbitals*. It has the form of a polyhedron centered at the Γ-point, or the center of the Brillouin zone, $\mathbf{k} = (0,0,0)$. Its component in, e.g., the x direction is in the range

$$-\pi/a < \mathbf{k}_x < \pi/a$$

for the first Brillouin zone, where a is the repeat distance along that direction.

Canonical molecular orbital (synonymous with *self-consistent orbitals*)—The *molecular orbitals* which produce a Fock matrix in the canonical (diagonal) form. These orbitals are delocalized over the whole molecule and form the basis for an irreducible representation of the *point group* defined by the symmetry of the molecule.

Characteristic polynomial—is defined for an arbitrary square matrix $\mathbf{A}$ of order n as

$$P_n(x) = \det(x\mathbf{E}_n - \mathbf{A})$$

where $\mathbf{E}_n$ is the unit matrix of order n and det stands for the determinant of the matrix. The chemical term equivalent to characteristic polynomial is a secular polynomial.

Charge decomposition analysis (CDA)—A fragment *molecular orbital* partioning scheme for analyzing the electronic interactions between closed-shell fragments A and B in terms of donation A → B, backdonation A ← B, and repulsive polarization A ↔ B. The three terms are given by the mixing of the occupied orbitals of the fragments (donation and backdonation) and by mixing of the occupied orbitals of both fragments (repulsive polarization). The rest term Δ, which is given by the mixing of the unoccupied orbitals of the fragments, is a probe which shows if A–B may be considered a donor-acceptor bond [37].

Charge density—see *Electron density*.

Charge-transfer complex—A *ground state* adduct which exhibits an observable charge transfer absorption band [38].

Chemical bond—when forces acting between two atoms or groups of atoms lead to the formation of a stable independent molecular entity, a chemical bond is considered to exist between these atoms or groups. The principal characteristic of a bond in a molecule is the existence of a region between the nuclei of constant potential contours that allows the potential energy to improve substantially by atomic contraction at the expense of only a small increase in kinetic energy. Not only directed *covalent bonds* characteristic of organic compounds, but also bonds such as those existing between sodium cations and chloride anions in a crystal of sodium chloride or the bonds binding aluminium to six molecules of water in its environment, and even weak bonds that link two molecules of O_2 into O_4, are to be attributed to chemical bonds [28,39,40].

See also *Coordination, Covalent bond, Dative bond, Hydrogen bond, Ionic bond, Van der Waals systems*.

Chirality—The property of an object due to which it cannot be superimposed on its mirror image by translation or rotation. A molecule is chiral if it lacks S_n mirror-rotational axes. The notion of chirality has also been extended to displacements in space and other processes. A chiral process consists of successive states all of which are chiral.

Chromatic graph—see *Molecular graph*.

Closed shell molecular systems—Even-electron atomic or molecular systems whose *electron configurations* consist of doubly occupied orbitals.

Complete Active Space (CAS)—A computational scheme employed in *Multiconfiguration SCF methods* especially suitable for studies of *excited states*. The *wavefunction* is defined by selecting a set of active *orbitals*, and is constructed as a linear expansion in the set of configuration functions that can be generated by occupying the active orbitals in all ways consistent with an overall spin and space symmetry (full *Configuration Interaction*) [41].

Complete active space self-consistent field second-order perturbation theory (CASPT2)—Theoretical scheme that in the first step takes *electron correlation* into account only to a certain extent by using a CAS formalism, while the remaining electron correlation is included through the use of second-order *perturbation theory*.

Complete basis set (CBS) theory—Set of methods developed for computing very accurate energies. These methods use extrapolations of the *Hartree–Fock* and the second order *correlation energies* to the complete basis set limit.

Computational chemistry—Those aspects of molecular research that are expedited or rendered practical by computers [42].

Concerted reaction—A single step reaction through which reactants are directly transformed into products, i.e. without involvement of any intermediates [43].

Configuration interaction (CI)—The mixing of many-electron *wavefunctions* constructed from different electronic configurations to obtain an improved many-electron state. In the CI method, an *n*-electron *wavefunction* is expanded as a linear combination of *Slater determinants*. CI proceeds by constructing other determinants through replacing one or more occupied *orbitals* within the Hartree–Fock determinant (see *Hartree–Fock method*) with a virtual orbital. In the full CI method, the wavefunction Ψ

is represented by a linear combination of the Hartree–Fock determinant Ψ_0 and all possible substitutions Ψ_i. The c_i are the set of coefficients to be solved for by minimizing the energy of the resultant wavefunction.

$$\Psi = c_0\Psi_0 + \sum_i c_i\Psi_i$$

In practical calculations, CI methods are usually used which augment the HF method by only a limited set of substitutions: the CIS method adds single excitations to the HF determinant, CID adds double excitations, CISD adds single and double excitations, and so on [23,24].

Conical intersection (synonymous with the term 'funnel')—An n–2 dimensional subspace of n nuclear coordinates in which two *electronic states* are degenerate. Such type *potential energy surface* crossings of two singlet (or two triplet) surfaces or singlet-triplet surface intersections provide a very efficient channel for *radiationless transition* or for chemical transformation occurring from the lowest *excited state* of polyatomic molecular systems, even in the case when two electronic states possess the same symmetry (contrary to the *noncrossing rule*, which is rigorously valid only for diatomics) [44,45].

Conjugation—In a topological sense, the indication that each pair of multiple (double or triple) bonds in a polyunsaturated molecule is separated by one single (or double) bond. In a conjugated system one multiple bond can be replaced by a centre with a fully or incompletely occupied orbital, (i.e. an atom with a lone pair, an unpaired electron, or a vacant orbital). The term conjugation was extended to orbital language to describe particular *orbital interactions* (π-conjugation, σ-conjugation) given by the topology of the molecule. Conjugation implies an alternation between stronger and weaker orbital interactions leading to a corresponding alternation of the *resonance integrals* [46].

Conservation of orbital symmetry—The orbital symmetry control of *concerted reactions*; this requires transformation of the *molecular orbitals* of reactants into those of products to proceed continuously by following a *reaction path* along which the symmetry of these orbitals remains unchanged. Reactions which adhere to this requirement are classified as *symmetry allowed reactions*, and those which do not as *symmetry forbidden reactions* [43].

Consistent Force Field (CFF)—A *force field* for calculating structures, energies and vibration frequencies of both small organic molecules and large biomolecular systems, including peptides, proteins, nucleic acids, carbohydrates and lipids. The CFF differs from empirical force fields in that its force constants are derived from a rigorous quantum mechanical procedure [47].

Coordination—The bonding of a Lewis base to a Lewis acid via a *dative* or coordinate *covalent bond*.

Coordination number of an atom—The number of atoms by which that atom is directly surrounded, and to each of which it is attached by the direct sharing of electrons.

Core approximation (synonymous with *Pseudopotential approximation*)—The approximation treating atoms as being subdivided into a core composed of a nucleus and tightly bound inner electrons (which form a cloud of negative charge representing the time averaged motion of inner electrons) and a valence shell of electrons that are less tightly bound and may be delocalized over a molecular entity. This simplification allows one to greatly reduce the number of electrons that must be taken into account in the calculation of molecular properties. It is used in all *semiempirical quantum mechanical methods* and in some of *ab initio quantum mechanical* methods.

Correlation consistent basis sets—Sets of contracted gaussian functions specially designed to account as much as possible for the *correlation energy* of valence electrons [48].

Correlation diagram—A diagram which shows the relative energies of orbitals, configurations, valence bond structures or states of reactants and products of a reaction as a function of molecular geometry or another suitable parameter.

Correlation energy—The difference between the energy of a system calculated as the minimal value within the Hartree–Fock approximation (see *Hartree–Fock limit*) and the exact nonrelativistic energy of that system. The correlation energy arises because the *Hamiltonian* in the *Hartree–Fock method* includes an averaged interelectronic potential which does not account for the *electron correlation* in a molecular system.

Coulomb integral (see *Coulomb repulsion*). In the *Hückel molecular orbital theory*, is treated as an empirical parameter supposed to have a value α_m characteristic of the AO ϕ_m and the atom of which it is an AO, and independent of the rest of molecule. In the HMO theory, it is usually assumed that α_m is equal to *ionization potential* of an electron occupying the AO ϕ_m of the corresponding atom [49].

Coulomb repulsion—The potential energy component corresponding to the electrostatic interaction between each pair of charged particles:

$$V = (1/4\pi\epsilon_0) \sum_i \sum_{j<i} e_i e_j \Delta r_{ij}$$

where ϵ_0 is the permittivity of a vacuum, Δr_{ij} is the distance between the two particles, and e_i and e_j are the charges on particles i and j. In *molecular orbital theory*, the electrostatic repulsion between the two electrons occupying the *orbitals* Ψ_i and Ψ_j. In the *Hartree–Fock method* the mean Coulomb repulsion is determined by the value of the *Coulomb integral*

$$J_{ij} = \int\int \Psi_{i*}(\mathbf{r}_1)\Psi_i(\mathbf{r}_1)(e^2/r_{12})\Psi_{j*}(\mathbf{r}_2)\Psi_j(\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = <ij|ij>$$

See also *Exchange repulsion*.

Counterpoise correction—Approximate method to estimate the value of the *basis set superposition error*. For a complex A–B formed by two interacting monomers, A and B, the BSSE is estimated as the difference between monomer energies with the regular *basis set* of each monomer and the energies calculated with the full basis functions for the whole complex. The latter energies for each monomer are calculated by adding to the normal basis set the basis functions of the other monomer located at the corresponding nuclear positions, but without the nuclei present. These additional basis are called *ghost orbitals*.

Coupled cluster (CC) method—An *ab initio quantum mechanical* method in which *electron correlation* effects are introduced by acting with the exponential operator *exp*(T) on the *zero-order wavefunction*, and where T consists of the sum of all possible excitation operators. A CCSD(T) calculation provides for a higher-level treatment of electron correlation beyond MP4 (see *Møller–Plesset Perturbation Theory*) [23].

Covalent bond—A type of bonding associated with the sharing of two electrons usually between two atomic centers of a molecular entity. The mechanism of covalent bonding that causes decrease in the total potential energy of a molecule as its constituent atoms move towards each other is orbital contraction, which increases the localization of the electrons around the nuclei and decreases the accumulated charge in the bonding region(s) [39,50].

Crystal field—The average static electric field experienced by an ion, molecule or atom in a crystal generated by all the other surrounding atoms, molecules, or ions. The concept introduced by Becquerel and developed by Bethe has been extended to refer to the field generated by the ligands (anions or neutral species) surrounding a transition metal ion in a coordination compound. With the understatement that some covalency (see *Covalent bond*) may exist in the metal–ligand bond, it is often referred to as *ligand field*.

Crystal orbital (synonymous with *band orbital*)—One-electron function extended throughout a crystal. Typically a linear combination of *Bloch orbitals*:

$$\Psi_j = \sum_\mu a_{j\mu} \phi_\mu$$

The Bloch orbitals incorporate the translational symmetry by application of boundary conditions:

$$\phi_\mu(\mathbf{r}) = \sum_n e^{ikr} \chi_\mu(\mathbf{r})$$

where $\chi_\mu(\mathbf{r})$ is the *n*-th atomic orbital at the *unit cell* defined by the translation vector **r**. The different values adopted by the *wave vector k* determine the symmetry and nodal properties of the crystal orbital.

Crystal orbital overlap population (COOP)—The overlap population weighted *density of states*. For a solid, COOP serves as the differential version of the *bond order* concept. The integral of the COOP curve up to the *Fermi level* is the total overlap population of the specified bond in a solid, whereas the value of COOP(E)dE represents the contribution to the total overlap population of those *crystal orbitals* whose energy levels lie in the range of E and $E + \mathrm{d}E$ [51].

Curve-crossing model—Model of organic reactivity that generates a *reaction profile* from curves that describe the energies of reactant, product, and intermediate *electronic configurations* (or, alternatively, reactant, product and intermediate *electronic states*) as a function of the *reaction coordinate*. The crossing reflects the electronic reorganization that accompanies the transformation of reactants and products [52–54].

Dative bond—The coordination bond formed upon interaction between molecular species one of which serves as a donor and the other as an acceptor of the electron pair to be shared in the complex formed, e.g. the $N \rightarrow B$ bond in $H_3N \rightarrow BH_3$. In spite of the analogy of dative bonds with *covalent bonds* in that both types imply sharing a common electron pair between two vicinal atoms, the former are distinguished by their significant polarity, lesser strength, and greater length. The distinctive feature of dative bonds is that their minimum-energy rupture in the gas phase or in inert solvent follows the *heterolytic bond cleavage* path [55].

See also [38].

Degenerate electronic states—*Electronic states* whose energies are equal.

Degenerate orbitals—*Orbitals* whose energy levels are equal in the absence of external fields. Any linear combination of the functions corresponding to a given set of degenerate orbitals serves as an equivalent representation of this set of orbitals.

Degenerate rearrangement—see *Automerization*.

Delocalization—Redistribution of the valence-shell electron density throughout a molecular entity as compared with some localized models (individual atoms in their valence states, separated bonds or fragments). Different topological modes of the electron delocalization include: (a) *ribbon delocalization* of either π- or σ-electrons (i.e. electrons occupying respectively π- and σ-orbitals); (b) *surface delocalization* of σ-electrons occurring through an overlap of radially oriented σ-orbitals of a cyclic molecule, as is the case of cyclopropane; and (c) *volume delocalization* of σ-electrons through an overlap of σ-orbitals directed inside a molecular polyhedron, as is the case in tricyclo $[1.1.0.0^{2,4}]$ butane (tetrahedrane) [56,57].

Delocalization energy (DE)—The difference between the actual π-electron energy of a molecular entity and the π-electron energy of a hypothetical species with a localized form of the π-electron system. These energies are normally evaluated within *Hückel molecular orbital theory*. See *Hückel resonance energy*.

Density functional theory (DFT)—A theory which is concerned with a quantum mechanical description of atomic and molecular systems in terms of the *electron density*. All properties are functionals of it including the electronic kinetic energy $T[\rho]$ and the electron–electron repulsion energy $V_{ee}[\rho]$. The total electronic energy of a given system having N electrons is expressed as a functional of its single particle density $\rho(\mathbf{r})$

$$E[\rho] = T[\rho] + \int \nu(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + V_{ee}[\rho]$$

where $\nu(\mathbf{r})$ is the potential due to the nuclei, is a minimum when ρ is the correct ground-state density. In DFT, the exact exchange term for a single determinant is replaced by a more general expression, the exchange-correlation functional, which can include terms accounting for both *exchange repulsion* energy and the *electron correlation* which is omitted from the *Hartree–Fock method*. DFT provides the conceptual basis to a number of important chemical concepts such as *electronegativity, absolute hardness* and *softness, frontier orbital* theory, etc. [1,58].

Density matrix—The one-electron density matrix the elements of which are defined as

$$P_{\mu\nu} = \sum_{i=1} n_i C_{\mu i}^* C_{\nu i}$$

where subscripts μ,ν are for *basis function*, i that of *molecular orbitals*, n_i is the occupation number if the ith orbital. The asterisk denotes complex conjugation (required if the molecular orbitals are not real functions).

Density of states (DOS)—In a solid, the number of energy levels in a given energy interval defined as follows:

$DOS(E)dE$ = number of levels between E and $E + dE$

In general, DOS (E) is proportional to the inverse of the slope of the *dispersion diagram*. The integral of DOS up to the *Fermi level* is the total number of occupied *molecular orbitals* in a solid. The DOS curves, therefore, plot the distribution of electrons in energy in the solid [51].

Dewar resonance energy—see *Resonance energy, various types of*.

Diabatic reaction—Within the *adiabatic approximation*, a reaction beginning on one *electron state* (ground or excited) *potential energy surface* and ending, as a result of *radiationless transition*, on another surface.

Diatomics in Molecules (DIM)—A quantum chemical method based on the assumption that the energy of molecule may be expressed from diatomic contributions [59].

See also *Atoms in molecules, theory of*.

Differential overlap, neglect of—see *Zero differential overlap approximation*.

Diffuse functions—Large size versions of s- and p-type *atomic orbitals* (as opposed to the normal, contracted functions). They allow orbitals to occupy a larger region of space; this makes them important for inclusion into *basis sets* or systems where electrons are relatively far from the nucleus: molecules with lone pairs, anions, systems in their *excited states* etc.

See also *Basis set*.

Dipole hyperpolarizability—see *Hyperpolarizability*.

Dipole moment—The electric dipole of a molecule, μ, is the first derivative of the energy with respect to

an applied electric field. It is a measure of the asymmetry in the molecular charge distribution and is defined by the relation

$$\mu = -e \int \rho(x, y, z)\mathbf{r}\,dV + e \sum_a Z_a \mathbf{r}_a$$

where $\mathbf{r}$ is the radius vector of electrons, $\mathbf{r}_a$ is the vector from the origin to the nucleus of atomic number Z_a and $\rho\,(x,\,y,\,z)$ is the *electron density*. The dipole moment of a complex molecule can be represented approximately in the form of the vectorial sum of the moments belonging to the individual bonds. Dipole moment is independent of origin for a neutral molecule but origin dependent for an ion [60,61].

Dispersion diagram (synonymous with *band diagram*)—Representation of the energy of the *crystal orbitals* of a solid as a function of the *wave vector*. For three-dimension solids, such representations are given for only a few projections of the wave vector, or symmetry lines of the *Brillouin zone*.

Dispersion energy—An attractive component of the energy of intermolecular interaction resulting from the interaction between the instantaneous, time-variable dipole of one system and the induced multipole of the second system. This interaction cannot be interpreted in terms of classical electrostatics and corresponds to the intersystem component of the *correlation energy*. For two neutral atoms, the dispersion energy is proportional to the sixth power of the reciprocal distance:

$$E_D \approx -1/\mathrm{R}^6$$

[62].

Distonic ion—An ion with formally separated charge and radical sites. Distonic ions may be divided into two distinct classes: those possessing coordinatively and electronically-saturated charge site (usually of the onium type) and the ionized *biradicals* with two coordinatively-unsaturated sites containing one or three electrons [63].

See also *Distonic radical cation* [38].

Double zeta (DZ basis set)—See *Basis set*.

Dynamic reaction path (DRP)—a classical trajectory method based on *molecular orbital* calculations which determines atomic accelerations, velocities and positions using the energy gradient, and does not require prior knowledge of the *potential energy surface* [64].

Dynamic spin polarization (see *spin polarization*).

Dyotropic rearrangement—A class of *pericyclic reactions* in which migration of two σ-bonded groups occurs. Two different types of dyotropic rearrangements are distinguished: (a) those in which two migrating groups interchange their positions (Eqn 1) and (b) those which involve migration to new bonding sites in a manner that avoids positional exchange (Eqn 2) [65].
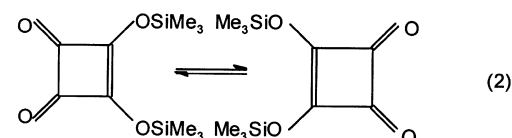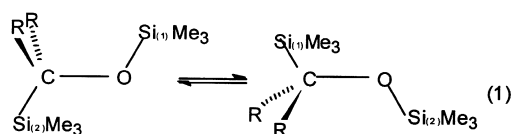
ECW model for donor-acceptor interaction—An approach to obtaining a quantitative scale of bond strengths of Lewis acid-base complexes. Each acid is characterized by electrostatic, E_A, and covalent, C_A enthalpy parameters as is each base (E_B and C_B) which are combined according to the equation

$$-\Delta H = E_A E_B + C_A C_B + W$$

to produce the enthalpy of formation of the AB complex. The E, C parameters are chosen in such a way as to have minimal contributions from solvation or lattice energies. The W term incorporates any constant contribution to the reaction of a particular acid (or base) that is independent of the base (acid) it reacts with [66,67].

**Effective Atomic Number (EAN) rule**—see *18-Electron rule*.

Effective Hamiltonian—A model *Hamiltonian*, H_{eff} used for an approximate description of a certain part of the total electronic system of a molecular entity, e.g. valence electrons or p_π electrons. It is related to the exact Hamiltonian, H, for the same problem by means of a factorizing similarity transformation: $H_{eff} = W^{-1} H W$ such that H_{eff} has the same eigenvalues as H (usually for a small subset of the eigenvalues of H), but much simpler eigenfunctions. In the *Hartree–Fock method* H_{eff} replaces electron-electron repulsion by an average over occupied *orbitals*. The *Hückel MO theory* can be interpreted as a method based on H_{eff} [68].

See also *Kohn–Sham orbitals*.

Effective molecular symmetry group—The appropriate group in which the energy levels of molecules undergoing rearrangements on a given experimental time scale are to be classified. The operations of the molecular symmetry group of such molecules consist of permutations of identical nuclei amongst themselves, and permutation-inversions, where a permutation is combined with the inversion of all particle coordinates through the origin of a space-fixed axis system. The complete nuclear permutation-inversion group contains all such operations, which all commute with the full molecular *Hamiltonian* [69,70].

See also *Symmetry point group*, *Symmetry operation*.

Electron affinity—The energy (A_X) released upon attachment of an electron to an atom or a molecule (X) resulting in the formation of the negative ion X^-, i.e.

$$X + e^- \rightarrow X^- + A_X$$
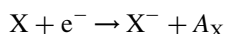
As with the case of *ionization potential*, there may be defined *adiabatic electron affinity* and a *vertical electron affinity*. The adiabatic A_X is equal to the difference between the total energies of a neutral system (X) and the corresponding anion (X^-). The vertical A_X is equal to the difference between total energies of X and the anion X^- in the equilibrium geometry of X.

Electron correlation—The adjustment of electron motion to the instantaneous (as opposed to time-averaged) positions of all the electrons in a molecular system i.e. the tendency of electrons to correlate their motions in order to keep as far apart as possible because of the restrictions set by the *Pauli exclusion principle* (exchange correlation) and because of the electrostatic repulsions (coulombic correlation).

See also *Correlation energy*.

Electron-counting rules—Rules establishing correspondence between the topology of a *molecular structure* and the number of electrons which may be placed into its *bonding molecular orbitals*. In the origin of various electron-counting rules lies a general assumption that the completeness of the valence electron shell of a molecular entity belonging to a certain structural type serves as the major criterion of *structural stability*.

See *18-Electron rule*, *Hückel rule*, *Lewis octet rule*, *Wade's rules*, *Woodward–Hoffmann rules*.

Electron deficient compounds—Molecules or ions that contain too few electrons to allow their bonding to be described exclusively in terms of two-center, two-electron, i.e. *covalent*, *bonds*. Such molecules or

certain fragments in these are often held together with the *multicenter bonds*. The compounds containing atoms with incompletely filled but spin-paired electron shells (carbenes, carbenium ions) may also be regarded as electron deficient ones.

Electron density—(synonymous with *charge density*), see *Electron density function*.

Electron density function—The electron probability distribution function, ρ defined as

$$\rho(\mathbf{r}) = n \int \Psi^*[\mathbf{r}(1), \mathbf{r}(2) \dots \mathbf{r}(n)] \Psi[\mathbf{r}(1)\mathbf{r}(2) \dots \mathbf{r}(n)] d\mathbf{r}(2) \dots d\mathbf{r}(n)$$

where Ψ is an electronic *wavefunction* and integration is made over the coordinates of all but the first electron of n. The physical interpretation of the electron density function is that $\rho d\mathbf{r}$ gives the probability of finding an electron in a volume element $d\mathbf{r}$, i.e. electron density in this volume.

18-Electron rule—for mononuclear transition metal complexes the *electron-counting rule* derived from the fact that transition metals have nine valence AOs which can be used either for metal-ligand binding or for accommodating non-bonding electrons. An extension of the rule to transition metal cluster compounds is known as the *effective atomic number rule*.

Electron transfer (ET) reaction—A redox process in which the overall change that has occurred is the transfer of one or more electrons.

Electronegativity—The power of an atom in a molecule to attract electrons. The two widespread empirical scales of electronegativity are those developed by L. Pauling and R. Mulliken. The Pauling scale is thermochemical; it is based on the values of *bond energies* of type X–Y, X–X and Y–Y molecules from much the ionic contributions to the X–Y bond is defined as

$$\Delta_{XY} = E_{XY} - (1/2)(E_{XX} + E_{YY}).$$

From this value the relative electronegativity of X with respect of Y is defined (in $eV^{1/2}$ units) as

$$\chi_X - \chi_Y \approx (\Delta_{XY})^{1/2}.$$

The Mulliken electronegativity (in eV units) is given by the equation:

$$\chi_X = (1/2)(I_X + A_X)$$

where I_X and A_X are respectively *ionization potential* and *electron affinity* in a suitable valence state (see *valence state ionization potential*, *valence state electron affinity*). Both scales are linearly interrelated. These are useful for estimating bond polarities and strengths of bonds between different atoms. Many other scales of electronegativity are known, among which that of A. Allred and E. Rochow, where electronegativity is defined as the electrostatic force between the nucleus and its valence electrons, is most frequently used. Accounting for the observation that the position of *bond points* relates to the polarity of a bond, a scale of atomic and group electronegativities, which are comparable in magnitude to the Pauling values, was derived (R. Boyd) on the basis of topological properties of the *electron density* distributions in model hydrides R–H [71–76].

See also *Absolute electronegativity, Equalization of electronegativity*.

Electronic chemical potential—The quantity that measures the escaping tendency of electrons from a species in its *ground state*. It is the negative of the *absolute electronegativity* [77].

Electronic configuration—The allocation of electrons within an atom or a molecule to a set of correspondingly *atomic* or *molecular orbitals* complying with the *Pauli exclusion principle*. One electronic configuration may give rise to several *electronic states* with different multiplicities. A *wavefunction* for a given *electronic configuration* which is an eigenfunction of the electron spin operators S^2 and S_z represents an electronic state of the atom or molecule.

Electronic state—An arrangement allowed by the laws of quantum mechanics of electrons within an atom, molecule (or system of molecules).

See also *Electronic configuration*.

Electronic stability—Unavailability of another electronic structure (different *electronic state*) of lower energy with the same number of electrons.

Electrostatic potential—A physical property equal in magnitude to the electrostatic energy between the static charge distribution, $\rho(\mathbf{r})$, of an atomic or molecular system (in the latter case the term *molecular electrostatic potential* is commonly used) and a positive unit point charge located at $\mathbf{r}$. The electrostatic potential $V(\mathbf{r})$ that is produced at any point $\mathbf{r}$ by the electrons and nuclei (A) of the system is given by:

$$V(\mathbf{r}) = \sum_{A} Z_A/|\mathbf{R}_A - \mathbf{r}A| - \int \rho(\mathbf{r}')\mathrm{d}\mathbf{r}'/|\mathbf{r}' - \mathbf{r}|$$

See [78,79].

Energy gradient—First derivatives of the total energy with respect to nuclear coordinates, i.e. negative values of forces on the nuclei. Evaluation of energy gradient plays a central role in searching *potential energy surfaces* for *stationary points*. A widespread technique is based on the minimization of the *gradient norm* (the square of energy gradient) [80].

Energy hypersurface (synonymous with *potential energy surface, PES*)—The notion of hypersurface is used to stress the multidimensionality of PESs. In a molecular system consisting of N atomic nuclei, the number of the independent coordinates that fully determine the PES is equal to $3N$–6 (or $3N$–5 if the system is linear) [81].

Energy profile—A schematic plot of the energy of a reacting system as a function of the *reaction coordinate*. The term energy may refer to enthalpy, free energy or internal energy. Energy profiles are intended to illustrate the energies of reactant, intermediate, transition and product states of the system in the order in which they are formed; they are useful for depicting reaction mechanisms.

Equalization of electronegativity, principle of—The postulate that in a molecule all the constituent atoms should have same *electronegativity* value, which would be the geometric mean of the electronegativities of isolated atoms [82].

Equilibrium geometry—Molecular geometry that corresponds to the true minimum on the respective *potential energy surface*. While information relating to the equilibrium geometry is provided by calculations within the *adiabatic approximation* (minimization of the *total energy* with respect to any independent geometrical parameter), various experiments yield some effective geometries for the molecule which are averaged over molecular vibrations.

See also *Bond length*.

Exchange integral—see *Exchange repulsion*.

Exchange repulsion—The correlation to the *Coulomb repulsion* between two electrons in *orbitals* Ψ_i and Ψ_j for the case when the electrons possess parallel spins. It is to be substracted from the *Coulomb repulsion* to give the total energy of the electron–electron interaction. In the *Hartree–Fock theory* the magnitude of the exchange repulsion is given by the *exchange integral*

$$K_{ij} = \int \int \Psi_i^*(\mathbf{r}_1)\Psi_j^*(\mathbf{r}_1)(e^2/r_{12})\Psi_i(\mathbf{r}_2)\Psi_j(\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 = <ij\,|\,ji>$$

For the case of electrons with opposite spins K_{ij} vanishes.

Excimer—A dimer stable only in the electronically *excited state* formed by the interaction of an excited molecular entity with a *ground state* partner of the same structure.

Exciplex—An electronically excited complex stable only in the electronically *excited state* formed by the interaction of an excited molecular entity with a *ground state* partner of a different structure.

Excited configuration—An *electronic configuration* that makes a predominant contribution to the quantum mechanical description of an *excited state* of a system.

Excited state—An *electronic state* other than the lowest energy state of a system.

Exciton—A quasiparticle invoked to describe the migration through the crystal lattice of the excitation of one molecule in the crystal. The rate of the migration depends on the width of the *band orbital*: the wider bands provide for faster migration. The migration of the excitation is analogous to the migration through the crystal of a spin-free particle [83,84].

Exclusion principle—see *Pauli exclusion principle*.

Extended basis set—see *Basis set*.

Extended Hückel MO method (EHMO)—A *semiempirical* all-valence electron *quantum mechanical method* which uses the same approximations, apart from π-approximation and neglect of overlap integrals, as those of the *Hückel molecular orbital theory*. The method reproduces relatively well the shapes and the order of energy levels of *molecular orbitals*. The account for overlap makes it possible to describe the net destabilization caused by interaction of two doubly occupied orbitals, which effect is not reproduced by HMO theory [85].

Extended transition state method (ETS)—An energy partioning scheme of the bond energy DE between two atoms of fragments A and B into four different terms:

$$\Delta E(A-B) = \Delta E_{prep} + \Delta E_{elst} + \Delta E_{ex} + \Delta E_{orb}$$

where ΔE_{prep} is the energy which is necessary to promote the fragments A and B from the respective equilibrium geometry in the electronic *ground state* to the geometry and electronic reference state in the molecule A–B. The three terms ΔE_{elst}, ΔE_{ex} and ΔE_{orb} give the interaction energy ΔE_{int}. They are calculated in three subsequent steps. ΔE_{elst} is the electrostatic interaction energy which is calculated in the first step with a frozen electron density of the fragments. ΔE_{ex} then gives the repulsive energy caused by *exchange repulsion*, which is calculated when the frozen *wavefunction* of step one becomes orthogonalized and antisymmetrized. ΔE_{orb} is calculated in the third step. It gives the stabilization which comes from the *orbital interaction* when the wavefunction is completely relaxed. The latter term can be broken down into orbital contributions with different symmetry. The ETS method is similar to *Morokuma analysis* [86].

Fermi hole—A region around an electron where the probability of finding another electron with the same spin is very small due to the action of the *antisymmetry principle*. The Fermi hole describes the manner in which the charge of the reference electron is spread out in space, thereby excluding the presence of an identical amount of same-*spin density* [87].

Fermi level—In an extended structure (solids, metals, semiconductors or insulators), the average for the highest occupied and the lowest unoccupied levels. In chemistry, the Fermi level is usually considered as the highest occupied *crystal orbital*.

Fluxional molecules—A subclass of *structurally nonrigid* molecules in which all the interconverting species that are observable are chemically and structurally equivalent. The classic example of the phenomenon of fluxionality is the rapid *automerization* of tricyclo[3.3.2.0^{2,8}]deca-3,6,9-triene (bullvalene), the rapid interconversion of 1 209 600 (10!/3) degenerate isomers [88].

Force field—Within the *molecular mechanics* approach, a set of potential functions defining bond stretch, bond angle (both valence and dihedral) distortion energy of a molecule as compared with its nonstrained conformation (that characterized by standard values of *bond lengths* and angles). A set of

transferable empirical force constants is preassigned and the *harmonic approximation* is usually employed. Some force fields may contain terms for interactions between nonbonded atoms, electrostatic, hydrogen bond and other structural effects as well as account for inharmonicity effects.

In vibrational spectroscopy, the inverse problem is solved by determining a set of force constants and other parameters of a chosen potential energy function which would match with experimentally observed vibrational frequencies of a given series of congeneric molecules.

Fractional bond number (synonymous with the *Pauling's bond order*)—The formal bond order, *n* defined in terms of the difference between a standard single bond distance r_0 and an interatomic distance *r*, and an empirical constant *c*.

$$c \ln n = r_0 - r$$

Fragment molecular orbital analysis—(Synonymous with reconstruction molecular orbital analysis)—The procedure based on the theory of *orbital interactions* for the construction of *molecular orbitals* of a complex molecular system from the *orbitals* of its fragments with the same geometry and symmetry properties as these fragments have in the molecule [89].

Franck–Condon principle—Classically, the approximation that an electronic transition is most likely to occur without changes in the positions of the nuclei in a *molecular entity* and its environment. The resulting state is called a *Franck–Condon state*, and the transition involved is called a vertical transition. The quantum mechanical formulation of this principle is that the intensity of a *vibronic transition* is proportional to the square of the *overlap integral* between the vibrational wavefunctions of the two states involved in the transition [30].

Frank–Condon State—see *Franck–Condon principle*.

Free radical—see *Radical*.

Free valence—A reactivity index applied mostly to radical reactions of conjugated systems. An atom in such a system can exert only a certain maximum of π-bonding power as measured by a sum of the π-bond orders P_{AB} of bonds formed by it. In the *Hückel molecular orbital theory*, the maximum π-bonding power for a carbon atom is $\sqrt{3}$; hence the free valence of a carbon atom in a molecule is defined by

$$F_A = \sqrt{3} - \sum_B P_{AB}$$

Frontier function (synonymous with *Fukui function*)—The function which provides a description of *electron density* in the *frontier orbital* as the initial response in the electron density at position $\mathbf{r}$, $\rho(\mathbf{r})$, due to infinitesimal perturbation in the total number of electrons N in the *molecular entity* [90,91].

$$f(\mathbf{r}) = \partial \rho(\mathbf{r}) / \partial N$$

Frontier orbitals—The *highest occupied molecular orbital (HOMO)* and the *lowest unoccupied molecular orbital (LUMO)* of a given molecular entity. In the case of an odd-electron molecular entity, when its HOMO is occupied by a single electron such a molecular orbital is termed a *singly occupied molecular orbital (SOMO)*. Depending on the properties of the reactive partner, the SOMO of a given species may function as either HOMO or LUMO. The special importance of the frontier orbitals is due to the fact that a broad variety of chemical reactions takes place at a position and in a direction where the overlap of HOMO and LUMO of the respective reactants is maximal.

Frozen core approximation—Approximation commonly used in post-SCF calculations which implies that only the contributions of the valence electrons to the correlation energy are evaluated.

Fukui function—see *Frontier function*.

Gaussian type orbital (GTO)—An exponential function centered on an atom, the general expression for

which is given by

$$\chi(\alpha, \mathbf{r}) = N x^i y^j z^k \exp(-\alpha r^2)$$

where *i, j, k* are positive integers or zero and α is the orbital exponent. Orbitals of s, p and d type result when $i + j + k = 0$, 1, 2 respectively. Linear combinations of primitive gaussians are used to form the actual *basis functions* that are called contracted gaussians. The great convenience of GTOs lies in the fact that evaluation of the molecular integrals needed in *ab initio quantum mechanical methods* of calculation is performed much more efficiently as compared with *Slater type atomic orbitals*.

Generalized Valence Bond (GVB) method—A muilticonfigurational method that uses a limited set of valence bond configurations in the conventional *multiconfiguration SCF method*.

Ghost orbitals—see *Counterpoise correction*.

Gradient norm—see *Energy gradient*.

Graph—A representation consisting of points (vertices) connected by lines (edges). A graph is a topological, but not a geometric object.

Graph automorphism group—The set of all permutations of *graph* vertices in which adjacent vertices remain adjacent.

Ground state—The lowest energy state of a chemical entity.

Half-electron (HE) model—An approach to treating open-shell molecular systems by a closed-shell formalism which utilizes the similarity between the SCF equations (see *Hartree–Fock method*) and those for a fictitious closed-shell system in which the odd electron is replaced by two half-electrons. The model is applied for calculating energies of *radicals* by use of *semiempirical quantum mechanical methods* [92].

Hamiltonian—A differential operator of the *total energy*. For any normalized *wavefunction* ψ, the energy is the expectation value of the Hamiltonian operator.

$$E = \int \psi^* \mathbf{H} \psi \mathrm{d}\tau$$

Hard and Soft Acid and Base (HSAB) principle—A structure-reactivity concept formulated in terms of acid-base interaction. According to this principle soft acids react faster and form stronger bonds with soft bases, whereas hard acids react faster and form stronger bonds with hard bases, everything else being assumed approximately equal. Hardness is associated with low *polarizability*, high *electronegativity* and energy low-lying HOMO (bases) or energy high-lying LUMO (acids). Softness is related to high polarizability, low electronegativity, energy high-lying HOMO (bases) and energy low lying LUMO (acids). The soft-soft preference is characteristic mostly of the reactions controlled by the *orbital interaction*, and the hard-hard preference relates to reactions in which electrostatic factors prevail [93–95].

    See also *Absolute hardness*.

Harmonic approximation—The approximation of the full nuclear potential of a molecular system in its *equilibrium geometry* and in the vicinity of the respective minimum on the *potential energy surface* by the function

$$V = (1/2) \sum_{i,j=1}^{3N} \partial^2 \mathrm{V}/\partial q_i \partial q_j$$

where q_i are mass-weighted cartesian displacements of nuclei relative to their equilibrium positions. The approximation allows one to describe vibrational motion in terms of independent vibrational modes normal modes) each of which is governed by a simple one-dimensional harmonic potential.

Hartree–Fock limit—The lowest energy that would be obtained via the SCF procedure (see *Hartree–Fock method*) if there were no restrictions on the sorts of function that *molecular orbitals* could adopt.

Hartree–Fock (Self-Consistent Field, SCF) method—Method for determination of the spatial orbitals ψ_i of the many-electron determinantal wavefunction (see *Slater determinant*) based on reducing coupled nonlinear differential equations for the optimum forms of the *molecular orbitals* by use of the variational method (see *variational principle*). The Hartree–Fock *hamiltonian* operator is defined in terms of these orbitals through the operators of *coulomb* and *exchange repulsion*. The general procedure for solving the Hartree–Fock equations is to make the orbitals self-consistent with the potential field they generate. It is achieved through an iterative trial-and-error computational process, for which reason the entire procedure is called the *self-consistent field-method*. In the case of *open-shell systems* one should distinguish between the spin-*restricted Hartree–Fock (RHF) method* and spin-*unrestricted Hartree–Fock (UHF) method*. In the former approach a single set of molecular orbitals is preset, some being doubly occupied and some being singly occupied with an electron of spin. In the UHF approach different spatial orbitals are assigned to electrons with α and β spins and the orbitals ψ_i doubly occupied in the RHF method are replaced by two distinct orbitals $\psi_i(\alpha)$ and $\psi_i(\beta)$ [13].

Heat of atomization—The negative value of the *heat of formation*. It is equal to the total *bond energy* of a compound.

Heat of formation—the heat absorbed or released upon formation of a compound from the elements in their standard states (i.e. the most stable form of the elements under standard temperature and pressure, 25°C and 1 atm).

Hessian matrix (synonymous with force constant matrix)—The matrix of second derivatives of energy. At any local minimum, all eigenvalues of the Hessian matrix are positive. At a first-order saddle point, only one eigenvalue is negative and all others are positive.

Heterolytic bond cleavage—A bond-dissociation reaction of the type $R–X \rightarrow R^- + X^+$ resulting in the splitting of the electron pair of the ruptured bond in a way which leaves the pair with one of the fragments formed upon dissociation.

High-spin state—When the separation between *highest occupied* and *lowest unoccupied molecular orbitals* is not large, two alternative *electronic states* may be considered for the two uppermost electrons. The state with the largest number of unpaired electrons is called the *high spin state*. In the cases where the one-electron energy needed to promote an electron to the LUMO is smaller than the *Coulomb* and *exchange repulsion* energies required to pair up two electrons in the HOMO, the high-spin state is the *ground state*.

For compounds with more than two unpaired electrons, several spin states may exist, but in octahedral (or tetrahedral) transition metal complexes (e.g. organometallic compounds), the high degeneracy of the MOs results in only one low-spin and one high-spin state.

Whether a given compound is in its *low-spin* or high-spin *state* can be usually determined from magnetic susceptibility or ESR experiments, although in some cases both states have similar energies and are thermally populated, giving rise to a peculiar temperature dependence of the compound's magnetic behavior.
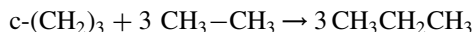
See also *Hund's rule*.

Low Spin
S = 0

High Spin
S = 1

e_g

t_{2g}

Low Spin

High Spin
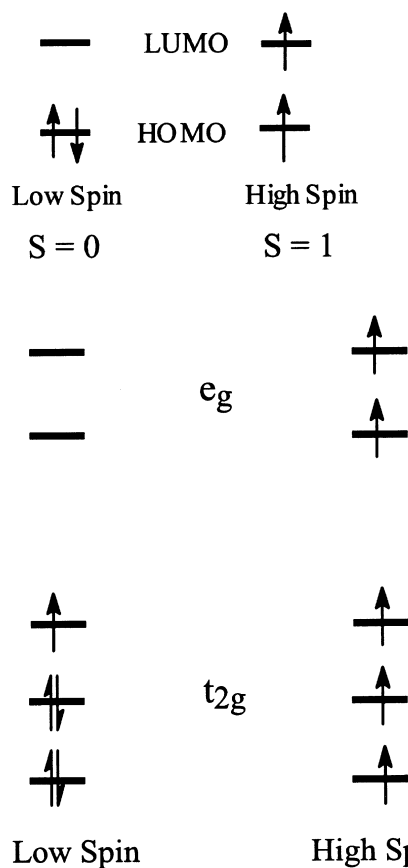
Highest Occupied Molecular Orbital (HOMO)—see *Frontier orbitals*.

Homoaromaticity—The aromatic stabilizaiton of cyclic conjugated systems with $4n + 2$ π-electrons is partly preserved when one or more methylene (or other saturated) groups are inserted into the ring. The molecules and ions thus formed are regarded as homoaromatic structures. Examples are cyclobutenyl **1** and cyclooctatrienyl (homotropylium) **2** cations. Trishomocyclopropenyl cation **3** represents a trishomoaromatic structure.

1   2   3
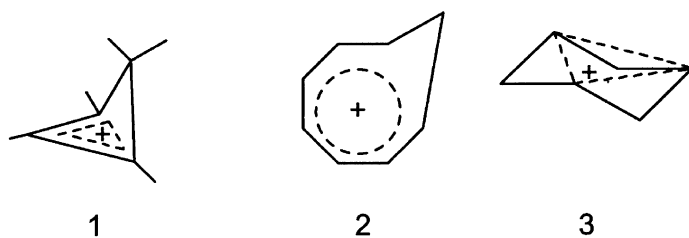
Homodesmotic reaction—A subclass of *isodesmic reactions* in which reactants and products contain equal numbers of carbon atoms in corresponding states of *hybridization*; moreover, there is matching of the carbon-hydrogen bonds in terms of the number of hydrogen atoms joined to the individual carbon atoms. To achieve all this matching, one should significantly extend the number and types of reference molecules. In the aliphatic series of hydrocarbons these are propane, isobutane and neopentanes as well as propene and isobutene; for aromatics—buta-1,3-diene, 3-methylidenepenta-1,4-diene (2-vinylbutadiene)

and 3,4-bismethylidenehexa-1,5-diene (2,3-divinylbutadiene). Thus to assess *strain energy* of cyclopropane and aromatic stabilization of benzene the following homodesmotic reactions are to be respectively analyzed.

$$c\text{-}(CH_2)_3 + 3\,CH_3{-}CH_3 \rightarrow 3\,CH_3CH_2CH_3$$

$$\Delta H^0_{exp} = -26.5\,\text{kcal/mol}\ (110.9\,\text{kJ/mol})$$

$$C_6H_6 + 3\,CH_2{=}CH_2 \rightarrow 3\,CH_2{=}CH{-}CH = CH_2\,(trans)$$

$$\Delta H^0_{calc}(MP2/6{-}31G^{**}) = 23.9\,\text{kcal/mol}\ (100.0\,\text{kJ/mol})$$

Due to closer matching of the hybridization states of the atoms of reactants and products as compared to isodesmic reactions, the homodesmotic reactions give more accurate estimates of the intrinsic strain and the cyclic delocalization. The definition may be extended to molecules with heteroatoms [96].

Homolytic bond cleavage—The bond-dissociation reaction of the type $R\text{–}X \rightarrow R^{\cdot} + X^{\cdot}$ resulting in the splitting of the electron pair of the ruptured bond in a way that leaves by one electron on each of the fragments formed upon dissociation.

Hot ground state photoreaction—A photochemical *diabatic reaction* which occurs as the jumps from the *potential energy surface* of the *excited state* of a molecule to the *ground state* surface with excess of thermal energy, large enough to overcome the potential energy barrier between the reactant and the product.

Hot state reaction—A reaction proceeding from an ensemble of molecular entities possessing a higher average vibrational, rotational or translational energy than they would at thermal equilibrium with the surrounding medium [30].

See also *Hot ground state photoreaction*.

Hückel molecular orbital (HMO) theory—The simplest *molecular orbital theory* of π-conjugated molecular systems. It uses the following approximations: *π-electron approximation*; LCAO representation of the π-molecular orbitals; neglect of electron–electron and nuclear–nuclear repulsions (in fact, the assumption that these cancel). The diagonal elements of the *effective Hamiltonian, coulombic integrals*, and the off-diagonal elements, *resonance integrals*, (accounted for only directly bonded atoms) are chosen as empirical parameters, all *overlap integrals* being neglected [97,98].

Hückel resonance energy—see *Resonance energy, various type of*.

Hückel rule—(also known as the $4n+2$ rule). The *electron-counting rule* which states that those monocyclic π-conjugated molecules and ions are stable which contain $(4n+2)$ π-electrons, where $n = 0$, $1, 2 \ldots$ While being originally formulated on the basis of the simple *Hückel molecular orbital theory*, the rule is not limited by the conditions of this theory and proved to be valid also in the framework of the *self-consistent-field* approximation with *electron correlation* taken into account. From the structural point of view, the rule has certain limitations when applied to polycyclic systems and heterocycles with highly electronegative or highly electropositive heteroatoms.

Hund's rule—A rule for building up the *electronic configuration* of atoms and molecules: where a species possesses degenerate orbitals one electron is placed into each of these before two electrons are placed in any one of the degenerate set, and the electrons in the singly occupied orbitals have parallel spins. Thus, the *ground state* electron configuration of the nitrogen atom is represented by $N(1S^2 2S^2 2p_x p_y 2p_z)$. Apart from this rule (called sometimes Hund's multiplicity rule), two other rules of determining ground *electronic states* from the magnitudes of the total orbital angular momentum are referred to as Hund rules [30,99].

Hybrid orbital—An *atomic orbital* derived through *hybridization* of atomic orbitals with different angular momentum quantum numbers located at a given atom.

Hybrid Quantum Mechanics/Molecular Mechanics (QM/MM) methods—A procedure for the treatment of large molecular systems in such a way that part of the system is treated explicitly by quantum mechanical (QM) techniques, while the rest of the system is approximated by a classical or molecular mechanics (MM) *force field* [100,101].

Hybridization—The vectorial type mixing of *atomic orbitals* with different angular momentum quantum numbers on the same atomic center. Mathematically, the hybridization corresponds to an orthogonal transformation of a given *basis set* (e.g. $\chi_1 = 2s$, $\chi_2 = 2p_x$, $\chi_3 = 2p_y$, $\chi_4 = 2p_z$) to an equivalent basis set $\{\lambda_l\}$. In simple cases, it may involve the mixing of two $(2s, 2p_x)$, three $(2s, 2p_x, 2p_y)$ and four $(2s, 2p_x, 2p_y, 2p_z)$ AOs, the respective types of hybrid orbitals being referred to as sp, sp^2 and sp^3 AOs. For inequivalent ligands or unequal *bond lengths* more general sp^λ hybrid orbitals have the form:

$$h_\lambda(\theta) = N(s + \lambda^{1/2} p_\theta)$$

where p_θ is a normalized p orbital pointing in the direction θ, N is a normalization constant, and λ is generally noninteger.

Hydrogen bond—A particular type of *multicenter* (*three center–four electron bond*) X–H . . . Y in which the central hydrogen atom covalently linked to an electronegative atom X (C,N,O,S. . .) forms an additional weaker bond with atom Y (N,O,S. . .) in the direction of its lone electron pair orbital. The energy of hydrogen bonds, which is usually in the range of 3–15 kcal/mol (12–65 kJ/mol), results from the electrostatic interaction and also from the *orbital interaction* of the *antibonding* $\sigma^*(XH)MO$ of the molecule acting as the hydrogen donor and the *nonbonding* lone electron pair MOn_Y of the hydrogen acceptor molecule [102–104].

Hydrophobic effect—The tendency of nonpolar species to aggregate in water solution so as to decrease the hydrocarbon–water interfacial area. The effect is a principal factor determining the structures of proteins and nucleic acids, the binding of substrates to enzymes, and the binding of antigens to antibodies [105].

Hyperconjugation—The effect of donation of electron density from the symmetry adapted σ-orbitals of saturated groups to vacant π^*-orbitals of conjugated fragments of a molecular entity; this builds π-character into bonds that nominally possess only σ-character.

See also *Negative hyperconjugation*.

Hypercoordination—A property of main-group atoms in molecular entities to acquire *coordination numbers* greater than four (which would comply with the *Lewis octet rule*). Hypercoordination may be associated with *hypervalency*, but usually is referred to peculiar atomic centres in the *electron-deficient species* with multicenter σ-bonding, in which the bonding power of a pair of electrons is spread over more than two atoms. An example of a hypercoordinated atom is the five-coordinate carbon atom in the cation methanium, where three C–H bonds may be regarded as normal two center–two electron bonds and the bonding in the remaining CH_2 fragment is governed by the *three-center, two-electron bond*.
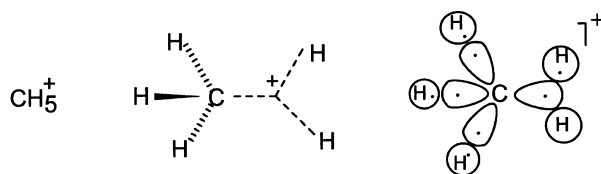
A particular case of a hypercoordinated atom is the hydrogen atom included into a *hydrogen bond* [106].

Hyperfine coupling—The interaction between the spin magnetic moment of an unpaired electron and the nuclear spin magnetic moments resulting in the splitting of the α (spin up) and β (spin down) energy

levels in an external magnetic field and, thus, in the multiplet pattern of the ESR spectra of radical-like species and transition metal compounds.

The main contributions to the hyperfine coupling are usually considered, Fermi contact and dipolar interactions. The contact interaction is isotropic and related to the unpaired *spin density* at the nucleus, $|\Psi_\sigma^2|$. The dipolar interaction is anistropic, and related to r^3, where r is the distance between the atom holding the unpaired electron and the nucleus with non-zero spin.

Hyperpolarizability (of *n*th order)—The energy of a molecule in an external electrostatic field can be expanded as

$$E = E^o - \mu_i F_i - (1/2)\alpha_{ij}F_iF_j - (1/6)\beta_{ijk}F_iF_jF_k| - (1/24)\gamma_{ijkl}F_iF_jF_kF_l - \dots$$

where E^o is the unperturbed energy, F_i is the component of the field in the i direction, μ_i is the permanent *dipole moment*, α_{ij} is the *polarizability* tensor, and β_{ijk} and γ_{ijkl} are the first and second hyperpolarizability tensors, respectively. β is a third order symmetric tensor that measures the second order response of the molecular electric dipole moment to the action of an external electric field and thus often referred to as *dipole hyperpolarizability* [107,108].

Hypervalency—The ability of an atom in a molecular entity to expand its valence shell beyond the limits of the *Lewis octet rule*. Hypervalent compounds are common for the second and subsequent row elements in groups 15–18 of the periodic table. A description of the hypervalent bonding implies a transfer of the electrons from the central (hypervalent) atom to the *nonbonding molecular orbitals* which it forms with (usually more electronegative) ligands. A typical example of the hypervalent bond is a linear *three-center, four-electron bond*, e.g. that of F_{ap}-P-F_{ap} fragment of PF_5 [109,110].

Imaginary frequency—The frequency of the normal vibration related to a negative eigenvalue (force constant) of the *Hessian matrix. Transition state* structure possesses only a single imaginary frequency.

Individual Gauge for Localized Orbitals (IGLO)—A method of calculation of nuclear shieldings, in which *localized molecular orbitals* associated with inner shell, bonding orbitals, and lone pairs have unique origins for the calculation of the diagmagnetic and paramagnetic terms. With this method, satisfactory estimates of NMR chemical shifts for elements in the first and second rows can be achieved in ab initio calculations with *basis sets* of moderate size provided sufficiently accurate molecular geometrics are used [111,112].

Inductive effect—The polarization of chemical bonds due to shifts of their electron pairs in the direction of the electronegative group. Within a molecule, the inductive effect is transmitted through space and is determined by electrostatic forces between the interacting sites. Another original (G. Lewis) model of inductive effect relates to through-bond transmission by successive polarization of the bonds between a dipolar or charged substituent and the reaction site. A quantitative assessment of the inductive effects of groups (substituents) is given by the Taft σ^*-constants (for aliphatic) and the inductive σ_I-constants (for aromatic) compounds.

Instability of Hartree–Fock solution—Existence of additional solutions to the equations of the *Hartree–Fock method* occurring usually in the case when *potential energy surfaces* of different *electronic states* are drawn close together. Within the *spin-restricted Hartree–Fock method (RHF)*, singlet and triplet instabilities are distinguished. The former involves the existence of another solution with lower energy and the electron distribution of lower symmetry. It may be regarded as an indication that the initially assumed molecular shape needs correction. The triplet instability involves rejection of the condition of double occupancy of *molecular orbitals* and thus transition to the *spin-unrestricted Hartree–Fock method (UHF)*. The triplet instability is a necessary, but insufficient, condition for the conclusion as to the *biradical* character of the *ground state* of a given system [113,114].

Internal conversion—Isoenergetic *radiationless transition* between two *electronic states* of the same *multiplicity*.

Internal rotation—The interconversion of stereoisomers through rotation of groups of atoms about a single bond. The internal rotation is called 'free' when the energy barrier is so low that different rotational isomers are not perceptible as individual chemical species (i.e. the characteristic time of the method of observation is longer than the lifetime of the rotational isomers). The inhibition of internal rotation by a sufficiently high rotational barrier makes the phenomenon observable on the time scale of the experiment, and is termed restricted or hindered rotation.

Intersystem crossing—Isoenergetic *radiationless transition* between two *electronic states* of different *multiplicity*.

Intrinsic barrier—The activation free-energy barrier associated with a reaction whose free-energy change is zero.

Intrinsic reaction coordinate—*A minimum-energy reaction path* on a *potential energy surface* in mass-weighted coordinates, connecting reactants to products via the *transition state* [115].

Ionic bond—The bond between atoms with sharply different *electronegativities*. In strict terms, an ionic bond refers to the electrostatic attraction experienced between the electric charges of a cation and an anion, in contrast with a purely *covalent bond*. In practice, it is preferable to consider the amount of ionic character of a bond rather than referring to purely ionic or purely covalent bonds. The relationship was proposed (L. Pauling) for the estimation of ionic character of a bond between atoms A and B;

Amount of ionic character $= 1 - e^{-1/4}(\chi_A - \chi_B)$

where χ_A and χ_B are the Pauling *electronegativities* of atoms A and B. This type of bonding is realized mostly in solids.

Ionization potential of an atom or a molecule—The minimal energy (I_X) needed for the detachment of an electron, i.e. $X + I_X \rightarrow X^+ + e^-$. When the ion is produced in its most stable state, (which is the case in e.g. photoionization or photoelectron spectroscopic techniques), the values I_x correspond to *adiabatic ionization potentials*. When a technique such as fast electron bombardment is used, where the ionization occurs during the period of collision, so that the ion X^+ retains the geometry of the initial X, the value of I_X is referred to as the *vertical ionization potential*.

See also *Koopmans' theorem*.

Isoconjugate systems—Molecular entities with similar conjugate networks which have the same number of π-electrons, e.g. cyclopentadienide and pyrrole or benzene and pyridine.

Isodesmic reaction—A reaction (sometimes hypothetical) in which the number of bonds of each given formal type, e.g. C–H, C–C, C=C, is conserved, but the relationship among the bonds is altered. An example is given for a formally conceivable reaction

$F_3C-C(=O)H + CH_4 \rightarrow CH_2F_2 + H_3C-C(=O)F$
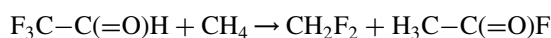
where three C–F, one C=O, and C–C and five C–H bonds are present in both reactants and products; only the environment in which bonds are located has changed. Due to the conservation of the number of electron pairs in the reactants and products the changes in their *correlation energies* are usually small, so that the energies of isodesmic reactions are generally well reproduced even by simple computational methods. This mades isodesmic reactions important interpretive tools and a means of providing thermochemical data [116,117].

Isogyric reaction—A reaction in which the number of electron pairs is conserved, for example [13]:

$CH_4(^1A_1) + H(^2S) \rightarrow CH_3(^2A_2') + H_2(^1\Sigma_g^+)$
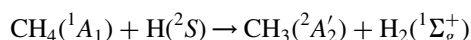
Isolobal analogy—The concept allowing one to establish relationships between the *isolobal groups* of organic, main-group and transition metal inorganic and organometallic compounds. The utility of the isolobal analogy is that, if an ML_n fragment is isolobal with a particular AL'_m arrangement, then one should be able to replace the former in a molecule with the latter to form a new compound possessing a very similar valence electron shell and even displaying similar reactivity. The isolobal analogy makes it possible to establish qualitative correspondence between the energy and the spatial (nodal) characteristics of *orbitals* of the groups formed by the main-group and transition elements as well as to analyze in an approximate manner the structure and reactivity of inorganic and organometallic compounds by analogy with those of simple organic compounds [118].

Isolobal groups—Molecular moieties for which the number, symmetry properties, occupation by electrons and approximate energy of *frontier orbitals* are similar. The isolobal relationship between the groups is denoted by a double-headed arrow with a tear-drop, for example [119]:

CH_2 ⟷ $Fe(CO)_4$ ⟷ $Ni(PPh_3)_2$ ⟷ $Co(\eta^5-C_5H_5)CO$ ⟷ $Cu(\eta^5-C_5H_5)$
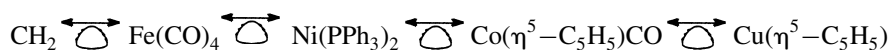
Isostructural reaction—A ligand exchange reaction, where the structural type of the metal complex remains the same.

$$ML_n + X \rightarrow ML_{n-1}X + L + \Delta E$$

Although these types of reactions are not necessarily *isodesmic reactions*, a substantial degree of error cancellation for the calculation energy, ΔE, is achieved because the coordination sphere of the metal atom M is conserved [120].

Isotopologues—Species that differ only in the isotopic composition of their molecules or ions.
See also *isotopomers* [121].

Isotopomers—Isomers due to the positions of nuclear isotopes, for example CH_2DOH and CH_3OD.

Jahn–Teller (JT) effect—Deals with molecular distortions due to an electronically degenerate *ground state*. For nonlinear molecular entities in a geometry described by a *symmetry point group* possessing degenerate irreducible representations there always exists at least one nontotally symmetric vibration that makes the *electronic states* with orbital degeneracy unstable at this geometry. The nuclei are displaced to new equilibrium positions of lower symmetry causing a splitting of the originally degenerate electronic states (first-order Jahn–Teller effect). In the case of molecules with a nondegenerate ground electron state, but with a very low lying *excited state*, distortions of proper symmetry arise which mix ground and excited states, and thereby lower the *ground state* energy (*pseudo Jahn–Teller* or *second-order Jahn–Teller effect*). The closer the states in energy, the more effective is the mixing. The pseudo Jahn–Teller effect manifests itself in fluxional behaviour (see *fluxional molecules*) and *stereochemical nonrigidity* of molecules and ions [122,123].
See also *Vibronic coupling, Peierls distortion*, and *Renner effect*.

Kinetic stability—The propensity of a molecular system not to undergo chemical changes in a reasonable period of time even in the presence of small external perturbations, owing to a high activation barrier.

Kohn–Sham orbitals—The functions $\Psi(r)$ in a set of one-electron equations derived by Kohn and Sham, from which one can obtain the exact *electron density* and hence the *total energy*.

$$\mathbf{H}^{eff}\Psi_i(r) = \epsilon_i\Psi(r) \qquad i = 1, 2, \dots n$$

where $\mathbf{H}^{eff}$ is the *effective* one-electron *hamiltonian*, generally expressed as a functional of electron density, $\rho(r)$ and ϵ_i are the energies associated with the $\Psi_i(r)$. The Kohn–Sham equations are fundamental

in *density functional theory* as they serve as a starting point for approximate methods. The electron density $\rho(r)$ can be calculated from the Ψ_is according to

$$\rho(r) = \sum_{i=1} |\Psi_i(r)|^2$$

The Kohn–Sham orbitals Ψ_i should not be confused with the *molecular orbitals* obtained in *Hartree–Fock method*. They have no physical significance other than in allowing the exact $\rho(r)$ to be calculated by the above equation [1,124,125].

Koopmans' theorem—Directly relates experimental *ionization potentials* with energy levels of *molecular orbitals*. The theorem states that the ionization potential required to remove an electron from the *orbital* Ψ_i is given by the negative value of the energy of the orbital, $-\epsilon_i$, as calculated within the *Hartree–Fock* approximation. The theorem is not applied to *localized molecular orbitals*, which are not eigenfunctions of the *effective hamiltonian*.

Landau–Zener model—A semiclassical model for the probability, P, of a *diabatic reaction* occurring by hopping from a *potential energy surface* for one *electronic state* to that of another at an *avoided crossing*.

$$P = \exp(-4\pi^2 \epsilon_{12}^2 / hV|s_1 - s_2|)$$

where ϵ is the energy gap between the two adiabatic electronic states at the crossing point, $|s_1 - s_2|)$ is the difference in slopes between the intersecting potential curves at this point, and V is nuclear velocity along the *reaction coordinate* [127].

Laplacian of the electron density—A characteristic used to reveal the distribution of electrons in molecular systems and crystals. It is defined as the sum of the three principal curvatures of the *electron density function* at each point in space, that is

$$\nabla^2 \rho(\mathbf{r}) = \partial^2 \rho/\partial x^2 + \partial^2 \rho/\partial y^2 + \partial^2 \rho/\partial z^2$$

When $\nabla^2 \rho(\mathbf{r}) < 0$, the value of ρ at point $\mathbf{r}$ is greater than its average value at neighboring points, and when $\nabla^2 \rho(\mathbf{r}) > 0$, ρ at $\mathbf{r}$ is less than its average value at neighboring points. Thus, the Laplacian of the electron density identifies regions of molecular space where $\rho(\mathbf{r})$ is locally concentrated or depleted; this information can be used to study directions of electrophilic and nucleophilic attacks. A negative value of $\nabla^2 \rho(\mathbf{r})$ in the internuclear region indicates the formation of *covalent bond*, while a positive value characterizes the interaction between *closed-shell molecular* (or atomic) *systems* [15].

Least motion, principle of—The statement that those elementary reactions are the most favored which exhibit the fewest possible alterations in the positions of the atomic nuclei and in the *electronic configuration*. The most frequently used mathematical formulation of the principle rests on a mechanical model of a molecule in which the energy of structural deformation, when reactants (r) turn into products (p), is assumed to be proportional to the sum of the squares of the change sin the positions of the nuclei common to both reactants and products

$$E = \sum_i f_i (q^p i - q^r i)^2$$

where f_i is the force constant (in many applications set equal to unity). The equation coincides with the relationship for the potential energy of small vibrations, hence it is valid only at a very early stage of a reaction. This is one of the reasons why many reactions violate the principle of least motion [126].

Lennard–Jones potential—see *van der Waals interactions*.

Lewis octet rule—A classical rule for describing the *electronic configuration* of atoms in molecules: the

maximum number of electron pairs that can be accommodated in the valence shell of a first-row element is four. For the second and subsequent row elements there are many exceptions to this rule. See *Hypervalency*.

Ligand field—see *Crystal field*.

Linear Combination of Atomic Orbitals (LCAO)—The approximation of the *molecular orbital* function as a linear combination of *atomic orbitals* chosen as the *basis functions*.

Localized molecular orbitals (LMO)—The *molecular orbitals* located on certain fragments of a molecular system and spatially separated from each other as much as possible. The LMOs are derived from the electron occupied *canonical molecular orbitals* by subjecting them to a unitary transformation determined by an appropriate physical criterion, e.g. by maximizing the sum of squares of the centroids of occupied MOs (the Foster–Boys procedure) or by minimizing the sum of the *exchange* (or *Coulomb*) *repulsion integrals* between the occupied MOs (the Edmiston–Ruedenberg procedure) [127,128].

Low-spin state—When the separation between the *highest occupied* and the *lowest unoccupied molecular orbitals* is not large, two alternative *electronic states* may be considered. The state with two electrons paired up in the HOMO is called a *low-spin state*. The low-spin state is the *ground state* when the one-electron energy needed to promote an electron to the LUMO is larger than the *Coulomb* and *exchange repulsion* energies required to pair up two electrons in the HOMO.

See also *High-spin state*.

Lowest Unoccupied Molecular Orbital (LUMO)—see *Frontier orbitals*.

Many body perturbation theory (MBPT)—In quantum mechanics, methods of *perturbation theory* which use an independent particle approximation to obtain the *zero-order wavefunction*.

Marcus equation—A relationship correlating free activation energy, $\Delta G^{\#}$, with the standard free energy, ΔG_o of a reaction in the particular solvent

$$\Delta G^{\#} = \omega^r + \lambda(1 + \Delta G'_o/\lambda)^2/4$$

where $\Delta G'_o = \Delta G_o + \omega^p - \omega^r$, ω^r (or ω^p) is the work required to bring the reactants (or products) together to the mean separation distance in the *transition state* structure, and the vertical *reorganization energy*, λ, is equal to the fourfold *intrinsic barrier*. Originally developed for treatment of outer-sphere electron transfer reactions, the Marcus equation has later been found to be applicable to proton transfer and group-transfer reactions [129,130].

Maximum hardness, principle of—A chemical system at a given temperature will evolve to a configuration of maximum *absolute hardness*, η, provided that the potential due to the nuclei, plus any external potential and the electronic chemical potential remain constant. In terms of *molecular orbital theory*, the highest value of η reflects the highest possible energy gap between the *lowest unoccupied* and *highest occupied molecular orbitals*; this value correlates with the stability (see *structural stability*, *electronic stability*, *thermodynamic stability* and *kinetic stability*) of a system [131,132].

Mesomeric effect (synonymous with *Resonance effect*)—The intramolecular polarization of a conjugated molecular system brought about by a substituent whose p_π or π-orbitals overlap with the π-MOs of the conjugated moiety. A distinctive feature of the mesomeric effect, as compared with the *inductive effect*, is that it causes alternation of the *electron density* in the conjugated chain or ring to which the mesomeric substituent is attached. Electron-releasing substituents with lone electron pairs (e.g. hydroxy, amino groups) are said to exert positive mesomeric effects, whereas substituents with low-lying *lowest unoccupied molecular orbitals* are characterized by negative mesomeric effects.

Metropolis algorithm—see *Monte Carlo, method of.*

Microscopic reversibility, principle of—For a system in thermodynamic equilibrium not only the total number of molecules leaving a given quantum state in unit time will equal the number arriving in the state in unit time, but also the number leaving by any one particular path will be equal to the number arriving by the reverse of that path. The principle was widely applied to the analyses of reaction mechanisms, in particular of substitution reactions. In the case of S_N2 reactions at tetrahedral centers implying a formation of the trigonal bipyramid *transition state* (or intermediate) structure, the original formulation of the principle was extended in the following way: if a molecule or reactant enters a trigonal bipyramid at an apical position, this (or another) molecule or reactant must likewise leave the trigonal bipyramid from an apical position [133,134].

Minimal basis set—see *Basis set.*

Minimum energy reaction path (MERP)—The trajectory orthogonal to the equipotential contours of a *potential energy surface*, which connects the energy minima through a common *saddle point* (*transition state*) from which it slopes downward along the steepest descent lines in $3N-6$ configurational space (N is the number of nuclei in the reacting system). The methodology of MERP allows one to transform the large number of nuclear coordinates needed to specify the geometry of a polyatomic system to a unique coordinate. The remaining coordinates vary smoothly between their values at each end point of the MERP [135].

Möbius system—A cyclic π-conjugated ribbon-like (see *Ribbon delocalization*) delocalized molecular system whose basis *atomic orbitals* are organized in a Möbius strip. In contrast to Hückel systems, whose orbital basis sets of a ring have zero or even number of phase inversions, Möbius type systems are characterized by an odd number of nodes. The *electron counting rule* for the stability of Möbius systems is opposite to the *Hückel rule*: the $4n$ electron Möbius systems have a closed electron shell, while the shell of the $(4n+2)$ electron Möbius systems is open (97,136].

Molecular dynamics (MD), method of—A method of computational modeling of the static (equilibrium) and dynamic (kinetic) properties of many-particle systems by solving numerically the classical Newtonian equation assuming a predetermined force potential and a protocol for preparation of the system from a rational starting configuration to monitor the movement of molecules in liquid or solution, define the phase trajectories and then average over time, and obtain the magnitudes of the functions examined [137,138].

See also *Monte Carlo*, *method of.*

Molecular electrostatic potential (MEP)—see *Electrostatic potential.*

Molecular entity—A general term applied to any constitutionally or isotopically distinct atom, molecule, ion, ion pair, radical, radical ion, complex, conformer etc., identifiable as a separately distinguishable entity [38].

Molecular graph—The *graph* with differently labeled (colored) vertices (*chromatic graph*) which represent different kinds of atoms and differently labeled (colored) edges related to different types of bonds. Within the *topological electron distribution theory*, a complete network of the *bond paths* for a given nuclear configuration.

Molecular graph theory—The theory which deals with analyses of all consequences of connectivities inherent in molecular structure and chemical transformations. The theory does not produce numerical data but uses available data and searches for regularities that can be attributed to combinatorial and topological origins [139,140].

See also *Molecular graph*, *Reaction graph.*

Molecular graphics—Rendering a molecule as output by a computer for display. Sometimes molecular properties are also shown.

Molecular mechanics (synonymous with *force field* method)—Method of calculation of geometrical and energy characteristics of molecular entities on the basis of empirical potential functions (*force field*) the form of which is taken from classical mechanics. The method implies transferability of the potential functions within a network of similar molecules. An assumption is made on 'natural' bond lengths and angles, deviations from which result in bond and angle strain respectively (see *Strain energy*). In the simplest models, the total potential energy, V_{total}, is broken down into four components:

$$V_{\text{total}} = \sum V_{\text{r}} + \sum V_{\Theta} + \sum V_{\phi} + \sum V_{\text{vdW}}$$

where the sums represent respectively contributions due to bond stretching and compression terms, valence angle bending terms, internal rotation or torsional terms and van der Waals interactions. In practice, electrostatic terms and some other terms (improper torsion or out-of-plane bending terms, various cross-terms) are also taken into account [141].

Molecular modeling—Generation, manipulation, and/or representation of molecular structures and associated physicochemical properties on a computer.

Molecular orbital (MO)—*see Orbital*.

Molecular orbital (MO) theory—An approach to molecular quantum mechanics which uses one-electron functions (*orbitals*) to approximate the full *wavefunction*.

Molecular Rydberg state—An excited *electronic state* which is composed primarily of *atomic orbitals* with principal quantum numbers greater than that of the *ground state* and the valence excited states. Such electronic states typically have a large *polarizability* [142].

Møller-Plesset (MP) perturbation theory—An approach to *electron correlation* which adds higher excitations to *Hartree–Fock method* using the technique from many body *perturbation theory*. Whereas the first perturbation to the HF energy (MP2 method) will always lower the *total energy*, the higher-level MP orders may be positive. They are also capable of overcorrecting the energy, since the theory is not variational (see *Variational principle*) [23].

Monte Carlo (MC), method of—In mathematics, a method originally used for calculating multiple integrals by means of a random sample. The method is used for numerical modeling of many-particle chemical systems, in particular liquids; it is based on the equilibrium statistical mechanics theory. Observables A are calculated as mean values over a great number ($\cong 10^5 - 10^6$) of instant configurations as determined by coordinates of the particles.

$$<A> = 1/N \sum_{i=1}^{N} A\{r_i\}$$

where N is the number of configurations. At the first stage, various configurations are randomly generated and then those energetically unrealizable eliminated. An efficient search for the most probable configurations to be entered into the above expression is provided by the *Metropolis algorithm* based on the principle of Markov's chain theory. While being elaborated for the study of equilibrium chemical systems, MC method is also applied to studies of the dynamics of chemical reactions.

   See also *Molecular dynamics, method of*.

Morokuma analysis—An energy partitioning scheme for the interaction energy between atoms or

fragments A and B in the molecule A–B. The interaction energy is given as sum of three terms: electrostatic (which gives the interaction between the frozen charge distribution of A and B in the geometry of A–B), exchange interaction and the orbital relaxation energy (the energy change when the orthonormal orbitals of the fragments change into the final MO's of A–B). The latter term is decomposed further into a polarizaiton term, which arises from the mixing of occupied and empty orbitals of the same fragment, and a charge transfer term which gives the mixing of occupied orbitals of one fragment with the empty orbitals of the other fragment. The Morocuma analysis is similar to the *Extended transition state* method [143].

Morse potential—The empirical function relating the potential energy of a molecule to the interatomic distance r accounting for the anharmonicity (see *harmonic approximation*) of bond stretching:

$$E(r) = D_e\{1 - \exp[-a(r - r_e)]\}^2$$

where D_e is the *bond-dissociation energy*, r_e is the equilibrium *bond length*, and a is a parameter characteristic of a given molecule.

Mulliken population analysis (MPA)—A partitioning scheme based on the use of density and overlap matrixes of allocating the electrons of a molecular entity in some fractional manner among its various parts (atoms, bonds, *orbitals*). As with other schemes of partitioning the *electron density* in molecules, MPA is arbitrary and strongly dependent on the particular *basis set* employed. However, comparison of population analyses for a series of molecules is useful for a quantitative description of intramolecular interactions, chemical reactivity and structural regularities [13,144].

See also *Atomic charge*, *Bond order*.

Multicenter bond—A type of chemical bonding for which a localized description requires involvement of more than two atomic centers. See also *Three-center*, *two-electron* and *Three-center*, *four-electron bonds*.

Multiconfiguration SCF (MC SCF) method—The *configuration interaction* method in which simultaneous optimization of both the shapes of *molecular orbitals* and contributions from different *electronic configurations* is carried out by use of the *variational method*. The MC SCF method with a large enough set of configurations allows better estimation of the *correlation energy* as compared with the conventional CI method.

Multiplicity—The existence of several degenerate *wavefunctions* distinguished only by the relative orientation of the angular spin momentum. Defined by the total angular spin momentum S, it is given by $2S + 1$.

Multi-reference configuration interaction (MRCI)—*Configuration interaction* method in which the configurations are built by excitations out of a wavefunction obtained by using *multiconfiguration SCF method*.

Narcissistic reaction—The degenerate transformation in which the structure of the products can be viewed as a reflection of the structure of the reactants in a mirror plane, which is a symmetry element absent in both the reactants the products. An example is the pyramidal inversion of ammonia [145].
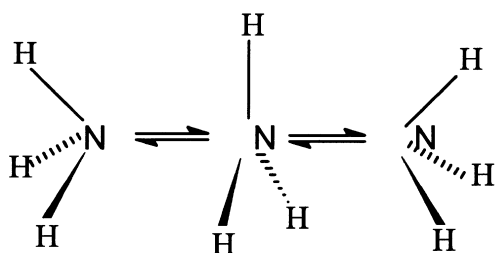
Natural atomic orbital (NAO)—A valence-shell *atomic orbital* whose derivation involves diagonalizing the localized block of the full density matrix of a given molecule associated with *basis functions* $\chi_i(A)$ on that atom. A distinguishing feature of NAOs is that they meet the simultaneous requirement of orthonormality and maximum occupancy. For isolated atoms, NAOs coincide with *natural orbitals*. In a polyatomic molecule the NAOs (in contrast to natural orbitals that become delocalized over all nuclear centers) mostly retain one-center character, and thus are optimal for describing the molecular *electron density* around each atomic center [146].

Natural bond orbital (NBO)—The *orbital* which is formed from *natural hybrid orbitals*. For a localized σ-bond atoms A and B, the NBO is:

$$\sigma_{AB} = c_A h_A + c_B h_B$$

where h_A and h_B are the natural hybrids centered on atoms A and B. NBOs closely correspond to the picture of localized bonds and lone pairs as basic units of molecular structure, so that is possible to conveniently interpret *ab initio wavefunctions* in terms of the classical Lewis structure concepts by transforming these functions to NBO form [110].

Natural hybrid orbital (NHO)—Symmetrically orthogonalized directed *hybrid orbital* derived through unitary transformation of *natural atomic orbitals* centered on a particular atom.

Natural orbital—The *orbitals* defined (P. Löwdin) as the eigenfunctions of the spinless one-particle *electron density* matrix. For a *configuration interactions wavefunction* constructed from orbitals ϕ, the *electron density function*, ρ, is of the form:

$$\rho = \sum_i \sum_j a_{ij} \phi_i^* \phi_j$$

where the coefficients a_{ij} are a set of numbers which form the density matrix. The NOs reduce the density matrix ρ to a diagonal form:

$$\rho = \sum_k b_k \phi_k^* \phi_k$$

where the coefficients b_k are occupation numbers of each orbital. The importance of natural orbitals is in the fact that CI expansions based on these orbitals have generally the fastest convergence. If a CI calculation was carried out in terms of an arbitrary *basis set* and the subsequent diagonalization of the density matrix a_{ij} gave the natural orbitals, the same calculation repeated in terms of the natural orbitals thus obtained would lead to the *wavefunction* for which only those configurations built up from natural orbitals with large occupation numbers were important [33,147].

Natural population analysis (NPA)—The analysis of the *electron density* distribution in a molecular system based on the orthonormal *natural atomic orbitals*. Natural populations, $n_i(A)$ are the occupancies of the natural atomic orbitals. These rigorously satisfy the *Pauli exclusion principle*: $0 < n_i(A) < 2$. The population of an atom $n(A)$ is the sum of natural populations.

$$n(A) = \sum_A n_i(A).$$

A distinguished feature of the NPA method is that it largely resolves the *basis set* dependence problem encountered in the *Mulliken population analysis* method [110].

Negative hyperconjugation—The effect of donation of electron density from filled π or n_π-orbitals to the symmetry adapted σ*-orbital(s) of σ-bond(s) of a molecular entity resulting in building π-character into bonds that nominally possess only σ-character. The consequences of the effect are, for example, in elongation of the C–F bond in the β-fluoroethyl anion and stabilization of the antiperiplanar conformation of fluoromethylamine [110,148].
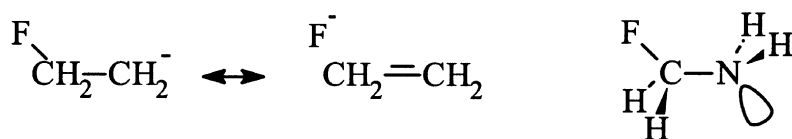
Nodal plane—A plane of a system in which the value of the orbital *wavefunction* equals zero. This plane defines a region of zero *electron density* for the *orbital*.

Nonadiabatic reaction—Synonymous with *Diabatic reaction*.

Nonbonding molecular orbital—A *molecular orbital* whose occupation by electrons does not contribute (or contributes insignificantly) to the *binding energy* of the molecule. Generally, a nonbonding MO represents the *highest occupied molecular orbital* of a molecule.

Nonclassical structure—The structure of molecules or molecular ions that escapes description in terms of conventional rules of valency and stereochemistry. Nonclassical structures are characteristic of carbonium ions with hypercoordinated (see *hypercoordination*) carbon atoms, e.g. the ion methanium **1**, pyramidal dication $C_6H_6^{2+}$, **2** (isomeric to benzene dication), and the molceular species whose structure cannot be adequately represented by the equilibrium (2-norbornyl cation, **3**) or resonance of two or more classical structures. From the stereochemical point of view, those structures are assigned to the nonclassical type for which all tetracoordinate carbon bonds extend into a single hemisphere, i.e. the valence angle of a carbon atom is greater than 180°. A hypothetical example is tetracyclo[2.1.0.0^{1,3}.0^{2,5}] pentane (pyramidane), **4**, the structure of which corresponds to a local minimum on the C_5H_4 potential energy surface [149,150].
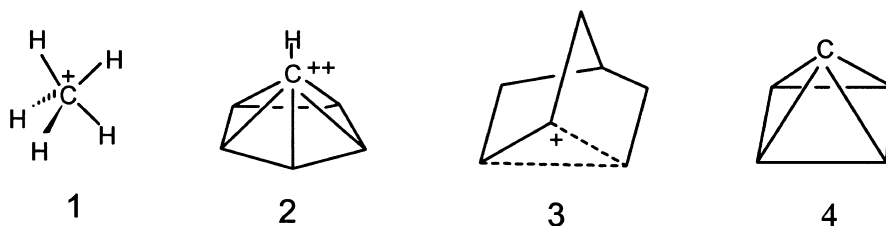
Noncrossing rule—Energy levels of orbitals of the same symmetry cannot cross each other along a *reaction coordinate*. The rule is applied also to the energy variation of *electronic states* [21,43].

Nonempirical quantum mechanical methods—see *Ab initio quantum mechanical methods*.

Non-Kekulé molecules—Molecules that are fully conjugated, but each of those Kekulé structures contains at least two atoms that are not π-bonded. Examples of non-Kekulé hydrocarbons are trimethylenemethane (2-methylidenepropane-1,3-diyl) **1**, *m*-benzoquinodimethane (benzene-1,3-diyldimethyl) **2**, and 1,2,4,5-tetramethylenebenzene (benzene-1,2,4,5-tetrayltetramethyl) **3** [99,151].
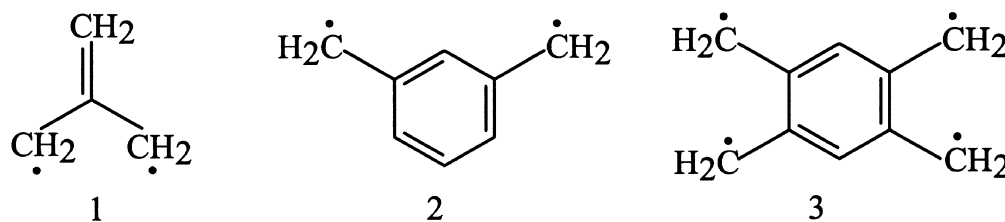
Normalization—A mathematical procedure which ensures that the integral of the square of modulus of a *wavefunction* over all space equals 1. The constant required to ensure that a wavefunction is normalized is termed the normalization constant.

Open-shell systems—Atomic or molecular systems in which the electrons are not completely assigned to *orbitals* in pairs.

Orbital (Atomic or Molecular)—A *wavefunction* which depends explicitly on the spatial coordinates of only one electron.

Orbital correspondence analysis in maximum symmetry (OCAMS), method of—An extension of the *correlation diagram* procedure for determining *reaction paths*. The reactant(s) and product(s) are set up in their highest common *symmetry point group*. The preferred reaction path retains the symmetry of a subgroup in which all of the occupied *molecular orbitals* correlate across the diagram. Inclusion of the symmetry properties of the components of the *spin-orbit coupling* operator allows application of the method to thermal and photochemical reactions that do not conserve electron spin [152].

Orbital interaction—Interaction of two orbitals due to their overlap which results in the formation of two new orbitals, one of which is lower in energy than the lowest energy level of the initial orbitals, while the energy level of another new orbital lies higher than the highest energy level of the initial orbitals. The notion may be extended to the interaction of several orbitals. In *perturbation theory*, the energy of the orbital interaction is proportional to the square of the *overlap integral* and inversely proportional to the energy difference between the interacting orbitals [119].

Orbital interaction diagram—A diagram which portrays in a qualitative or quantitative manner the splitting of the energy levels due to an *orbital interaction*.

Orbital isomers—Species distinguishable by different occupation of a set of available MOs [153].

Overlap integral—The integral defining the summation over the space of the overlap of the electron density of two *orbitals*: $S_{\mu\nu} = \int \phi_\mu \phi_\nu d\tau$.

Pariser–Parr–Pople (PPP) method—A *semiempirical quantum mechanical method* of calculation of the properties of conjugated molecules and ions from *self-consistent-field* theory and the *π-electron approximation*.

Pauli exclusion principle—A rule, complementary to the *aufbau principle*, of building up the *electronic configuration* of atoms and molecules: a maximum of two electrons can occupy an *orbital* and then only providing that the spins of the electrons are paired, i.e. opposed. The principle demands that the *wavefunction* for a many-electron system must be asymmetric with respect to the permutation of the space-spin coordinates for every pair of electrons.

Pauling's bond order—see *Fractional bond number*.

Peierls distortion—The distortion of a regular one-dimensional structure with a partially occupied band to give bond alternation, eventually leading to dimerization or oligomerization. The degree of oligomerization λ depends on the *electronic population* of the conduction band indicated by *wave vector* of the *Fermi level*, k_F

$$\lambda = 2\pi/k_F$$

A Peierls distortion opens a gap at the Fermi level, producing a net stabilization of the distorted structure. The Peierls distortion for chain compounds is analogous to the *Jahn–Teller effect* for molecules. The prototypical example of the Peierls distortion in organic chemistry is the bond alternation present in polyacetylene.
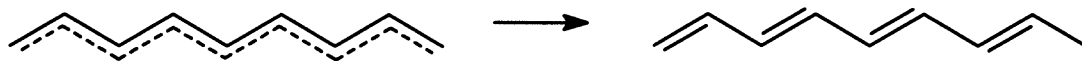
Perfect pairing—The term used to describe corollaries of the Coulson–Rushbrooke pairing theorem for *alternant hydrocarbons*: (a) the *molecular orbitals* of an even alternant hydrocarbon occur on pairs with energies $\alpha \pm E_\mu$, α being the *Coulomb integral* for carbon; (b) the coefficients at *atomic orbitals* of the paired molecular orbitals are numerically the same, but their signs at atomic orbitals of starred atoms are reversed in going from one molecular orbital to the other; (c) in an odd alternant hydrocarbon, with the total number of molecular orbitals odd, all but one of the molecular orbitals is paired. the odd molecular orbital has energy α (see *nonbonding molecular orbital*) and is confined to the starred atoms.

Pericyclic reaction—Reactions in which all first-order changes in bonding relationships take place in concert on a closed curve, i.e. throughout a cyclic array of continually bonded atoms forming a fully conjugated cyclic *transition state*. An example of a pericyclic reaction is the 3,3-sigmatropic (Cope) rearrangement of hexa-1,5-diene [43].

Permutation group of the set of n objects—The set of all possible permutations that can be applied to a given set of objects, together with the composition operation. For example for a set of three objects (vertices of a graph, atomic centers etc.) the permutation group consists of six permutations: id, ((1,2)), ((1,3)), ((2,3)), ((1,2,3)), ((1,3,2)), where id is the permutation which leaves each object fixed.

Permutational isomerization—see *Automerization*.

Perturbation theory—Along with *variational method*, the second major quantum-mechanical approximation method. The methods of perturbation theory are based on representation of the *Hamiltonian* of a system under study, H, through the Hamiltonian, H^0, of a system, whose Schroedinger equation is solvable, and its relatively small perturbation H': $H = H^0 + H'$. Numerous techniques are derived allowing one to relate the unknown eigenvalues and eigenfunctions of the perturbed system to the known eigenvalues and eigenfunctions of the unperturbed system. As distinct from the variational method, the methods of perturbation theory are applicable to all the *electronic states* of an atom or molecule. When H' is time-dependent, the perturbed system does not have *stationary states*. In this case time-dependent perturbation theory, which is the method of approximate calculation of the expansion of *wavefunctions* of the perturbed system over wavefunctions of stationary states of the unperturbed system must be employed. The applications of this method are associated mostly with studies of light emission and absorption by atoms and molecules.

See also *Møller-Plesset (MP) Perturbation Theory*.

Phonon—A quantized vibration of a crystalline lattice. In contrast to *photons*, phonons are quasiparticles.

Photon—The quantum of electromagnetic energy at a given frequency.

Pi (π) electron approximation—The assumption that in planar unsaturated molecular entities, whose π-*molecular orbitals* do not mix with σ-molecular orbitals, the molecular *wavefunction* is rigorously separated into $\Psi = \Psi_\sigma \Psi_\pi$. The σ-electron shell serves as a nonpolarizable core (see *core approximation*) merely providing part of the effective potential for the motion of π-electrons, i.e. Ψ_σ remains the same for any state of the π-system.

Point group—see *Symmetry point group*.

Polarizability (static dielectric polarizability)—A measure of the linear response of the electronic cloud of a chemical species to a weak external electric field. For isotropic molecules, the *dipole moment*, μ_i, produced by a field, $\mathbf{E}$, of unit strength

$$\mu_i = \alpha\mathbf{E}$$

In the general case, the polarizability is anisotropic, i.e. dependent on the position of the molecule with respect to the field and α is replaced by a function (symmetrical tensor) which defines the induced dipole moment for each possible direction of the electric field. The polarizability defined on an experimental basis is the average polarizability, i.e. the sum of polarizabilities (b_i) in three principal directions, b_1 being collinear with the external field [107,154].

$$\alpha_{ave} = (1/3)(b_1 + b_2 + b_3)$$

Polarization—The readjustment of a charge distribution when it experiences an external *electrostatic potential*. Polarization, $\mathbf{p}$, is usually measured as the *dipole moment* induced in a unit volume

$$\mathbf{p} = Nd\alpha\mathbf{E}/M$$

where α is *polarizability*, M/d is the molar volume (M is the molecular mass and d is density), and $\mathbf{E}$ is applied electric field.

Polarized basis set—see *Basis set*.

Polarizable continuum model (PCM)—A *self-consistent reaction field method* to treat solvation effects, which employs a van der Waals surface type cavity instead of a spherical cavity in the standard SCRF procedures.

Polyhedral skeletal electron pair approach—see *Wade's rules*.

Potential Energy Surface (PES)—Within *the adiabatic approximation*, the function of the total energy of a molecular system (minus kinetic energy of the nuclei) of the coordinates of all nuclei which this system contains.

See also *Energy hypersurface*.

Predissociation—Dissociation of a molecule occurring through its excitation to a certain bound state which is coupled to a dissociative continuum. Predissociation is caused by interaction between discrete levels of a given *electronic state* and the dissociative continuum of another electronic state. Predissociation manifests itself by the appearance of the line broadening, a decrease in lifetime, an abrupt decrease of fluorescence (quantum yield and generation of dissociation products [155].

Prereactive complexes—Weakly bound complexes with a potential minimum that precede the activation barrier along the *reaction path*. In contrast with the *van der Waals complexes* which fall apart reversibly into their constituents, the prereactive complexes may undergo a vigorous reaction to form different products [156].

Prochirality—The property of an achiral object to acquire *chirality* through a single desymmetrization step, e.g. addition to it of a new atom or achiral group or substitution of an existing atom or achiral group by different ones.

Proton affinity (of a given base Z)—The negative of the enthalpy change at 298 K for the gas phase reaction of an atomic or molecular entity with a proton

$$H^+ + Z \rightarrow HZ^+$$
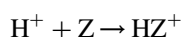
Pseudo Jahn–Teller effect (synonymous with *Second-order Jahn–Teller effect*)—see *Jahn–Teller effect*.

Pseudopericyclic reaction—A reaction from the subset of *pericyclic reactions* for which there is no cyclic orbital overlap. An example of pseudopericyclic orbital topology is given by the reaction of decarbonylation of furan-2,3-dione to give 4-oxoprop-2-enal [157,158].
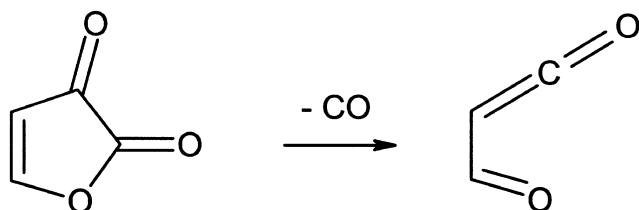
Pseudopotential approximation—see *Core approximation*.

Pseudorotation—A conformational change resulting in a structure that appears to have been produced by rotation of the entire initial molecule and is superimposable on the initial one, unless different positions are distinguished by substitution or isotopic labeling. No angular momentum is generated by this motion; this is the reason for the term. An example is the facile interconversion of the envelope and twist conformers of cyclopentane. A particular case is the *Berry pseudorotation*.

Quantitative structure-activity relationships (QSAR)—Mathematical models designed for the correlation of various types of biological activity, chemical reactivity, equilibria, physical and physicochemical properties with electronic, steric, hydrophobic and other factors of a molecular structure of a given series of compounds such as substituent constants, *topological indices* as well as with solvent and other physicochemical parameters [30,159].

Quantum mechanical resonance energy (QMRE)—see *Resonance energy, various types of*.

Radiationless transition—A transition between two states of a system without photon emission or absorption.

Radical—A *molecular entity* possessing an *atomic* or *molecular orbital* occupied by one electron. A radical (*free radical*) has a net electronic spin experimentally observable in paramagnetic behaviour. Paramagnetic metal ions are not normally regarded as radicals [38].

Reaction cordinate—A structural parameter or a certain function of several of these, the variation of which along the *reaction path* defines the *energy profile* of a given reaction. In mathematical terms, the arc length along the *minimum energy reaction path*.

Reaction field—The response field from the induced *polarization* charges of an outer medium which creates an extra potential at the immersed molecule. The reaction field interacts with the solute molecular system giving rise to a solvent effect (see also *solvation energy*).

Reaction graph—Topological representation of either all possible reactions that occur (or can occur) in a given chemical system or a subset of these reactions, for which each vertex stands for a component of the system (molecule or ion) and each edge connecting two given vertices stands for the reaction path. Most usable are the reaction graphs for intramolecular rearrangements, with vertices standing for isomers and edges standing for their isomerization paths [160].

Reaction path—The gradient line (or classic trajectory) in the configurational space interconnecting the reactant and product energy minima on the *potential energy surface* [161–164].
    See also *Intrinsic reaction coordinate*, *Minimum energy reaction path*.

Reaction path Hamiltonian (RPH)—A *Hamiltonian* that deals with the dynamics occurring in a small amplitude many-dimensional harmonic valley centered on the *reaction path* as determined by the *intrinsic reaction coordinate*. By calculating curvature properties of the reaction path and coupling between the small amplitude degrees of freedom, insight into the mechanism of energy disposal along the reaction path is conveniently gained [165].

Reaction profile—see *Energy profile*.

Relative hardness—The difference between the values of the absolute hardnesses (η) of a given molecule and the corresponding reference structure (η_a): $\eta_r = \eta - \eta_a$. The values of relative hardnesses correlate well with the *resonance energies* of cyclic compounds and may be used as an index of *aromaticity*.

Relativistic effects—Corrections to exact nonrelativistic energy from the fact that inner shell electrons in heavy atoms move with velocities comparable in order of magnitude to the velocity of light. The most important relativistic effect is *spin-orbit coupling*. See also *spin-spin coupling* [166].

Renner effect—The dynamic instability of linear molecular species in the *degenerate electronic states*. The Renner effect is a particular case of the *Jahn–Teller effect*.

Reorganization energy—The energy (term λ in the *Marcus equation*) required for all structural adjustments (in the reactants and in the surrounding solvent molecules) which are needed in order to arrange the reactants in the reactive configuration [38].

Resonance effect—see *Mesomeric effect*.

Resonance energy (RE), various types of—Part of the *total energy* due to electron *delocalization*. To find the value of the resonance energy (RE), the difference must be calculated between a quantity characterizing experimentally determined energy of a given molecule (such as *heat of atomization* or *heat of formation*) and the same characteristic obtained with the aid of an additive scheme, e.g. sum of the *bond energies* (*thermochemical resonance energy*). When the *total energy* or the heat of formation (atomization) is calculated with use of quantum mechanical methods, the RE value is referred to as the *quantum mechanical resonance energy* (QMRE). Various schemes for the determination of QMRE are distinguished by the choice of the reference structure which should have non-interacting π-bonds. In the framework of the *valence bond theory*, the reference structure is represented by a single (usually the most stable) *resonance structure*.

Hückel resonance energy, HRE, is equivalent to the *delocalization energy*, DE. For a conjugated hydrocarbon

$$HRE = DE = -[E_\pi - n_{C=C}(2\alpha + 2\beta)]$$

where n is the number of π-bonds and E_π is the total π-electron energy.

Dewar resonance energy, DRE, is the quantity which allows one to account for the effects of cyclic electron delocalization and thus serves as a measure of the aromatic stabilization (see *aromaticity*) of a cyclic molecular entity. The model reference structure is not a system of isolated π-bonds (as is the case for HRE), but a hypothetical cyclic polyene with the number of the π- and σ-bonds equal to that in a given molecule. The condition of the additivity of bond energies for cyclic polyenes is adopted.

$$DRE = \Delta H_a - H_a^{add}$$

where ΔH_a is the calculated heat of atomization of a given conjugated molecule and ΔH_a^{add} is the heat of atomization for the reference structure.

Topological resonance energy, TRE—The TRE scheme rests on the formalism of *graph theory*. A *characteristic polynomial* is constructed for the reference structure with only the acyclic Sachs graphs for

the given molecule taken into account. An advantage of the TRE scheme is in the fact that it can be easily extended to radicals and ions and applied to *excited states*.

For the purposes of comparison of the resonance energies of molecules of different sizes, the normalized quantity *resonance energy per electron*, REPE, has been introduced [8,49].

Resonance energy per electron (REPE)—see *Resonance energy, various types of*.

Resonance hybrid—A localized valence bond representation of a molecule. This describes pictorially an electronic *wavefunction* that makes some contribution to the state wavefunction of the system. Resonance hybrids are needed to describe the state of a system when that system is not adequately described by a single Lewis structure.

Resonance integral—In the *LCAO MO approximation*, the energy of the overlap electron density between the *atomic orbitals* χ_μ and χ_ν due to attraction by the core (see *Core approximation*).

In *semiempirical quantum mechanical methods* resonance integrals are adjustable parametric functions or parameters designed to achieve better agreement with experimental data.

Restricted Hartree–Fock (RHF) method—see *Hartree–Fock method*.

Ribbon delocalization—Electron *delocalization* realized in both acyclic and cyclic π-conjugated, **1**, and σ-bonded. **2**, ribbon-like systems.

1   **2**

For cyclic systems, a variety of linkage fashions between several ribbons (pericyclic, spirocyclic, longicyclic and laticyclic) is possible.

Rice, Ramsperger, Kassel and Marcus (RRKM) theory—A theory of unimolecular and recombination reactions based on the application of *transition state* theory to a microcanonical ensemble of excited reactant molecules.

Rydberg orbital—For an atom, an *orbital* whose principal quantum number is greater than that of any occupied orbital of the *ground state*. For a molecular entity, a *molecular orbital* which correlates with a Rydberg *atomic orbital* in an atomic fragment produced by dissociation.

Rydberg state—An *electronic state* that arises by the excitation of a valence electron to a diffuse atomic-like orbital. For instance, the lowest lying Rydberg state (n, 3S) of NH_3 can be described as resulting from the excitation of a nonbonding orbital to a 3S *Rydberg orbital* [167].

Saddle point—A point of lowest maximum energy on a valley (*reaction path*) connecting two minima on the *potential energy surface*. In mathematical terms, the stationary point on the PES in which the *Hessian matrix* has only one negative eigenvalue is assigned to the saddle point of the first rank. The saddle point is associated with the *transition state* structure.

Scaling factor—A variational parameter (see *variational method*) used as a multiplier of each nuclear Cartesian and electronic coordinate chosen to minimize the variational integral and to make a trial variation function to satisfy the *virial theorem*. In practical calculations, the numeral factor to scale computed values, e.g. vibrational frequencies, to those found in experiments.

Second-order Jahn–Teller (SOJT) effect—see *Jahn–Teller effect*.

Secular equation—In *molecular orbital theory*, the determinant of matrix elements whose solution leads to the set of energy levels of *molecular orbitals* for a given system.

Selection rule—A rule which states whether a given transition or process is allowed or forbidden (i.e. its intensity is high or zero, or close to zero) on the basis of the symmetry or spin of the *wavefunctions* of the initial and final states.

Self-Consistent Field (SCF) method—see *Hartree–Fock method*.

Self-Consistent Reaction Field (SCRF) methods—Methods designed to treat solvation effects which incorporate the essential elements of the reaction field theory in the conventional SCF approach. The classical reaction field is treated as a perturbation, so that the hamiltonian is given by

$$H_{SCRF} = H_O + H_{RF}$$

Semiempirical quantum mechanical methods—Methods which use parameters derived from experimental data to simplify computations. The simplification may occur at various levels: simplification of the *Hamiltonian* (e.g. as in the *Extended Hückel method*), approximate evaluation of certain molecular integrals (see, for example, *Zero differential overlap approximation*), simplification of the wavefunction (for example, use of a *Pi (π) electron approximation* as in *Pariser–Parr–Pople method*) etc. [168,169].

Singly occupied molecular orbital (SOMO)—see *Frontier orbitals*.

Size consistency—A property which guarantees that the method scales properly with the number of particles, i.e., when doubling the size of the system investigated and keeping the particle density constant, the energy of the system should double.

Slater determinant—The determinantal representation of many-electron *wavefunction* Ψ which conforms to the requirement of the *antisymmetry principle*.

Slater type atomic orbital (STO)—The exponential function centered on an atom; its radial dependence is given by $Nr^{n-1}\exp(-\zeta r)$, where n is the effective principal quantum number and ζ is the orbital exponent (screening constant) derived from empirical considerations. The angular dependence is usually introduced by multiplying the radial one by a spherical harmonic $\gamma_{1m}(\theta\Phi)$.

Soliton—Vibration coupled with longitudinal sound waves propagated as localized quasiparticles. From a chemical point of view, a solution can be regarded as a migrating region of conformational change.

Solvation energy—The change in Gibbs energy when an ion or molecule is transferred from a vacuum (or the gas phase) to a solvent. The main contributions to the solvation energy come from: (a) the cavitation energy of formation of the hole which preserves the dissolved species in the solvent; (b) the orientation energy of partial orientation of the dipoles; (c) the isotropic interaction energy of electrostatic and dispersion origin; and (d) the anistropic energy of specific interactions, e.g. *hydrogen bonds*, donor-acceptor interactions etc.

Spin conservation rule—see *Wigner rule*.

Spin contamination—In *unrestricted Hartree–Fock method*, the *wavefunctions* obtained are eigenfunctions of the *Hamiltonian* and the *spin projection S_z* operators, but not eigenfunctions of the S^2 operator. As a result, the wavefunctions of the doublet systems are spin contaminated to some extent by admixtures of quartet, sextet, and higher spin states. The eigenvalues of the S^2 operator are given as a measure of the spin contamination [170].

Spin crossover—A type of molecular magnetism that is the result of electronic instability (see *electronic stability*) caused by external constraints (temperature, pressure, or electromagnetic radiation), which induce structural changes at molecular and lattice levels. The phenomenon is most characteristic of first-row transition metal complexes, e.g. those of Fe(II). An example of spin-crossover complexes (the term of *spin-state isomers* is also used) is [Fe(2-pic)$_3$]Cl$_2$·EtOH (2-pic = 2-picolylamine). At the Fe–N distance of 203.2 pm (115 K), the complex has an electronic *low-spin state* (^{1}A$_1$), whereas stretching the bond up to 219.9 pm at 227 K induces the transition to a *high-spin state* (^{5}T$_2$) [171].

Spin density—The excess of the *electron density* related to the electron with α spin over that of the electron with β spin (see *spin-orbital*) at a given point of an *open-shell system*. For a *closed-shell system* spin density is zero everywhere.

Spin polarization—*Static* and *dynamic spin polarization* effects are distinguished. The static polarization of an electron spin occurs in the C–H bonds of aromatic radicals where the σ-electron closest to an unpaired π-electron tends to have its spin parallel to that of the π-electron. Likewise, static spin polarization arises in the π-system of conjugated radicals: the electron of the doubly occupied molecular orbital prefers to take a closer spatial position to the odd one, which spin is parallel to the latter. The effect reflects the energy unfavourable situation if an electron of opposite spin were to come nearby.

The dynamic spin polarization is the instantaneous *electron correlation* effect occurring in *biradicals* (e.g. in 90°-twisted ethene, cyclobuta-1,3-diene) leading to correlation of spins of electrons in inner-shell orbitals with those of odd electrons. Essentially, a molecule seeks out a local (π,σ) or (π,π) triplet configuration at each center (as is the case of *static spin polarization*) to decrease the overall *coulomb repulsion* energy of singlet states. The effect is termed dynamic since spin-polarized *electron configuration* has a counterpart where all the spins are reversed [29].

Spin projection—A component, M_S, of the angular spin moment S along an arbitrary axis (usually chosen as the z-direction). M_S can take the values between $-S$ and S: $-S+1, . . ., S-1, -S$. The term is also used to denote an operation (spin-symmetry projection) allowing one to eliminate *spin contamination* in the cases where *wavefunctions* are not eigenfunctions of the operator S^2.

Spin-coupled (SC) wavefunction—Representation of a *wavefunction* in the modified *valence bond theory*. A spin-coupled wavefunction describes a molecular system with a total number of electrons N_t by subdividing these into inactive core electrons placed in doubly occupied *orbitals* and N active (valence) electrons placed in N distinct, singly occupied, nonorthogonal orbitals, the spins of which are coupled together in all allowable ways to form the required overall resultant S [172].

Spin-orbit coupling—The interaction of the electron spin magnetic moment with the magnetic moment due to the orbital motion of the electron, and the consequent mixing of *electronic states* of different *multiplicity*.

Spin-orbital—The complete one-electron *wavefunction* given (in the absence or in the case of neglect of *spin-orbit coupling*) by a product of a spatial function (*orbital*) and a spin function. An orbital $\Psi_i(\mathbf{r})$ may be associated with either α(ξ) or β(ξ) spin functions, the spin coordinate ξ taking on one of two possible values (1/2 or –1/2) that measure the spin angular momentum component along the z-axis in the $h/2\pi$ units. This gives rise to the spin-orbitals $\Psi_i(\mathbf{r})\alpha(\xi)$ and $\Psi_i(\mathbf{r})\beta(\xi)$.

Spin-spin coupling—a small *relativistic effect* due to interaction between the spin magnetic moments of electrons or nuclei.

Spin-state isomers—see *Spin crossover*.

Split valence basis set—see *Basis set*.

Static spin polarization—see *Spin polarization*.

Stationary point (synonymous with critical point)—On the *potential energy surface* a point at which the *energy gradients* with respect to all coordinates vanish.

Stationary state—A state in which the expectation values of properties do not change with time. It is given by a *wavefunction* representing one of the solutions of the time-independent Schroedinger equation.

Stereochemical nonrigidity—The capability of a molecule to undergo fast and reversible intramolecular isomerization, the energy barrier to which is lower than that allowing for the preparative isolation of the individual isomers at room temperature. It is conventional to assign to the stereochemically nonrigid systems those compounds whose molecules rearrange rapidly enough to influence NMR line shapes at temperatures within the practical range (from –100°C to 200°C) of experimentation. The energy barriers to thus defined rearrangements fall into the range of 5–20 kcal/mol (21–85 kJ/mol). A more general term for this phenomenon is *structural nonrigidity*. See also *Automerization, Fluxional molecules, Pseudorotation* [173,174].

Steric energy—see *Strain energy*.

Strain energy—The excess energy due to steric strain of a molecular entity or *transition state* structure, i.e. distortions relative to a reference (real or hypothetical) 'strainless' structure with the standard *bond lengths*, bond angles and dihedral angles. The strain energy components involve the following destabilizing terms: non-bonded repulsions, bond-angle distortions, bond stretch or compression, rotation around or twisting of double bonds, and electrostatic strain. In general, the contributions of these components are inseparable and interdependent. A quantitative assessment of strain and strain energies can be made by taking the difference between the heat of formation of the substance under consideration and that of a hypothetical strain-free model. Several approaches to the assessment of strain energies have been developed based on the use of energies of *isodesmic* and *homodesmotic reactions* and on the so-called 'strainless increments', i.e. *heats of formation* of certain groups (CH_3, CH_2, CH, C etc). A synonymous term is *steric energy* [175].

Structural nonrigidity—see Stereochemical nonrigidity.

Structural stability—Within the *Born–Oppenheimer (adiabatic) approximation*, this is associated with an energy minimum on a *potential energy surface*. Structural stability implies that any change in the coordinates of the nuclei can only increase the total energy.

Sudden polarization—The occurrence of a large intramolecular charge separation in the singlet *excited state* of polyenes and their derivatives twisted about a double bond. Unsymmetricla substitution or geometrical distortion is effective in polarizing the system. An example is the stabilization of the zwitterionic structure of 90° twisted ethane (ethan-2-ylium-1-ide) with on methylene group pyramidalized [21]:
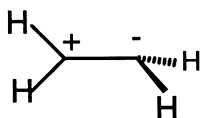
Supermolecule—A discrete oligomolecular species that results from the intermolecular association of its components.

Supramolecular chemistry—A field of chemistry related to species of greater complexity than molecules, that are held together and organized by means of intermolecular interactions. The objects of supramolecular chemistry are *supermolecules* and other polymolecular entities that result from the spontaneous association of a large number of components into a specific phase (membranes, vesicles, micelles, solid state structures etc.) [176].

Surface delocalization—see *Delocalization*.

Symmetry allowed reaction—see *Conservation of orbital symmetry*.

Symmetry breaking—Instability of the *wavefunction* which appears when it has a lower symmetry than the nuclear framework. It is found, for instance, in the allyl radical or in the hydrogen peroxide radical cation. In the former, the nuclear geometry has a C_{2v} symmetry, but the ROHF wavefunction has only C_s symmetry.

Symmetry element—A geometrical entity (mirror plane, proper and improper rotation axes, center of inversion) with respect to which one or more *symmetry operations* may be carried out [177].

Symmetry forbidden reaction—see *Conservation of orbital symmetry*.

Symmetry point group—(synonymous with *Point group*)—All the symmetry operations that leave a particular object (e.g. molecular entity or function) unchanged constitute together the symmetry point group for that object.

Symmetry operation—An operation associated with a *symmetry element* that is carried out on some object and which leaves the object unchanged.

Synchronous reaction—A *concerted reaction* in which all the changes in bonding take place in parallel.

Thermochemical resonance energy—see *Resonance energy*, *various types of*.

Thermodynamic stability—Those species are considered to be thermodynamically stable whose free energies are sufficiently low compared to all reasonable decomposition products so that detectable amounts of the former may exist in equilibrium.

Three-center, four-electron (3c–4e) bond—see *Hypervalency*.

Three-center, two-electron (3c–2e) bond—A kind of *multicenter* σ-bond in which three atomic cores are held together by two electrons. The 3c–2e bonds are particularly common in the boron hydrides, carbocations (for example, the bond in the CH_2 fragment of the methanium cation, see *Hypercoordination*), bridged metal alkyls and metal halides. The simplest example of the 3c–2e bond is in the H_3^+ ion.

Through-bond interaction—An intramolecular *orbital interaction* of spatially separated *orbitals*, where the orbitals interact through their mutual mixing with σ-orbitals of the intervening framework.

Through-space interaction—The *orbital interaction* that results from direct spatial overlap of two *orbitals*.

Tight binding method—Approximation of *crystal orbitals* in solids by a *Linear Combination of Atomic Orbitals*. In general, tight binding is approximation in quantum chemical methods by retaining *resonance integrals* only for neighboring atoms.

Topological principle—Reactions in the crystalline phase proceed under minimal atomic and molecular displacement.

Topological distance matrix—see *Topological index*.

Topological electron distribution theory—The theory of molecular structure based on the analysis of the topological properties of scalar fields of the *electron density function* $\rho(\mathbf{r})$ and the *Laplacian of the electron density* $[\nabla^2\rho(\mathbf{r})]$, which are summarized in terms of their critical points, r_c, i.e. the points were

$\nabla\rho(\mathbf{r})$ and $(-\nabla^2\rho(\mathbf{r}))$ are equal to zero. The critical points are classified according to their rank (number of non-zero eigenvalues) and signature (algebraic sum of their signs) of the *Hessian matrix* of $\rho(\mathbf{r})$. Thus, a (3, −3) critical point corresponds to a maximum of $\rho(\mathbf{r})$ related to an atomic nucleus, whereas a (3, −1) critical point (*bond point*) is a saddle point that exists between every pair of neighboring bonded atoms [15,16].

See also *Atoms in molecules, theory of*.

Topological index—A numerical value associated with chemical constitution purporting for correlation of chemical structure with various physical properties, chemical reactivity or biological activity. The numerical basis for topological indices is provided (depending on how a *molecular graph* is converted into a numerical value) by either the *adjacency matrix* or the *topological distance matrix*. In the latter the topological distance between two verices is the number of edges in the shortest path between these.

Topological resonance energy (TRE)—see *Resonance energy, various types of*.

Topomerization—see *Automerization*.

Total energy of a molecular system—The sum of the total electronic energy, E_{ee} and the energy of internuclear repulsion, E_{nr}. In the *Hartree–Fock (SCF) method*, the value of E_{ee} for a *closed-shell molecular system* is given by

$$E_{ee} = 2\sum_i \epsilon_i + \sum_i \sum_j (2J_{ij} - K_{ij})$$

where ϵ_i stands for orbital energies and J_{ij} and K_{ij} stand for respectively *Coulomb* and *exchange integrals*, the summation being done over all occupied *molecular orbitals*. The repulsion between the nuclei (A, B...) is defined by the expression:

$$E_{nr} = \sum_A \sum_{<B} Z_A Z_B / R_{AB}$$

Transition state (TS) (also transition state structure, transition structure)—The structure corresponding to the highest point on the *minimum energy reaction path*, i.e. first order *saddle point* on the *potential energy surface*. In *transition state spectroscopy*, the definition of the transition state is broader. It embraces the entire process of bond breaking and bond making and is used to denote the full family of configurations through which the reacting particles evolve along the route from reagents to products.

See also *Hessian matrix*.

Transition State Theory (TST)—The theory which provides a conceptual framework for understanding all chemical reactivity. It serves as a powerful computational tool for translating molecular structures and energetics into prediction of chemical reaction rates [178,179].

Transition state spectroscopy (TSS)—The femtosecond temporal resolution (10^{-14}–10^{-13} s = 10–100 fs) laser spectroscopy that enables one to detect the intermediate configurations (*transition states*) of a reacting system in real time and follow the nuclear motion and energy redistribution [180].

Transition vector—The eigenvector associated with the only negative eigenvalue of the *Hessian matrix* representing the single direction in which the *potential energy surface* is a maximum. The transition vector is also a path of the *intrinsic reaction coordination* through the *saddle point*.

Transmission factor—In the equation of the theory of absolute reaction rates that relates the reaction constant k with the height of the energy barrier ΔE^{TS}, the value of the coefficient γ is equal to 1 when the conversion of reactants to products always occurs upon attaining the height of energy barrier, and less than 1 when this condition is not met.

$$k = \gamma\,\tau(k_B T/h)(Q_{TS}/Q_R)\exp(-\Delta E^{TS}/RT)$$

where k is the rate constant for the reaction of conversion of reactants R into products by proceeding through transition state TS; Q are partition functions per unit volume, and τ is the quantum mechanical *tunnelling* coefficient. In some descriptions $\kappa = \gamma\tau$ is referred to as the transmission factor.

Tunnelling effect—The passage of a particle through a potential energy barrier the height of which is larger than the energy of that particle. The effect is important for some processes involving the transfer of electrons and light atoms, particularly hydrogen atoms.

Uncertainty (Heisenberg) principle—The statement that two dynamical variables can be simultaneously well defined only if their quantum mechanical operators commute. If, for example the momentum of a particle is known with an uncertainty of Δp, the position of the particle cannot be determined with the precision better than $h/\Delta p$:

$$\Delta p_X \Delta x \geq h$$

Unit cell—The cell chosen to represent best the symmetry of a crystal lattice. The entire lattice can be derived from it by translations. The translations selected as the edges of the plane unit cell are denoted as a and b, and for a space lattice as a, b, c called the crystallographic axes. The angles between the edges of the three-dimensional unit cell are α, β and γ.

Unitary group—A group which consists of unitary matrices of fixed order with matrix multiplication as the group operation.

Unrestricted Hartree–Fock (UHF) method—see *Hartree–Fock method*.

Valence bond configuration mixing (VBCM) model—A model that provides a framework for conceptualizing reactivity trends through building up a *reaction profile* from its constituent VB configurations. Key configurations that are invariably employed are those that best describe reactants Ψ_R and products Ψ_P [52,53,130].

See also *Curve-crossing model*.

Valence bond (VB) theory—A method of approximating the total *wavefunction* of a molecule as a linear combination of functions related to certain pairings of electron spins. Each such function is given by a product of the *atomic orbitals* of the separated atoms. As a first approximation the covalent pairing scheme is employed, in which pairs of electrons between the atoms have their spins paired as much as possible. To account for *electron correlation* effects, mixing in of functions representing ionic pairing schemes, in which some of the separated atoms are replaced by positive and negative ions, is employed. The VB and MO methods, if carried out with the same *basis set* of orbitals, are entirely equivalent if all possible ionic structures are included in the VB and all possible configurations in the MO [181–183].

Valence state electron affinity—the *electron affinity* of an atom in its particular *electron configuration*.

Valence state ionization potential (VSIP)—The *ionization potential* of an atom in its particular *electronic configuration*.

Valence-shell-electron-pair repulsion (VSEPR) theory—A semiquantitative approach to the prediction of the geometries of compounds of main-group elements. The basic idea of the theory is that the geometric arrangement of the bonds around a central atom depends on the number of electron pairs in its valence shell. A given number of electron pairs adopt that arrangement which keeps them as far apart as possible, as a consequence of the operation of the *Pauli exclusion principle*. The arrangements of electron pairs are essentially retained independently of whether they are unshared pairs, or form single, double or triple bonds. The theory is concerned with the arrangement of predominantly *covalent bonds* around a single central atom. It does not apply to the compounds with *ionic bonds* and to molecules with *multicenter bonds* [184,185].

van der Waals complexes—Molecular systems in which the individual parts are held together by forces other than *covalent bonds*. These include ionic complexes (where the dominant attractive force is of electrostatic origin), complexes with *hydrogen bonds*, charge-transfer complexes, and true van der Waals molecules for which the dominant attractive contribution is the *dispersion energy* [62].

van der Waals (VDW) interactions—Noncovalent interactions (weak as compared to *covalent bonds*) due to dipole-induced dipole and dispersion forces (see *dispersion energy*) acting at molecules and atoms. In *molecular mechanics* models, the energy contributions from vdW interactions are commonly treated with potential functions of the distance, *r*, between each pair of nonbonded atoms, like the *Lennard–Jones potential*:

$$V_{vdW} = A/r^{12} - C/r^6$$

Variational method—see *Variational principle*.

Variational principle—The principle according to which for a molecular system an approximate *wavefunction*, when substituted into the Schroedinger equation, will always yield a higher energy than the actual energy of the system. The more precise the wavefunction that is chosen, the closer will the calculated energy be to the true energy. The computational method using this principle to obtain approximations to correct wavefunctions is called the *variational method*. The method is commonly restricted to the *ground state*, but can be extended to others provided they are orthogonalized to the (true) ground state.

Variational Transition State—In *variational transition state theory*, the optimized dividing surface (hypersurface in plastic state that separates reactants from products). If not all trajectories passing through the dividing surface and originated at reactants are directed to products *transition state theory* overestimates the rate. In variational transition state theory one optimizes the location of the dividing surface to minimize the rate [179,186].

Variational Transition State Theory (VTST)—see *Variational Transition State*.

Vertical electron affinity—see *Electron affinity*.

Vertical ionization potential—see *Ionization potential*.

Vibronic interactions, theory of—An approach to the analysis of molecular properties and molecular transformations which, unlike the *Born–Oppenheimer approximation*, assumes that *electronic states* depend strongly on nuclear coordinates. If stationary electronic states (*ground, first excited* etc.) are obtained as solutions of the Schroedinger equation for fixed nuclei, an accounting for vibronic coupling terms in the *Hamiltonian* (interaction of electrons with nuclear displacements) mixes these electronic states. This mixing is especially strong in the cases of electronic degeneracy (see *Jahn–Teller effect*) and pseudodegeneracy (*pseudo Jahn–Teller effect*) [122].

Vibronic transition—A transition which involves a change in both the electronic and vibrational quantum numbers of a molecular entity. The transition occurs between two *electronic states*, but involves a change in both electronic and vibrational energy [30].

Virial theorem—Interrelates the kinetic, *T*, and potential, *V*, energy of a system in its *stationary states*. The molecular electronic virial theorem is formulated (J. Slater) as follows:

$$2 < T_{el} > = - < V > - \sum_{\alpha} \sum_{\beta > \alpha} R_{\alpha,\beta} (\partial U / \partial R_{\alpha,\beta})$$

where $R_{\alpha\beta}$ is the distance between nuclei α and β, *U* is the potential energy function for nuclear motion and the sum runs over all internuclear distances. The true *wavefunctions* must satisfy the virial theorem [60].

Virtual orbital—An orbital from a set of MOs obtained as solutions of the SCF equations (see *Hartree–Fock method*) whose energies are higher than those of doubly occupied MOs producing the single determinant *wavefunction* of lowest energy for a given system. The virtual orbitals obtained from SCF calculations are not variationally correct approximations (see *variational principle*) to the *excited state* orbitals. Their energies are not related to *electron affinities* of the molecular system.

Volume delocalization—see *Delocalization*.

Wade's rules—The *electron-counting rules* for prediction of stable structures of polyhedral inorganic, organometallic, and organic compounds. So-called 'skeletal' electrons, i.e. valence electrons of atoms positioned in the vertices of a molecular polyhedron that form bonding electron pairs of the framework bonds, are taken into account, their number being determined as follows

Main-group elements $k = v + x - 2$

Transition metals $k = v + x - 12$

where v is the full number of valence electrons of an atom or group in a vertex and x is the number of one-electron ligands. For deltahedral *close* (closed) structures (characterized by triangle faces) with m vertices there exist $(m + 1)$ *bonding molecular orbitals* which may be filled with not more than $2m + 2$ skeletal electrons ($m = 4, 5...$). For *nido* (nest-like) structures derived from the *closo*-forms through truncation of one apex there are $(m + 2)$ bonding MOs which may be occupied with not more than $2m + 4$ skeletal electrons. For *arachno* (web-like) structures derived from *nido*-forms through truncation of one apex, there are $(m + 3)$ bonding MOs that may be occupied by $2m + 6$ electrons. The extension of Wade's rules is the *polyhedral skeletal electron pair approach* that makes allowance for the total electron count in condensed polyhedra derived by the condensation of smaller tetrahedral, octahedral, and trigonal-prismatic fragments. The total electron count in a condensed polyhedron is equal to the sum of the electron counts for the parent polyhedra A and B minus the electron count characteristic of the atom, pair of atoms, or face of atoms common to both polyhedra [187,188].

Walsh diagram (also called *Walsh–Mulliken diagram*)—A molecular orbital diagram where the *orbitals* in one reference geometry are correlated in energy with the orbitals of the deformed structure.

Walsh's rules—The summaries of observations that the shapes of molecules in a given structural class are determined by the number of valence electrons. The most important rule states that a molecule adopts the structure that best stabilizes its *highest occupied molecular orbital*. If the HOMO is unperturbed by the structural change under consideration, the occupied MO lying closest to it governs the geometric preference.

Wavefunction—A mathematical expression whose form resembles the wave equations of physics, supposed to contain all the information associated with a particular atomic or molecular system. When a wavefunction is operated on by certain quantum mechanical operators, a theoretical evaluation of physical and chemical observables for that system (the most important one being energy) can be carried out.

Wave vector—The vector which appears in the expression of a *crystal orbital* as a result of the application of the periodic boundary conditions to the *wavefunction* of a solid. It determines the symmetry and nodal properties of the crystal orbital. Given the periodic nature of the Bloch orbitals, all the non-equivalent wavefunctions are generated by the components of the wave vector with values within the *Brillouin zone*.

Wigner rule (also known as *spin-conservation rule*)—During an elementary chemical step, electronic and nuclear magnetic moments conserve their orientation.

Woodward–Hoffmann rules—*Electron-counting rules* allowing predictions of thermally and photochemically driven *symmetry allowed* and *symmetry forbidden concerted reactions*.

Zero differential overlap (ZDO) approximation—An approach to the systematic neglect of the small-in-value electron repulsion integrals which is used in a number of approximate *self-consistent field* molecular orbital schemes. It means that all the products of *atomic orbitals* $\chi_\mu \chi_\nu$ are set to zero and the *overlap integral* $S_{\mu\nu} = \delta_{\mu\nu}$ (where $\delta_{\mu\nu}$ is the Kronecker delta). The ZDO approximation greatly simplifies the computation of *wavefunctions* by eliminating many of two-electron integrals. At the ZDO approximation all three- and four-centered integrals vanish.

Zero-order wavefunction—Commonly, the *wavefunction* used as a starting point to include *electron correlation* effects. Very often the zero-order wavefunction is a single determinant SCF wavefunction as in MP2, coupled cluster and CI methods, but it can be a multideterminant wavefunction as in the MRCI approach.

Zero-point energy (ZPE)—synonymous with *zero-point vibrational energy*.

Zero-point vibrational energy (ZPVE)—The energy of vibration of a molecule at absolute zero (0 K). It is given by

$$E_{\text{vib}}(0) = (1/2)h \sum_i \nu_i$$

where ν_i is a normal-mode vibrational frequency. Even for a small molecule, the total ZPE can amount to several tens of kcal/mol. ZPE is a quantum mechanical effect which is a consequence of the *uncertainty principle*.

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APPENDIX. Glossary of acronyms of terms used in theoretical organic chemistry

AIM	Atoms In Molecules—*method of topological analysis of distribution of electron density*.
AM1	Austin Model 1—*semiempirical method of quantum chemistry* [189].
AO	Atomic Orbital.
AOM	Angular Overlap Model.
ASE	Aromatic Stabilization Energy.
BDE	Bond Dissociation Energy.
BEBO	Bond Energy Bond Order *method*.
B3LYP	Becke Lee, Yang and Parr *hybrid functional which defines the exchange functional as a linear combination of HF, local and gradient-corrected exchange terms* [190].
BO	Born–Oppenheimer *approximation*.
BRE	Bond Resonance Energy.
BSSE	Basis Set Superposition Error.
CAS	Complete Active Space.
CASPT	Complete Active Space Perturbation Theory.
CASPT2	CASPT *based method with second order perturbation theory* [191].
CASSCF	Complete-Active-Space SCF *method of solution of the electronic Schrödinger equation* [192].
CBS	Complete Basis Set *of orbitals*.
CC	Coupled Cluster.
CCSD(T)	Coupled Cluster Single, Double (Triple) *excitations*.
CDW	Charge Density Waves.
CEPA	Coupled Electron-Pair Approximation.
CHF	Coupled HF method.
CI	Configuration Interaction.
3×3 CI	CI *for all three possible singlet configurations in the two-electron two-orbital model*.
CID	CI, Double *excitations only*.
	Collision Induced Dissociation.
CIDNP	Chemically Induced Dynamic Nuclear Polarization.
CIS	CI, Single *excitations only*.
CISD	Single *and* Double *excitations, single reference* CI *method*.
CISDT	CISD *plus* Triple *excitations*.
CISDQ (or QCISD)	CISD *plus* Quadruple *excitations, see also* QCISD.
CISDTQ	CISD *plus* triple *and* quadruple *excitations*.
CMO	Canonical Molecular Orbital.
CNDO	Complete Neglect of Differential Overlap.
CNDO/2	Complete Neglect of Differential Overlap, *semiempirical method of quantum chemistry with paramerization according to Pople & Segal* [193].
CNDO/S	Complete Neglect of Differential Overlap/Spectroscopic *parametrization according to Del Bene & Jaffe* [194].
COOP	Crystal Orbital Overlap Population.

CSD	Cambridge Structural Database.
CT	Charge Transfer.
DE	Delocalization Energy.
DFT	Density Functional Theory.
DIM	Diatomics In Molecules.
DNMR	Dynamic NMR *spectroscopy*.
DOS	Density of States.
DRE	Dewar Resonance Energy.
DRP	Dynamic Reaction Path.
DZ	Double-Zeta *type of basis set*.
DZP	DZ *plus* Polarization *function basis set*.
EA	Electron Affinity.
EAN	Effective Atomic Number rule.
ECP	Effective Core Potential.
EFF	Empirical Force Field.
EHMO	Extended Hückel Molecular Orbital, *semiempirical method of quantum chemistry* [85].
EHT	Extended Hückel Theory.
EM	Effective Molarity.
EPR	Electron Paramagnetic Resonance.
ESR	Electron Spin Resonance *spectroscopy*.
ET	Electron Transfer.
EXAFS	Extended X-ray Absorption Fine Structure spectroscopy [195].
FSGO	Floating Spherical Gaussian Orbitals.
G1	Gaussian1, *a method for ab initio calculations based on the MP4/6-311G(d.p)/ MP2/6-31G(d) scheme with corrections of the incompleteness of the basis through inclusion of diffuse functions and extra d- and f-functions for non-hydrogen atoms* [196].
G2	Gaussian 2, *a method for ab initio calculations that improves the G1 methodology by including corrections for the larger 6-311 + G(3df, 2p) basis set and providing empirical correction for the number of valence electron pairs. The theory corresponds effectively to calculations at the QCISD(T)/6-311 + G(3df, 2p) level with zero-point vibrational energy (ZPE) and higher level correlations* [197].
GIAO	Gauge Invariant Atomic Orbitals.
GTO	Gaussian-Type Orbitals.
GVB	Generalized Valence Bond *method*.
GVB-CI	GVB *plus* CI *method*.
HAM	Hydrogenic Atoms *in* Molecules *method*. HAM/N (N = 1,2,3)—*versions of the method* [198].
HE	Half Electron *method*.
HF	Hartree–Fock *method*.
HMO	Hückel Molecular Orbital.
HOMO	Highest Occupied Molecular Orbital.
HOMAS	Harmonic Oscillator Model *of* Aromatic Stabilization.

HOSE	Harmonic Oscillator Stabilization Energy.
HRE	Hückel Resonance Energy.
HSE	Homodesmotic Stabilization Energy.
HSRE	Hess-Schaad Resonance Energy.
ICCI	Internally Contracted CI *method*.
IEPA	Independent Electron-Pair Approximation.
IGLO	Individual Gauge *for* Localized Orbitals.
IRC	Intrinsic Reaction Coordinate.
INDO	Intermediate Neglect *of* Differential Overlap. *A semiempirical method of quantum chemistry* [199].
INDO/S	Intermediate Neglect *of* Differential Overlap/Spectroscopic *parametrization* [200].
INDO/S-CI	Intermediate Neglect of Differential Overlap/Spectroscopic *parametrization accounting for Configuration Interaction* [201].
IP	Ionization Potential.
ISE	Isodesmic Stabilization Energy.
JT	Jahn–Teller *effect*.
KIE	Kinetic Isotope Effect.
LCAO MO	Linear Combination of Atomic Orbitals *representation* of Molecular Orbitals.
LDA	Local Density Approximation in DFT.
LE	Localization Energy.
LFER	Linear Free Energy Relationships.
LFSE	Linear Field Stabilization Energy.
LMO	Localized Molecular Orbital.
LORG	Localized Orbital, Localized Origin *method*.
LUMO	Lowest Unoccupied Molecular Orbital.
MBPT(n)	Many-Body Perturbation Theory of nth Order.
MC	Monte Carlo *method*.
MC SCF	MultiConfiguration SCF *theory*.
MC-IGLO	MultiConfiguration IGLO.
MCPF	Modified-Coupled-Pair-Functional.
MD	Molecular Dynamics *method*.
MEP	Molecular Electrostatic Potential.
MERP	Minimum Energy Reaction Path.
MIDI-N	MID*dle size split-valence type contracted* GTO *basis set (N = 1–4)*.
MINDO	Modified INDO, MINDO/N *(N = 1,2,3)—versions of the semiempirical method of quantum chemistry* [202].
MINI-N	MINI*mal-type contracted* GTO *basis set (N = 1–4)*.
MM	Molecular Mechanics.
MM2	Molecular Mechanics *force field*, 2d version of the parametric set and the program using molecular mechanics* [203].
MM3	Molecular Mechanics *force field*, 3d version of the parametric set and the computer program* [204].
MMX	Molecular Mechanics *empirical force field* [205].

MNDO	Modified Neglect of Diatomic Overlap. *A semiempirical method of quantum chemistry* [206].
MNDOC	MNDO *method with a perturbative treatment of electron* Correlation [207].
MO	Molecular Orbital.
MOVB	MO VB theory.
MPA	Mulliken Population Analysis.
MPN (N = 2–4)	Møller–Plesset *perturbation theory of order N for electron correlation* [208].
MP2/6-31G*//HF/6-31G*	*Example of abridged notation to specify the type of level used in a given calculation: the MP2 theory and of the 6-31G* basis set, at the geometry optimized at HF/6-31G* method.*
MRD	Multireference Double *substitution, method of.*
MRDCI	MRD *with inclusion of* CI.
N-31G, etc.	*Pople's basis set. Notations of this basis sets like N-ijG or N-ijkG should be encoded as follows: N—number of Gaussian primitives (GTOs) for the inner shells; ij or ijk—number of Gaussian primitives for contractions in the valence shell. The ij notations correspond to basis sets of valence DZ quality and ijk notations indicate split valence sets of triple zeta (TZ) quality. N-ijG* denotes a polarized basis set augmented with d type functions on heavy atoms only; N-ijG** (or N-ijG(d,p)—basis set with p-functions on hydrogen atoms.*
N-31 + G(d), etc[#].	*Pople's basis set with diffuse function. For example, 6-311 + G(2df,2pd) putting 2d functions and 1f function on heavy atoms (plus diffuse functions), and 2p functions and 1d function on hydrogens.*
	#) According to the IUPAC recommendation, the actual construction of the basis sets for each atom should be specified as (abc . . . , ghi . . . , lm . . . , o . . .), where a is the number of primitives usually GTOs) in the first contracted s function, b is the number of primitives in the second contracted s function, etc., g is the number of primitives in the first contracted p function, l is the number of primitives in the contracted d function, and o is the number of primitives in the first contracted f function. Thus, a 6-3 + G basis for carbon should be designated as (6311, 311, 1)*
	'Guidelines for the Presentation of Quantum Mechanical Computational Data in Organic Chemistry'. Prepared for publication by Albright & Halevi [209].
NAO	Natural Atomic Orbital.
NBO	Natural Bond Orbital.
NDDO	Neglect of Diatomic Differential Overlap. *A semiempirical method of quantum chemistry* [210].
NHO	Natural Hybrid Orbital.
NICS	Nuclear Independent Chemical Shift.
NMR	Nuclear Magnetic Resonance.
NPA	Natural Population Analysis.
OCAMS	Orbital Correspondence Analysis in Maximum Symmetry.
OFGF	Outer Valence Green's Fucntion *method.*
PA	Proton Affinity.
PCILO	Perturbative Configuration Interaction *using* Localized Orbitals *method.*

PCM	Polarizable Continuum Model *of solvation*.
PES	Potential Energy Surface.
	Photoelectron Spectroscopy.
PLM	Principle of Least Motion.
PM3	Parametric Method 3—*a semiempirical method of quantum chemistry based on the MNDO scheme* [211].
PMO	Perturbation MO *theory*.
PNO	Pair Natural Orbitals.
POAV	π-Orbital Axis Vector.
PPFMO	Polarized π-Frontier MO *theory* [212].
PPP	Pariser–Parr–Pople, *method of*.
PRDDO	Partial Retention of Diatomic Differential Overlap. *A semiempirical method of quantum chemistry* [213].
PT	Perturbation Theory.
QCI	Quadratic Configuration Interaction, *method of*.
QCISD	Quadratic CI *with* Single *and* Double *excitations, see also* CISD.
QCISD (T)	QCISD *with perturbational treatment of* Triple *excitations*.
QCISD (TQ)	QCISD *with perturbational treatment of* Triple *and* Quadruple *excitations*.
QMRE	Quantum Mechanical Resonance Energy.
QSAR	Quantitative Structure–Activity Relationships.
RCI	Ring Current Index.
RE	Resonance Energy.
REPE	Resonance Energy Per Electron.
RHF	Restricted HF theory.
ROHF	Restricted Open shell HF theory.
RPH	Reaction Path Hamiltonian.
RRKM	Rice–Ramsperger–Kassel–Marcus *theory*.
SAM1	Semi-Ab-initio Model 1. *Version 1 of a semiempirical method of quantum chemistry* [214].
SC	Spin-Coupled *method*.
SCD	State Correlation Diagram.
SCF	Self-Consistent Field, *method of*.
SCI-PCM	Self-Consistent Isodensity Polarizable Continuum Model *of solvation*.
SCRF	Self-Consistent Reaction Field, *method of*.
SDW	Spin Density Wave.
SE	Strain Energy.
SET	Single Electron Transfer.
SINDO	Symmetrically *orthogonalized* INDO *method*. SINDO1—*a version of the method* [215].
SOJT	Second-Order Jahn–Teller effect.
SO	Spin-Orbital.
SOMO	Singly Occupied Molecular Orbital.
STO	Slater-Type Orbital [216].
STO-NG	STO *approximation by the sum of* N (3-6) GTOs.

TCSCF	Two Configuration SCF *method, a special case of* MC SCF.
TRE	Topological Resonance Energy.
TS	Transition State.
TSS	Transition State Spectroscopy.
UHF	Unrestricted HF *method*.
UMNDO	UHF version of MNDO.
VAT	Vibration Assisted Tunnelling.
VB	Valence Bond *theory*.
VBCM	Valence Bond Configuration Mixing *model*.
VDW	van der Waals *interactions*.
VSEPR	Valence Shell Electron-Pair Repulsion *method*.
VSIP	Valence State Ionization Potential.
XPS	X-ray Photoelectron Spectroscopy.
ZDO	Zero Differential Overlap.
ZINDO	Zerner's INDO *method*.
ZPE	Zero Point *vibration* Energy.
ZPVE	Zero Point Vibration Energy.