*Introduction to AIM* notes

1.

\* QM provides us with a consistent and powerful mathematical formalism to predict any property of a molecule. *HF-SCF-MO-LCAO* [[1]](#footnote-1), supported with Gaussian basis sets and density functionals, may be used to solve the TISE *ab initio*.

\* *ρ* may be measured experimentally and computed – AIM uses *ρ* as an information source to bridge QM and chemistry. AIM needs no deformation (reference) densities to reveal chemical features.

2.

\* Use grad(*ρ*) to avoid invoking artificial reference density. grad(*ρ*) leads to partitioning of molecules into disjoint regions of space - molecular atoms.

\* grad(*ρ*) follows normal conventions: orth. to envelopes of const. *ρ*, originate at one point and end on another, points towards largest increase in *ρ* (i.e. from low to high *ρ*), do not cross except where grad(*ρ*) = 0 (at critical points (CPs)).

\* Nuclei are an example of a CP (a NA or nuclear attractor). There also exists (N)NA (non-nuclear attractors) which dominate regions uniquely traversed by gradient paths terminating at the NA. For example, in Li2, the two lithium nuclei never directly bond. Rather, each Li loses some electronic charge (since they are very electropositive) and ‘create’ an object in the centre (which looks like a charge nodule) to which they both bind.

3.

\* An atom is the union of an attractor (the nucleus) and its associated atomic basin (the region of space traversed by the gradient paths from infinity). An IAS (or zero-flux surface) is a topological manifold which separates atoms – it consists of a bundle of gradient paths terminating at the CP between two atoms.

\* Simple atomic properties, electronic population, volume) may be expressed as volume integrals over an atomic basin. Since atoms are finite, non-overlapping, space-filling entities, their properties may be added to obtain the properties of the whole functional group.

\* Perfect transferability of atoms from one system to another is an unattainable limit but a large degree of transferability should be observed in AIM.

4.

\* AIM can rigorously define a bond which is compatible with both calculated w.f.s and experimental densities. An AIL (atomic interaction line) points out the special interaction or link between two nuclei and is a line of maximum *ρ* with respect to neighbouring lines. AILs point from the BCP to the two nuclei whose atomic basins share an IAS.

\* Two atoms are bonded if their nuclei are linked via a bond path (BP) – defined as an AIL in a molecule which is in its (stable) minimum energy conformation (therefore all BPs are AILs but not all AILs are BPs). A collection of BPs is called a molecular graph (MG).

\* The BCP (bond critical point) is the ‘communication point’ between two atoms. Bonds can be characterized via properties evaluated at the BCP. The IAS, BCP and BP always appear as a topological triplet. Generally, the BCP is sought first (using ansatz) and the orientation of the plane tangential to the IAS found (and the orthogonal direction). The IAS may then be drawn iteratively of gradient paths from the BCP outward. The AIL is then drawn from the BCP, terminating at the nuclei.

\*MGs recover the conventional picture of Lewis bonding in standard molecules. They can also straightforwardly explain non-conventional cases (e.g. boranes, hypervalent carbon, propellanes, organolithiums). AIM can be used to study bonding as long as a w.f. or experimental density can be obtained.

\* The coordination number of an atom is defined as the number of BPs terminating at the nucleus it contains.

5.

\* The ring critical point (RCP) occurs if nuclei are topologically connected to form a ring structure. The ring surface is defined by the infinitely-many gradient paths which originate from the RCP, located in benzene at the centre of symmetry of the molecule, and terminate on the nuclei or BCPs[[2]](#footnote-2). Since gradient paths move from low to high *ρ*, the RCP is at the minimum of *ρ* within the ring surface. In the plane orthogonal to the ring surface (along the ring line), the RCP is maximum (note this is inverse to BCPs, where the saddle point is in the opposite sense to this; also note similarity of ring line to BP).

\* The cage critical point (CCP) is a minimum in 3D and therefore the counterpart to the (N)NA. It occurs in C4H4 (tetrahedrane) where the BPs mark the interior of the molecule as a cage. No gradient paths terminate at a CCP, they only originate there and terminate at a (N)NA, BCP or RCP[[3]](#footnote-3).

\* Generally, CPs are classified using the Hessian of the electron density. This second derivative matrix yields three eigenvalues and three associated eigenvectors. The former express the local curvatures at the CP, the latter the corresponding directions of curvature (the principal axes of curvature). The number of non-zero eigenvalues and their associated signs are sufficient to define the type of CP – encapsulated in (*r*, *s*). The rank of a CP, *r*, is the number of non-zero eigenvalues and the signature, *s*, is the sum of their signs (which are +1 or -1). Degenerate CPs have *r* < 3. A degenerate CP occurs in a topologically unstable gradient vector field on the verge of structural change – a small change in rho due to displacement of the nuclei can lead the degenerate CP to vanish or bifurcate into a number of stable *r* = 3 CPs. Note that a vanishing eigenvalue means zero curvature (i.e locally flat / point of inflexion).

\* The number of types of CP exceeds the rank of the CP by 1. As a result, there are four types of rank-three CP: (N)NA, BCP, ring critical point (RCP), and cage critical point (CCP).

\* Any type of gradient path always originates at a CP and terminates at a CP.

\* The Poincare-Hopf relationship, (where *n* is the number of (N)NAs, *b* of BCPs, *r* of RCPs and *c* of CCPs) enables a check of a given pattern of CPs for topological consistency but cannot guarantee the completeness of this pattern (since it could happen that *both* a BCP and RCP has not been detected). The tuple (*n*, *b*, *r*, *c*) is called the characteristic set.

\* The quantity is called the ellipticity of a BCP and measures the behaviour of the electron density in the plane tangential to the IAS – called the eigenplane (note ellipticity *only* applies to BCPs). Since it applies to BCPs and given the convention and the fact the and , which quantify the curvature in the eigenplane (tangential to the IAS), are negative for BCPs, then , so the ratio 1. The ratio effectively gauges how pronounced the elliptical shape of the contour diagram is in the eigenplane. It follows from above that the ellipticity may vary from zero to infinity.

6.

\* Geometry and structure are two different things. The former is determined by the exact nuclear positions (set of nuclear coordinates), the latter is a connectivity scheme governed by the topology of *ρ* (i.e. since the gradient vector fields of each geometry are topologically equivalent the MGs and CPs are preserved). It follows that moderate vibrations in a molecule change the geometry but not the structure; meanwhile, highly excited molecules may fluctuate between several structures.

\* If two MGs can be continuously mapped into each other (one-by-one) they are homoeomorphic (or topologically equivalent). A molecular structure is defined as an equivalence class of MGs.

\* There are only two types of structural change possible: the bifurcation mechanism and the conflict mechanism, each possessing a corresponding unstable structure. Any structural change is an abrupt and discontinuous process – two nuclei are linked by an AIL or not (hence binary logic of MG connectivity). It follows that a reaction where molecule A becomes molecule B (which has a different structure) must contain at least one discontinuous structural change.

\* The bifurcation mechanism is where a BCP and RCP annihilate and leave a degenerate (2,0) CP behind (or the reverse if a molecule is ‘pulled apart’). The curvature associated with the second eigenvector of the Hessian vanishes and the ellipticity of the BCP becomes infinite (topologically unstable when BCP and RCP are very close).

\* In the conflict mechanism a conflict structure occurs in which all the CPs have rank 3 but the MG is unstable. The conflict consists of two nuclei competing for a single BCP and can be resolved by an infinitesimal distortion of the conflict geometry.

\* Parameters controlling geometry changes (e.g. distances from an origin along different axes) constitute the control space affecting the topology of *ρ* which exists in a 3D behaviour space. Generally, the *M* internal nuclear coordinates make up an *M*-dimensional control space. Behaviour space is the space wherein the behaviour of the system is determined and observed through the properties of *ρ* (hence the space is three-dimensional since *ρ* is).

\* A structure diagram puts all the possible structures and structural changes on a common denominator. It contains structurally stable (regular points) and unstable regions (catastrophic points).

\* Catastrophe theory (the study of abrupt changes) may be used to obtain a full and precise understanding of the changes in chemical structure via an AIM topological analysis of *ρ*.

7.

\* The atoms recovered from the topology of *ρ* can also be justified in a rigorous QM sense.

\* Subspace QM is a generalisation of full space QM in that it introduces extra surface terms. These terms disappear for a topological atom, thereby making it a rigorously defined subspace. Variational calculus (which considers *functionals*) yields atomic subspace QM by stepping back and deriving full space and subspace QM in a common framework.

\* The hermiticity of operators does *not* hold for subspaces (i.e. for volumes not extending to infinity) by one of Green’s identities. A real expectation value can instead be obtained by taking the average of the expectation integral and its complex conjugate.

\* The KE of an atom, and of the whole system, can be shown to be unique and well-defined. There is more than one way to define a KE density at a point, examples are K(**r**) and G(**r**), where . Integrating over all space means the second RH term goes to zero, hence the KE *T*() is equivalent to (i.e. unique and well-defined).

\* The atomic equivalent of the hypervirial theorem contains surface contributions – from this theorem the atomic virial theorem can be derived (among other theorems, e.g. atomic force, atomic torque, atomic power). It relates the KE and PE of the atom via: .

8.

\* The Laplacian of *ρ*, Lap(*ρ*), reveals chemical features not evident in *ρ*. If it is < 0 at some point, then *ρ* is locally concentrated. If it is > 0, *ρ* is locally depleted.

\* The VSCC is the region of electronic charge concentration in the outer quantum shell of the atom. It persists upon chemical bond formation but may be punctured (such as in polar molecules).

\* The atomic graph is a connectivity scheme expressing the topology of -Lap(*ρ*) in the VSCC of the atom. It consists of three types of CP: (3,-3), (3,-1) and (3,+1).

\* The pair density which is rigorously derived from the w.f. shows that electron pair localisation occurs solely and only to some extent in atomic core regions. The mechanism of electron pair formation is indirect and governed mainly by Pauli. Loosely speaking, a pair of electrons with opposite spin arises as a by-product of the fact that same spin electrons avoid each other and the presence of a nucleus attracting both alpha and beta electrons.

\* It is observed that the (3,-3) CPs in the Laplacian can be associated with the electron pairs of the Lewis model, both bonding and non-bonding (or lone) pairs.

\* The topology of the Laplacian provides a physical basis for the empirical VSEPR model. The Laplacian supports and makes precise explanations offered by VSEPR.

\* The Laplacian principle of complementarity states that a maximum in L(**r**) of an atom in one molecule combines with a minimum (or saddle) in an atom in L(**r**) of another molecule. It supports the generalised acid-base principle of Lewis.

\* Lap(*ρ*) can be used to study both electrophilic and nucleophilic attack and to predict preferred directions of alignment.

\* There is a local version of the virial theorem which enables one to interpret Lap(*ρ*) as an energy density or pressure. Acidic regions can be associated with zones of high KE, and basic regions with high PE.

9.

\* AIM defines an electrostatic moment for an atom inside a molecule as a volume integral of a property density. The electronic monopole moment of an atom can be used to study charge transfer in molecules and molecular aggregates (complexes). AIM charges have the correct sign but tend to be large compared to other methods – yet they have proved to be reliable.

\* The total molecular dipole moment always consists of contributions from: a charge transfer term measured by the zeroth moment, and a polarization term measured by the first moment. Therefore, attempts to assign atomic charges on the basis of dipole moments is unrealistic. By convention, the dipole moment vector points from the negative charge to the positive.

\* The atomic quadrupole moment consists of five independent components. Their values have been proposed as an electron density analogue of the pi population of the orbital model.

\* The electrostatic potential generated by a (molecular) electron distribution can be expanded using multipole moments. The lower the rank of multipole, the higher the number of sites required to represent the potential accurately.

\* AIM enables the calculation of the contribution of an atom to the electrostatic potential generated by the molecule it is part of. Since an atom is a transferable piece, its associated electrostatic potential is transferable as well. This enables the construction of potential maps of large proteins from accurately computed oligopeptides.

10.

\* The topology of *ρ* determines the presence of a bond. The bond character, however, is determined not by the topology but by the properties evaluated at the BCP.

\* A shared interaction is one where Lap(*ρ*) < 0, a closed-shell interaction is one where Lap(*ρ*) > 0, and an intermediate one, where the BCP lies very close the to the surface, where Lap(*ρ*) = 0.

\* It is possible to define a bond order empirically, based on *ρ*, provided the nuclei participating in the bond are the same.

\* BCP properties reveal conjugation, hyperconjugation and anti-aromaticity in a wide range of hydrocarbons.

\* AIM allows the study of H-bonds independently from IR, NMR, neutron diffraction etc. Eight criteria, based on AIM properties, have been proposed to characterise both inter- and intramolecular H-bonds. Candidate H-bonds which fail one or more of these criteria can therefore *not* be designated as H-bonds.

1. Hartree-Fock, self-consistent field, molecular orbital, linear combination of atomic orbitals [↑](#footnote-ref-1)
2. A ring is defined as part of the MG which bounds the ring surface. [↑](#footnote-ref-2)
3. A cage is defined as the part of an MG which contains atleast two rings, where the union of these two rings forms a cage. Only cages constructed of at least three rings have been observed. [↑](#footnote-ref-3)