

The atom in a molecule as a mereological construct in chemistry

N. Sukumar

Department of Chemistry, Shiv Nadar University, Dadri, India

Abstract: In this paper I discuss some consequences and manifestations of a mereology of structured wholes in chemistry, with particular reference to the concept of atoms in molecules.

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The identification of an entity in a molecule as an “atom” is a mereological construct, one that is central to chemical theory, predating quantum mechanics or modern notions of atomic structure and the nature of the chemical bond. Understanding the properties of atoms and functional groups in molecules during chemical transformations is central to science of chemistry. An atom does not lose every shred of its identity when it combines with other atoms or a group of atoms to form a molecule. It is this identification that makes possible the systematic study of chemistry as a science. If not for this vestigial identity retained by an atom in different chemical environments, chemistry would be no more than an encyclopedic catalog of the properties of disparate substances. Classical mereology, however, fails for such structured entities as molecules, where the whole is not merely the sum of its parts. When the whole is greater than the mereological sum of its parts, we speak of emergence. Process Structural Realism (PSR), as formulated by Joseph Earley (Earley, 2008), describes how combinations of processes may produce ontologically significant coherences. PSR sees such diverse structures as viral capsids, flames, swarms, chemical reaction networks and circadian rhythms through the common lens of emergent phenomena or dissipative structures. The key concept in PSR is that the components act in concert because of their inclusion in a closed set of interactions that defines the coherence. Framing these concepts in process terminology enables one to move from a classical mereology of objects or stuff (Simons, 1987) to a mereology of potentialities (Whitehead, 1978).

Quantum mechanics provides a vivid illustration of the failure of classical mereology. In classical statistics, probabilities of independent events are additive. In the statistical interpretation of quantum mechanics, for which Max Born was awarded the Nobel prize in 1954, the squared wave amplitude $|\psi|^2$ determines the probability density of particles. However, in order to reconcile the statistical interpretation with the existence of quantum interference phenomena, one needs to modify the classical laws for compounding probabilities: If a wave function ψ_1 with probability density $P(\psi_1)=|\psi_1|^2$ is superposed with a wave function ψ_2 with probability density $P(\psi_2)=|\psi_2|^2$, the probability density of the superposed wave $\psi_1+\psi_2$ is given by:

$$P(\psi_1+\psi_2) = |\psi_1+\psi_2|^2 = |\psi_1|^2 + |\psi_2|^2 + \psi_1^*\psi_2 + \psi_2^*\psi_1 \quad , (1)$$

and not just by the sum of the individual probabilities $|\psi_1|^2 + |\psi_2|^2$. The cross terms in equation (1) are interference terms that determine whether the whole is more (constructive interference) or less (destructive interference) than the sum of its parts. Interference of probabilities in quantum mechanics is thus nothing more nor less than a special rule for compounding potentialities in the new mereology. Seen in this way, quantum mechanics is a modification of the basic laws of classical mereology to a mereology of potentialities. The indistinguishability of electrons requires a further modification of the laws of compounding potentialities: namely the antisymmetrization principle. In density functional theory, both these problems are handled through the introduction of an extra interaction term which has no classical analog: the exchange-correlation potential.

Similar considerations apply when dealing with the notion of the “atom” in chemistry, a term that is used in multiple contexts. While we may intuitively understand the concept of an atom in a molecule (AIM), its rigorous definition is the subject of considerable controversy. Several schemes for partitioning a molecule into atoms have been proposed and the merits and shortcomings of each have

been debated in the literature (Parr, Ayers and Nalewajski, 2005; Bader and Matta, 2012). Some requirements of an AIM would be that it contain a nucleus, that its electron density reduce to that of the free atom as the other atoms are removed and that its properties likewise reduce to that of the free atom in this limit. This would ensure transferability of AIM properties between different molecules containing that atom. Perfect transferability of an atom between different molecules is an unattainable limit (Riess and Münch, 1981; Bader and Becker, 1988), but it is the quasi-invariant subset of properties retained by an atom in different chemical environments that is commonly referred to as an AIM. For many-electron atoms, the core electron densities are largely unperturbed from those of the corresponding free atoms and are carried largely intact into the AIM. In the valence regions of atoms, however, there is considerable variation between atomic densities in different molecular environments.

If $\rho(\mathbf{r})$ is the electron density at the position \mathbf{r} in a molecule and we associate a density $\rho_A(\mathbf{r})$ with every atom A in the molecule, we can define a weight function $w_A(\mathbf{r})$ such that:

$$\rho_A(\mathbf{r}) = w_A(\mathbf{r}) \rho(\mathbf{r}) \quad (2).$$

Requiring that the AIM densities add up to the total molecular density $\rho(\mathbf{r})$ at every point \mathbf{r} :

$$\sum_A \rho_A(\mathbf{r}) = \rho(\mathbf{r}) \quad (3)$$

results in the normalization of the weights:

$$\sum_A w_A(\mathbf{r}) = 1 \quad (4),$$

where the summation is over all atoms in the molecule. The atomic electron population N_A for each AIM is defined as:

$$N_A = \int \rho_A(\mathbf{r}) \, d\mathbf{r} \quad (5).$$

Integrating the total electron density in the molecule gives the total number of electrons N :

$$N = \int \rho(\mathbf{r}) \, d\mathbf{r} \quad (6),$$

whereupon:

$$\sum_A N_A(\mathbf{r}) = N \quad (7).$$

Bader's Mereology:

Bader's topological atoms result from partitioning space exhaustively into disjoint regions $\Omega_A, \Omega_B \dots$ each associated with a particular AIM. This is equivalent to the specification:

$$\begin{aligned} w_A(\mathbf{r}) &= 1 \quad \text{for } \mathbf{r} \in \Omega_A \\ &= 0 \quad \text{otherwise.} \end{aligned} \quad (8)$$

The boundaries of the region Ω_A are specified in this scheme by requiring that the "zero-flux condition" (Bader, 1990):

$$\nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) = 0 \quad (9)$$

be satisfied at every point on the surface S_A bounding the region Ω_A , where $\mathbf{n}(\mathbf{r})$ is the normal to the surface. The surface integral of this quantity:

$$\oint dS_A \nabla\rho(\mathbf{r}) \cdot \mathbf{n}(\mathbf{r}) \, d\mathbf{r} = 0 \quad (10)$$

is the flux of the gradient vectors of the charge density ($\nabla\rho$) through the surface S_A . It vanishes over every atomic region Ω_A and, by extension, over the entire molecular space.

Bader's partitioning scheme is motivated by the observation that concentrations of electron density around nuclei are the most obvious features of X-ray diffraction patterns of crystals: each nucleus is generally associated with a maximum or a cusp in the electron density, with the slope of the density at the cusp $\nabla\rho(\mathbf{r})|_{r=0}$ proportional to the negative of the atomic number $-Z$. This is the feature that makes it possible to deduce or 'solve' a molecular structure from analysis of X-ray diffraction patterns and

visual inspection of electron-density maps calculated from these data; this forms the basis of quantitative crystal structure determination from X-ray diffraction experiments. The electron density in an isolated atom decreases away from the nucleus in any direction. This feature is generally retained when atoms combine to form a molecule, with the nuclei functioning as attractors of the electron density gradient vector field $\nabla\rho(\mathbf{r})$. Bader formally defines an AIM as the union of such an attractor and its basin of attraction Ω_A (Bader, 1990).

AIMs in Bader's partitioning scheme are cleanly separated in space by inter-atomic surfaces formed by all paths of the gradient vector field originating at the bond critical point between the pair of atoms and terminating at infinity. Using Bader's partitioning (8) in equation (3) gives:

$$\begin{aligned} \rho_A(\mathbf{r}) &= \rho(\mathbf{r}) && \text{for } \mathbf{r} \in \Omega_A \\ &= 0 && \text{otherwise.} \end{aligned} \quad (11)$$

Using equation (11) in equation (5) then yields for the atomic electron population N_A :

$$N_A = \int_{\Omega_A} \rho(\mathbf{r}) \, d\mathbf{r} \quad (12),$$

where the domain of integration is restricted to the region Ω_A , the basin of atom A. A bond path in Bader's theory is defined as a trajectory of the gradient vector field $\nabla\rho(\mathbf{r})$ connecting two atomic nuclei. A pair of bonded atoms is usually associated with a bond path and a bond critical point between them. A molecular graph can be defined as the network of bond paths, where the atomic nuclei are nodes or vertices of the graph connected by bond paths. Bader has clarified, however, that bond paths are not the same as chemical bonds (Bader, 2009). The topology of the electron density and its network of critical points provides a fairly reliable view of molecular structure, corresponding with chemical intuition. Bond paths and molecular graphs are clearly higher-level coherent structures that emerge from the non-classical mereology of AIM.

Hirshfeld's mereology:

A fundamentally different mereological partitioning of a molecule into atoms was proposed by Fred Hirshfeld (Hirshfeld, 1977). In this scheme, a “promolecule” is first constructed from the superposition of the electron densities of the isolated atoms:

$$\rho^0(\mathbf{r}) = \sum_A \rho_A^0(\mathbf{r}) \quad (13),$$

where $\rho_A^0(\mathbf{r})$ are the reference atomic densities to which the AIM densities $\rho_A(\mathbf{r})$ are compared. The molecular electron density is then partitioned among the atoms, in such a manner that each AIM contributes to the molecular density $\rho(\mathbf{r})$ at each point in proportion to its contribution to the promolecule's density at that point:

$$w_A(\mathbf{r}) = \frac{\rho_A^0(\mathbf{r})}{\rho^0(\mathbf{r})} = \frac{\rho_A(\mathbf{r})}{\rho(\mathbf{r})} \quad (14),$$

The second equality here is a restatement of the general definition (2) for the weight function. This partitioning is known as the stockholder partitioning scheme, as it is analogous to the way a company's shares (and profits) are apportioned among its stockholders: in proportion to each stockholder's original contribution to the corpus of the company. In contrast to Bader's partitioning, Hirshfeld's mereology results in spatially overlapping atoms, allowing for interpretation of chemical bonding in terms of the overlap electron density between atoms. This is the higher-level coherence that results from this mereology.

Hirshfeld's partitioning follows from the reasonable requirement that the loss of information be minimized upon formation of a molecule from neutral atoms (Nalewajski and Parr, 2000). Defining a shape function for each atom as a density per electron:

$$\sigma_A(\mathbf{r}) = \frac{\rho_A(\mathbf{r})}{N_A} \quad (15),$$

with an analogous expression for the promolecular atoms $\sigma_A^0(\mathbf{r})$ allows one to define an information loss function (Ayers, 2006; Parr, Ayers and Nalewajski, 2005):

$$I = \sum_A N_A \int \sigma_A(\mathbf{r}) \ln \left\{ \frac{\sigma_A(\mathbf{r})}{\sigma_A^0(\mathbf{r})} \right\} d\mathbf{r} + \sum_A N_A \ln \left(\frac{N_A}{N_A^0} \right) \quad (16).$$

The first term in equation (15) represents the information loss due to polarization, *i.e.* change in shape of the electron density upon molecule formation, while the second term is an entropy of mixing, reflecting the transfer of electronic charge between AIMs upon molecule formation. The shape functions are normalized to unity by virtue of equation (2):

$$\int \sigma_A(\mathbf{r}) d\mathbf{r} = \int \sigma_A^0(\mathbf{r}) d\mathbf{r} = 1 \quad (17),$$

supporting the interpretation of I as an information entropy. Each term also satisfies the condition of statistical independence (additivity of independent events), as expected of any measure of information.

The first serious problem with Hirshfeld's mereology is the arbitrariness involved in choosing neutral atoms as the reference densities (Davidson, 1992). This choice has no strict theoretical basis and is adopted merely for computational convenience. Thus for heteronuclear, strongly ionic molecules, it would seem more reasonable to use the ionic fragments as reference densities. These different choices of the promolecule density lead to very different electron populations on the atoms. These ambiguities are further exacerbated when dealing with ionic molecules.

Momentum Space Mereology:

The fundamental quantity analogous to $\rho(\mathbf{r})$ in momentum space is the electron momentum density $\gamma(\mathbf{p})$ (which is related to $\rho(\mathbf{r})$ through Fourier-Dirac transformation of the full N -electron wavefunction). A

momentum space formalism is useful in interpreting the results of electron momentum spectroscopy and Compton scattering experiments. However, atomic momentum densities are not spherically symmetric. Thus partitioning the momentum density of a molecule with respect to zero-flux surfaces of $\nabla\gamma(\mathbf{p})$ does not result in basins that can be identified with atoms. But a Hirshfeld-type partitioning of molecular momentum densities may be employed to define AIMs in momentum space (Balanarayan and Gadre, 2006):

$$\gamma_A(\mathbf{p}) = \frac{\gamma_A^0(\mathbf{r})}{\sum_A \gamma_A^0(\mathbf{r})} \gamma(\mathbf{p}) \quad (18),$$

where $\gamma_A(\mathbf{p})$ and $\gamma_A^0(\mathbf{p})$ are the momentum densities of the AIM and the free atom A, respectively, centered at $\mathbf{p}=0$. This scheme yields integrated atomic charges that agree well with atomic charges obtained from the corresponding Hirshfeld AIMs in coordinate space.

Conclusion:

We have thus seen that modification of the basic laws of classical mereology lead to different conceptions of the atom in a molecule, and to the emergence of ontologically higher-level coherences associated with the science of chemistry. We have here discussed three different formulations of the concept of the atom in a molecule: two in position space and one in momentum space. The first scheme, championed by Richard Bader (Bader, 1990), partitions position space exhaustively into disjoint regions, using boundaries defined by the zero flux condition (9). This scheme is theoretically appealing as it results in atoms that satisfy the virial theorem of quantum mechanics, and can be justified by appealing to Schwinger's action principle. Bader's formulation is the one that provides a physical conception of the notion of a chemical bond between atoms. The second scheme, first proposed by Fred Hirshfeld (Hirshfeld, 1977) and justified on information theoretic grounds – namely the requirement that the loss of information be minimized upon formation of a

molecule from neutral atoms (Nalewajski and Parr, 2000), results in spatially overlapping spherical atoms with fuzzy boundaries. The appeal of this scheme is that it allows for interpretation of chemical bonding in terms of the popular concept of overlap of electron density between atoms, but the partitioning is not unique unless performed self-consistently using an iterative scheme (Bultinck, *et al*, 2007) and there is the further arbitrariness involved in the choice of neutral atoms as the reference densities (Davidson, 1992). The third mereology discussed here is a fuzzy partitioning in the spirit of Hirshfeld's scheme, but performed now on the electron density in momentum space (Balanarayan and Gadre, 2006), where no zero flux condition similar to Bader's partitioning in position space holds. This momentum space partitioning has not found widespread utility as yet and has remained an interesting curiosity, but if the position space and momentum space pictures are to be regarded as complementary descriptions of the same ontological reality (as quantum mechanics asserts), there is no reason to not consider a momentum space mereology on the same footing as a position space mereology.

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