

# Atom in Molecules a Quantum Theory (AIM)

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“The primary purpose in postulating the existence of atoms in molecules is a consequence of the observation that atoms or groupings of atoms appear to exhibit characteristic sets of properties, which, in general, vary between relatively narrow limits.”

## Necessary criteria for a theory of atoms in molecules

The definition of a bound atom – an atom in a molecule – must be such that it enables one to define all of its average properties. For reason of physical continuity, the definition of these properties must reduce to the quantum mechanical definition of the corresponding properties for an isolated atom. The atomic values for a given property should, when summed over all the atoms in a molecule, yield the molecular average for that property.

## The role of charge density

The question “are there atoms in molecules” is equivalent to asking two equally necessary questions of quantum mechanics:

- (i) does the state function  $\psi(\mathbf{x}, t)$ , which contains all of the information that can be known about a system, predict a unique partitioning of a molecule into subsystems and if so
- (ii) can one define the observables, their average values, and their equation of motion for the subsystem?

**Answer: YES**

Subsystems are open systems defined in real space, their boundaries being determined by a particular property of the *electronic charge density* (Bader and Beddall 1972).

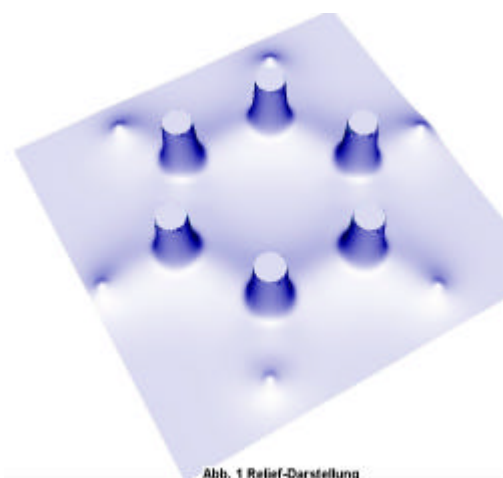


Abb. 1 Relief-Darstellung

The dominant morphological feature of the density defines an atom in a molecule. It is a **scalar field in a 3d space**. The topological properties of such a scalar field are conveniently summarized in terms of the **number und kinds of its critical points**.

## Critical points

These are points where the first derivatives of  $\rho(\mathbf{r})$  vanish and thus they determine the position of **extrema in the charge density** (minima, maxima, saddle points).

The structure of the density is made more evident through the study of the associated vector field. A representation of lines of forces is a display of a vector field. The null points referred to by Faraday are what is called a **critical points, points where the field of  $\tilde{\mathbf{N}}\mathbf{r}(\mathbf{r})$  vanishes**.

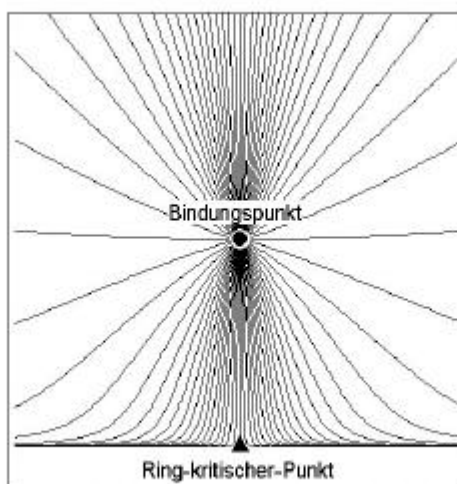


Abb. 5: Gradientenfeld der Grenzfläche zwischen C2 und C3

A display of  $\nabla\rho(\mathbf{r})$  for a molecule will make visible to the eye, without further mathematical analysis, the definition of its atoms and of a particular set of lines linking certain pairs of nuclei within the molecule – its **molecular graph**.

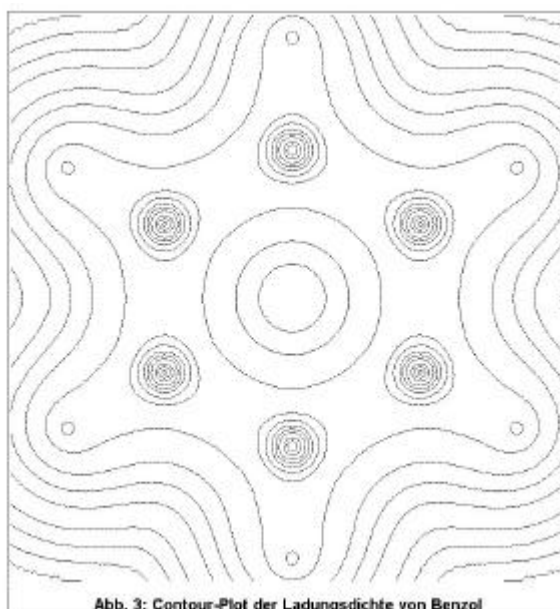
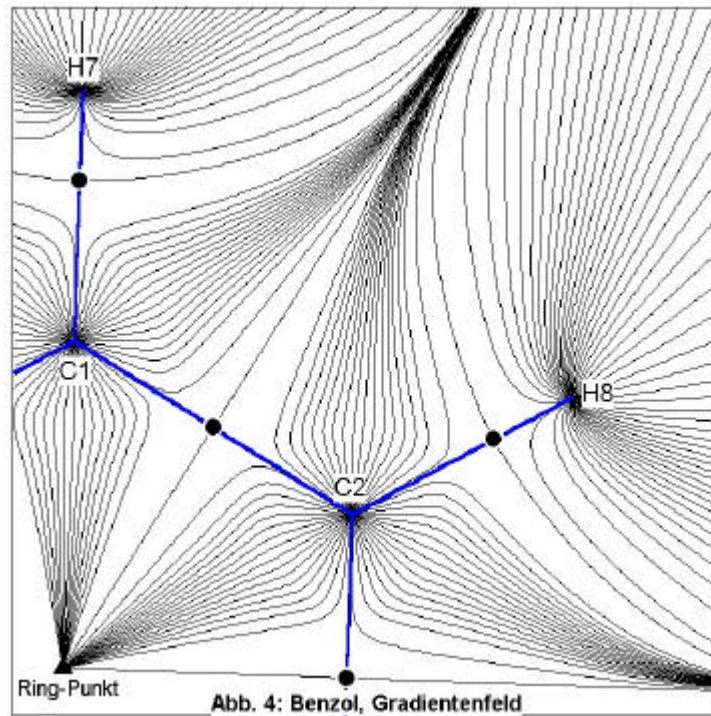


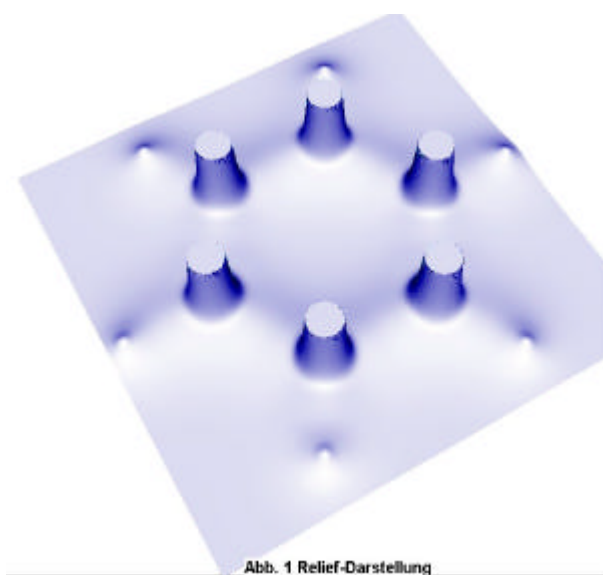
Abb. 3: Contour-Plot der Ladungsdichte von Benzol



There are **four possible kinds of stable critical points** in  $\rho(\mathbf{r})$  and each will be associated with a particular element of structure. From that one can conclude that atoms exist in molecules and they may be linked together to form structures consisting of chains, rings and cages.

## Topological properties of the charge density

The form assumed by the distribution of charge in a molecular system is the physical manifestation of the forces acting within the system. Dominant among these is the attractive force exerted by the nuclei, a consequence of the **localized nature of nuclear charge**. This interaction is responsible for the single most important topological property exhibited by a molecular charge distribution of a many-electron system –that, in general,  $\nabla\rho(\mathbf{r}, \mathbf{X})$  exhibits local **maxima** only at the positions of nuclei. This is an observation based on experimental results obtained from X-ray diffractions studies and on the results of theoretical calculations.



Besides the maxima **saddle points** are found at the midpoints along the C-C axis. In this case  $\rho(\mathbf{r})$  is a maximum in one particular plane. What is needed is a method of summarizing in a precise manner the principal topological features of a charge distribution.

## Classification of critical points

Laplacian:  $\nabla^2\rho = \partial^2\rho/\partial x^2 + \partial^2\rho/\partial y^2 + \partial^2\rho/\partial z^2$

$\omega$  rank of Hessian of  $\rho$  (number of non-zero eigenvalues)

$\sigma$  signature (sum of the signs of the eigenvalues)

**(w,s)**

**(3, -3)** All curvatures are negative and **r** is a **local maximum** at  $\mathbf{r}_c$ , **nucleus**

**(3, -1)** **Two curvatures are negative** and **r** is a **maximum** at  $\mathbf{r}_c$  in the plane defined by their corresponding axes.  $\rho$  is a minimum at  $\mathbf{r}_c$  along the third axis which is perpendicular to this plane, **bond critical point**

**(3, +1)** **Two curvatures are positive** and **r** is a **minimum** at  $\mathbf{r}_c$  in the plane defined by their corresponding axes.  $\rho$  is a maximum at  $\mathbf{r}_c$  along the third axis which is perpendicular to this plane, **ring critical point**

**(3, +3)** All curvatures are positive and  $\rho$  is a **local minimum** at  $\mathbf{r}_c$ , **cage critical point**

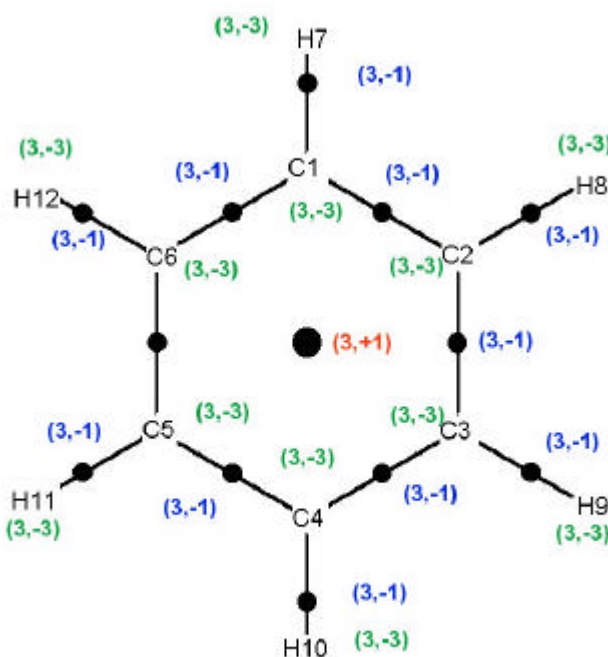


Abb.2: Benzol, Molekularer Graph

## Gradient vector field of the charge density

The gradient vector field of the charge distribution is represented through a display of the trajectories traced by the vector  $\nabla\rho$ . A trajectory of  $\nabla\rho$  is also called gradient path.

## Elements of molecular structure

A  $(3, -3)$  critical point exhibits the property which **defines a point attractor** in the gradient field of the charge distribution.

Since the  $(3, -3)$  critical points in a many-electron charge distribution are generally found only at the **positions of the nuclei**, the nuclei act as the attractors of the gradient field of  $\rho$ . The result of this identification is that the space of a molecular charge distribution, real space, is partitioned into disjoint regions, the **basins**, each of which contains one point attractors or nucleus.

### Boundaries

The presence of a  $(3, -1)$  critical point provides a boundary between the basins of neighbouring atoms. **The trajectories** associated with each  $(3, -1)$  critical point define a surface the **interatomic surface**.

### Chemical bonds and molecular graph

The existence of a  $(3, -1)$  critical point its associated atomic interaction line indicates that electronic charge density is accumulated between the nuclei that are so linked.

**Atomic interaction line:**  $(3, -3) \Leftrightarrow (3, -1) \Leftrightarrow (3, -3)$  linking two neighbouring atoms (attractors)

In this case the line of maximum charge density linking the nuclei is called a **bond path** and the  $(3, -1)$  critical point referred to as a **bond critical point**.

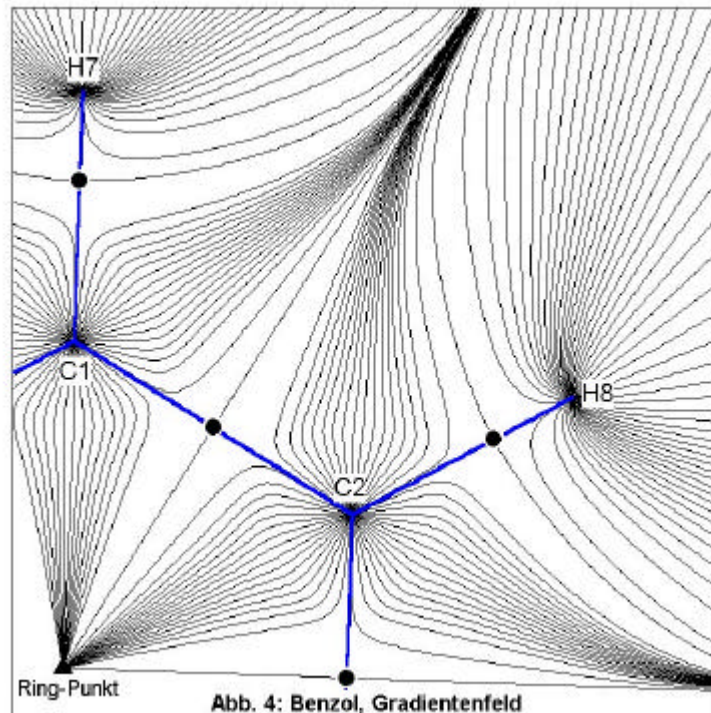
For a given configuration X of the nuclei, a **molecular graph** is defined as the union of closures of the bond paths or atomic interaction lines. Pictorially, the molecular graph is the network of the bond paths linking pairs of neighbouring nuclear attractors.

### Rings and cages

The remaining critical points of rank three occur as consequences of particular geometrical arrangements of bond paths and they define the remaining elements of molecular structure: rings and cages.

**Ring:  $(3, +1)$  critical point;** all of the trajectories which originate at the critical point at the enter of the ring of nuclei, the  $(3, +1)$  or ring critical point, terminate at the ring nuclei.

**Cage:  $(3, +3)$  critical point;** if the bond path are so arranged as to enclose the interior of a molecule with ring surfaces, then a  $(3, +3)$  or cage critical point is found in the interior of the resulting cage. The charge density is a local minimum at a cage critical point.



## Poincare-Hopf relationship

The number and type of critical points which can coexist in a system with a finite number of nuclei is limited:

$$n - b + r - c = 1$$

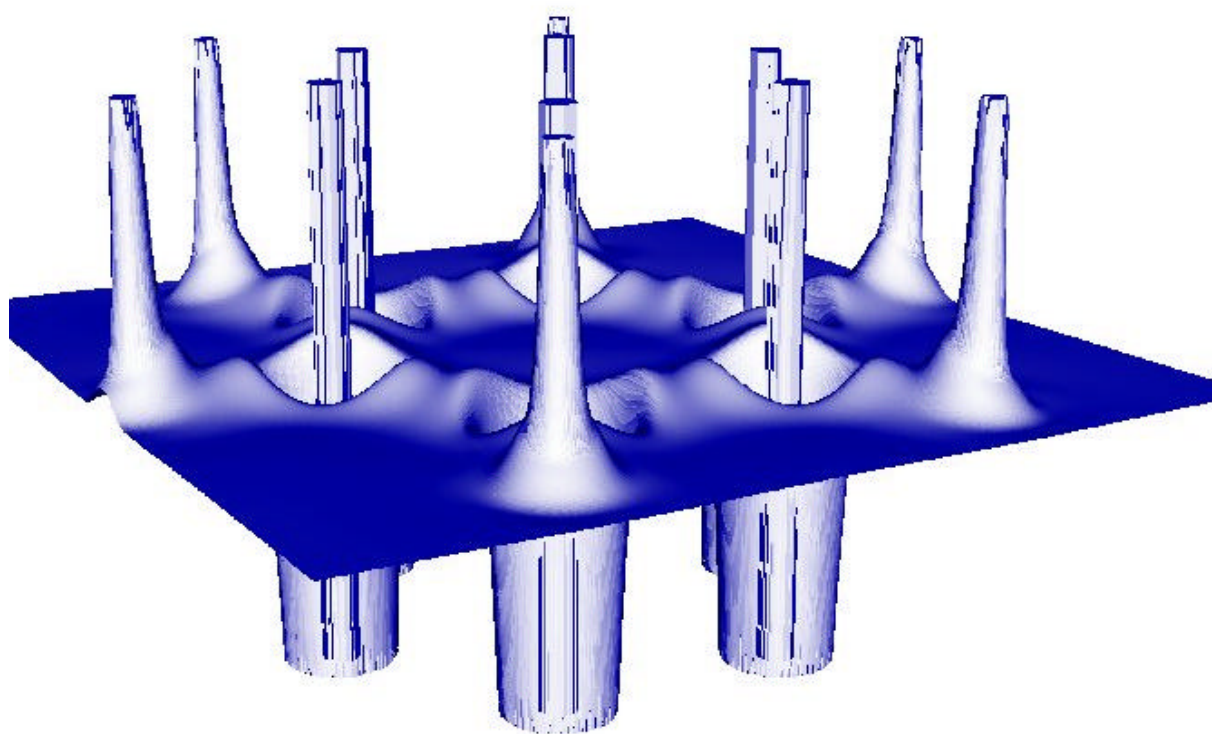
*n* = number of nuclei; *b* # bonds; *r* # rings; *c* # cages

**Example benzene:  $12 - 12 + 1 - 0 = 1$**



## Valence shell charge concentration

- Extrema in the Laplacian of the density are also classified by rank and signature resulting again in critical points.
- The topological discussion will always refer to the negative of the Laplacian  $-\nabla^2\rho$  • Since charge is concentrated where  $\nabla^2\rho < 0$ , a local maximum in  $-\nabla^2\rho$  is synonymous with a maximum in the concentration of electronic charge
- Division into inner and outer shell density possible (VSEPR)
- $\nabla^2\rho < 0$  of the outer shell is called the valence shell charge concentration



### 3D-Laplacian of benzene

- The Laplacian of the electron density recovers the **shell structure** of an atom by displaying a corresponding number of alternating shells of charge concentration and charge depletion. The uniform sphere of charge concentration present in the valence shell of a free atom is distorted upon chemical combination to form local maxima and minima. The number of local maxima in  $-\nabla^2\rho$  in the valence shell, the local valence charge concentrations, together with their relative positions and magnitudes, coincide with the number and corresponding properties of the localized electron pairs assumed to exist in the **VSEPR model** of molecular geometry.



## • Further Reading

1. R. F. W. Bader, [\*Atoms in Molecules - A Quantum Theory\*](#), [Oxford University Press](#), Oxford, 1990. ISBN: 0198558651  
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