Gradient Vector Fields

- ✔ AIM theory is concerned with the topology of a molecule's electron density, which is described as a *scalar field*.

- ✔ The scalar field describing ρ is usually represented by a series of envelopes of constant scalar value.

- ✔ Changes in the value of a scalar field are described by a *gradient*, which is a vector that points in the direction in which the scalar quantity is increasing most rapidly.

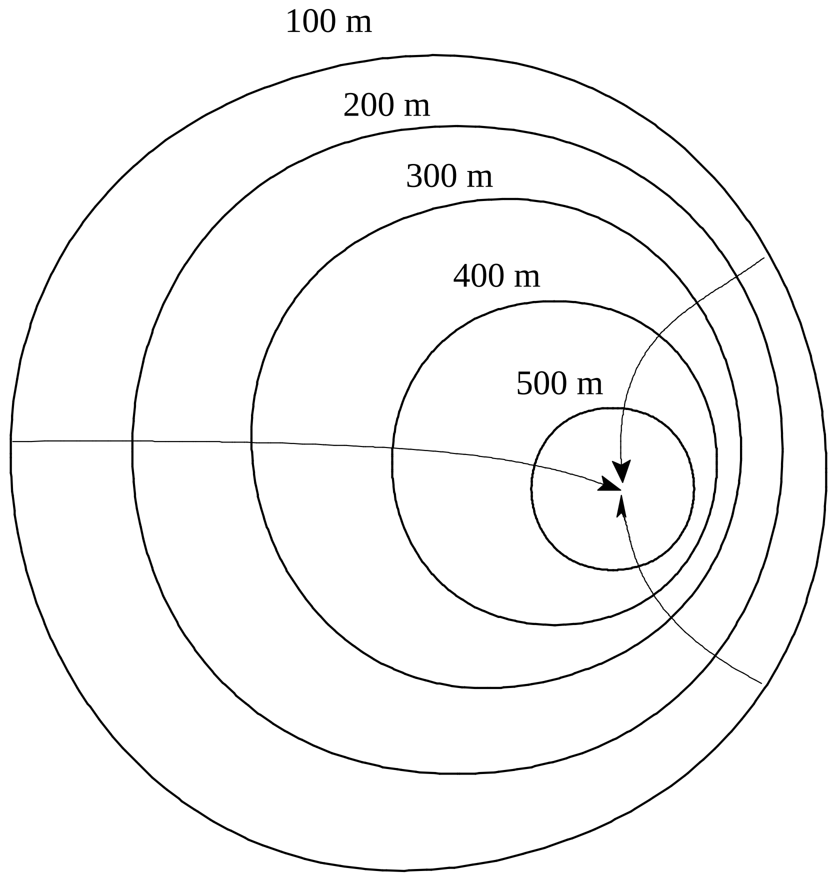
- ✔ A gradient vector is everywhere perpendicular to an envelope of constant scalar value.

- ✔ A *gradient path* traces a path of greatest change through a series of envelopes of varying constant scalar value.

- ✔ A gradient path is everywhere perpendicular to each of the contours of constant value.

- ✔ The collection of all gradient paths is called a *gradient vector field*.

Three Gradient Paths Up an Asymmetric Mountain



- ☞ All gradient paths cross each envelope of constant height at a right angle, thereby following the path of steepest ascent between each successive envelope.

- ☞ The collection of all gradient paths would describe the gradient vector field of the mountain.

The Gradient of ρ, $\nabla\rho$

☞ The gradient of electron density is defined as

$$\nabla\rho = \left(\partial\boldsymbol{\mu}_x/\partial x + \partial\boldsymbol{\mu}_y/\partial y + \partial\boldsymbol{\mu}_z/\partial z\right)\rho$$

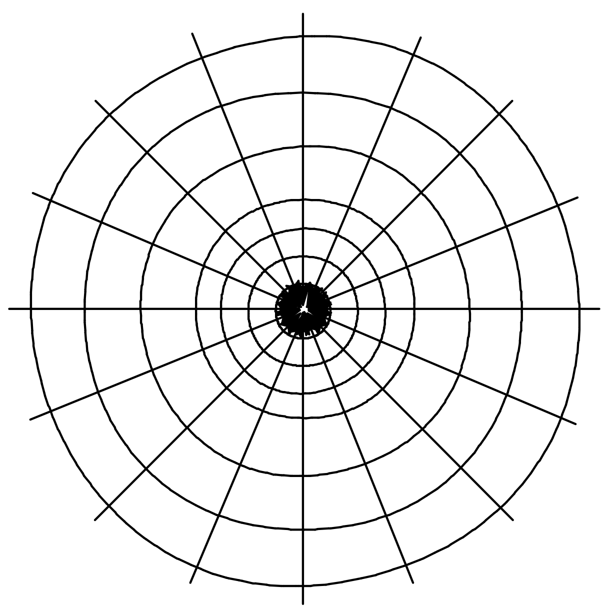
where $\boldsymbol{\mu}_x$, $\boldsymbol{\mu}_y$, $\boldsymbol{\mu}_z$ are unit vectors.

✔ $\nabla\rho$ is a vector that points in the direction of greatest increase in ρ.

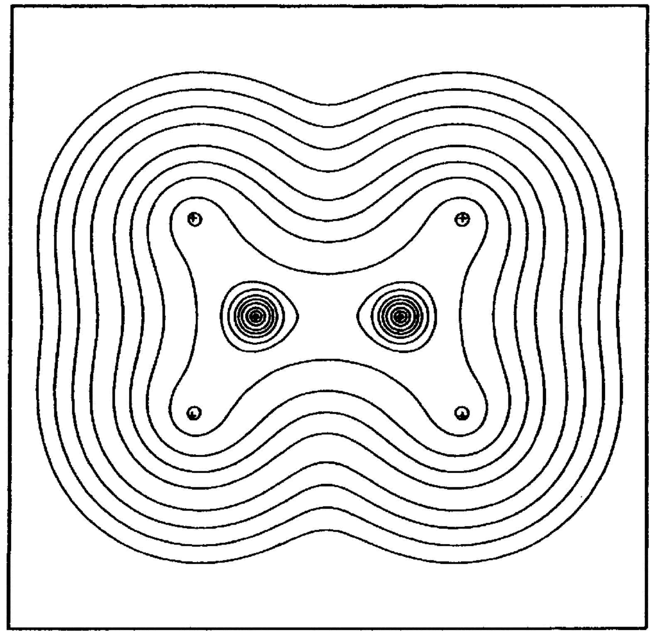
✔ From a given starting point, the gradient path is defined by following $\nabla\rho$, the direction of greatest change, from point to point.

✔ The collection of gradient paths constitutes the gradient vector field of the electron density.

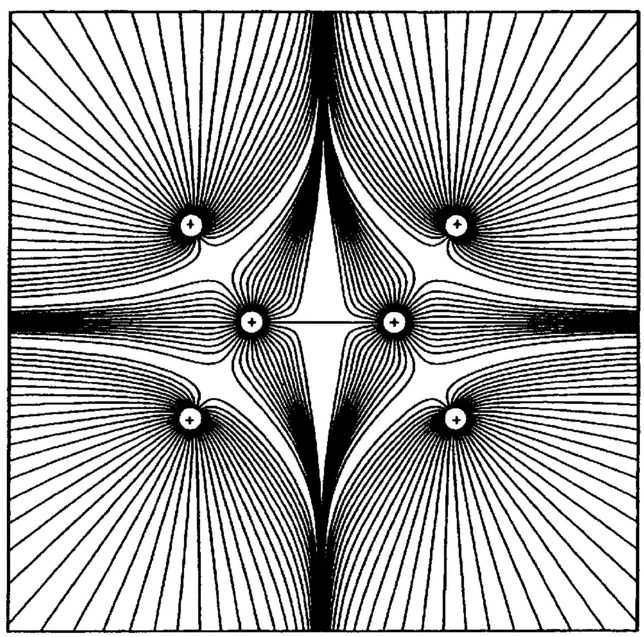
☞ For a spherical free atom, the gradient field is a symmetrical series of vectors pointing from infinity to the nucleus.



Contour Plot of ρ and Gradient Vector Field of C_2H_4



Contour plot of ρ for C_2H_4 in σ_h plane



Gradient vector field of $\nabla\rho$ for C_2H_4 in σ_h plane

General Features of Gradient Vector Field Maps

- ✔ All paths originate at infinity and terminate at a nucleus.

- ✔ Nuclei act as *attractors* for a series of gradient paths, defining a *basin* of the attractor.

- ✔ Basins do not overlap, thereby partitioning the molecule into individual atomic regions.

- ✔ The gradient vector field's partitioning can be used to define atoms as they exist in molecules.

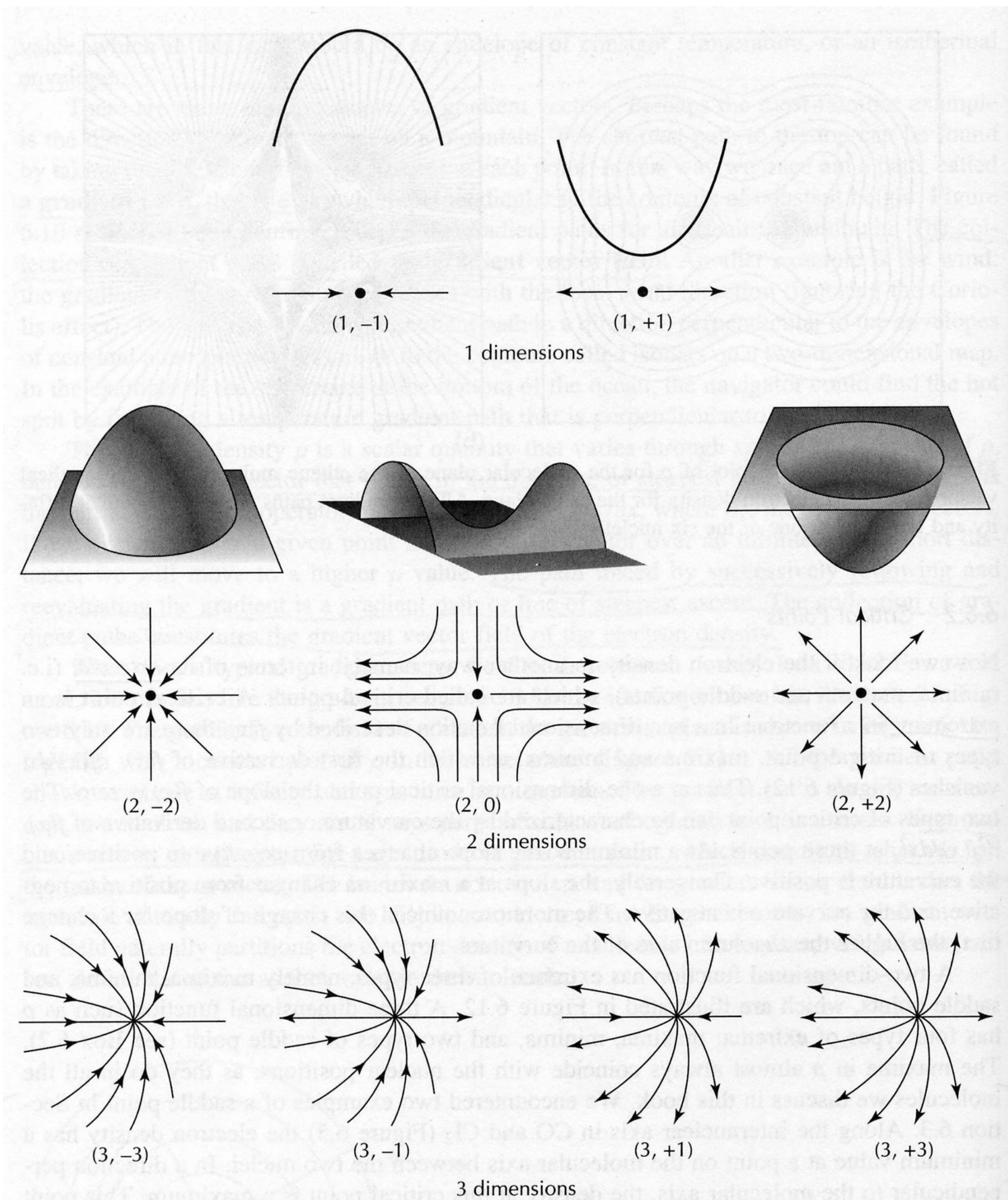
Critical Points

☞ A critical point is an *extremum* (maximum, minimum, saddle point) in a function.

① One-dimensional functions can have maxima and minima.

② Two-dimensional functions can have maxima, minima, and saddle points.

③ Three-dimensional functions (like ρ) can have maxima, minima, and two types of saddle points.



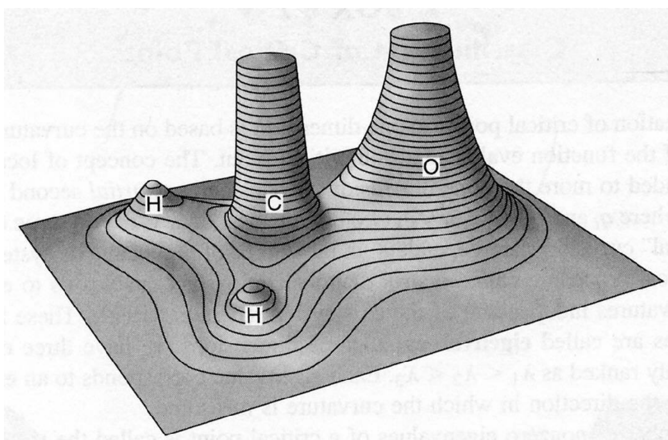
Notations of the type (r,s,) indicate rank (r) and signature (s) of the extremum. This notation is not important for our purposes.

Critical Points in ρ

✔ Maxima in ρ almost always occur at nuclear positions.

✔ The most important saddle point for our purposes is the *bond critical point*, which creates a minimum along the internuclear axis (bond line)

✔ When a value of ρ is chosen such that the corresponding constant density envelopes separate into individual envelopes that just touch, the point where the envelopes touch is the bond critical point.



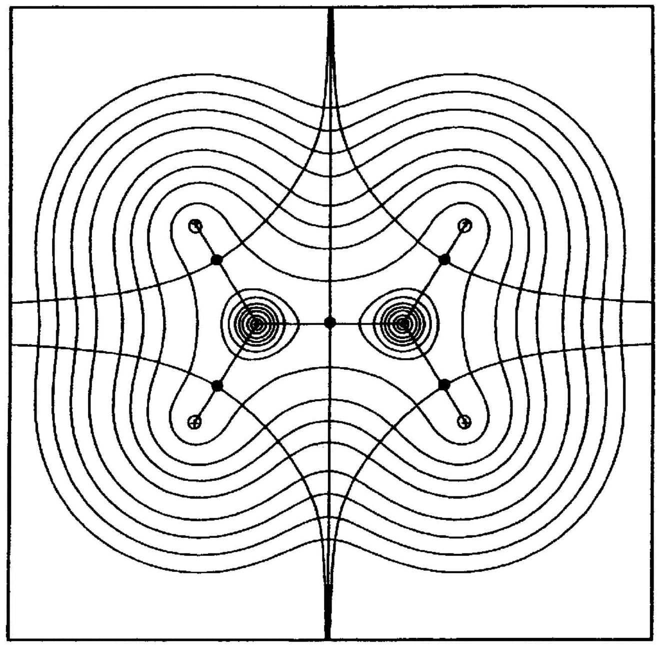
Relief map of H_2CO showing saddle points between C-O and C-H. Note lack of saddle point between the two H atoms.

Gradients Paths Through Bond Critical Points

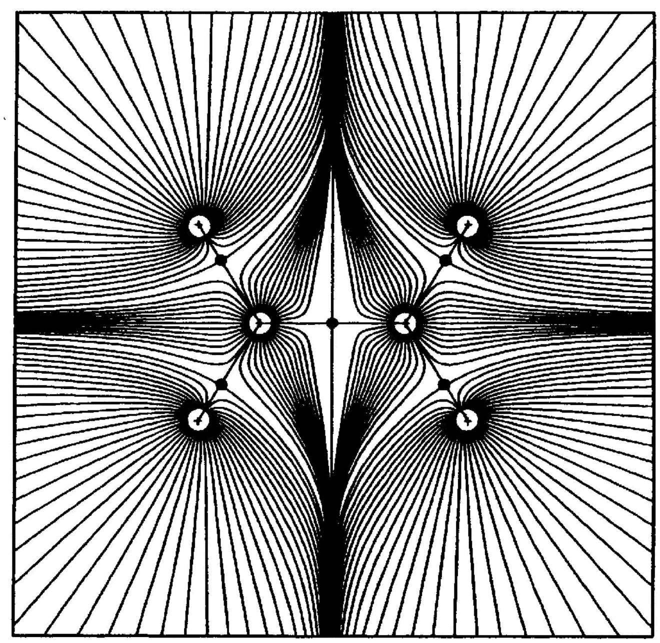
① Gradient paths that connect bond critical points with neighboring nuclei define bond lines.

② Gradient paths that originate at infinity and pass through a bond critical point define surfaces between two adjacent atoms, called the *internuclear surface*.

Gradient Paths Through Bond Critical Points in C_2H_4



Contour plot of ρ for C_2H_4 in σ_h plane with special gradient paths through bond critical points.

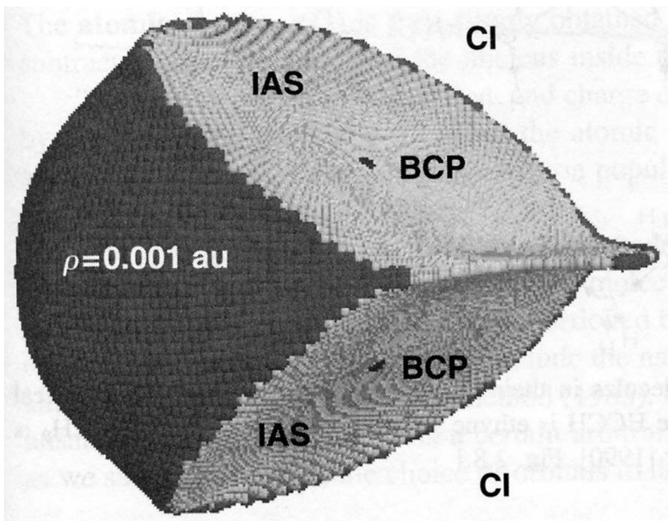


Gradient vector field of $\nabla\rho$ for C_2H_4 in σ_h plane with extra gradient paths through bond critical points.

AIM Definition of an Atom

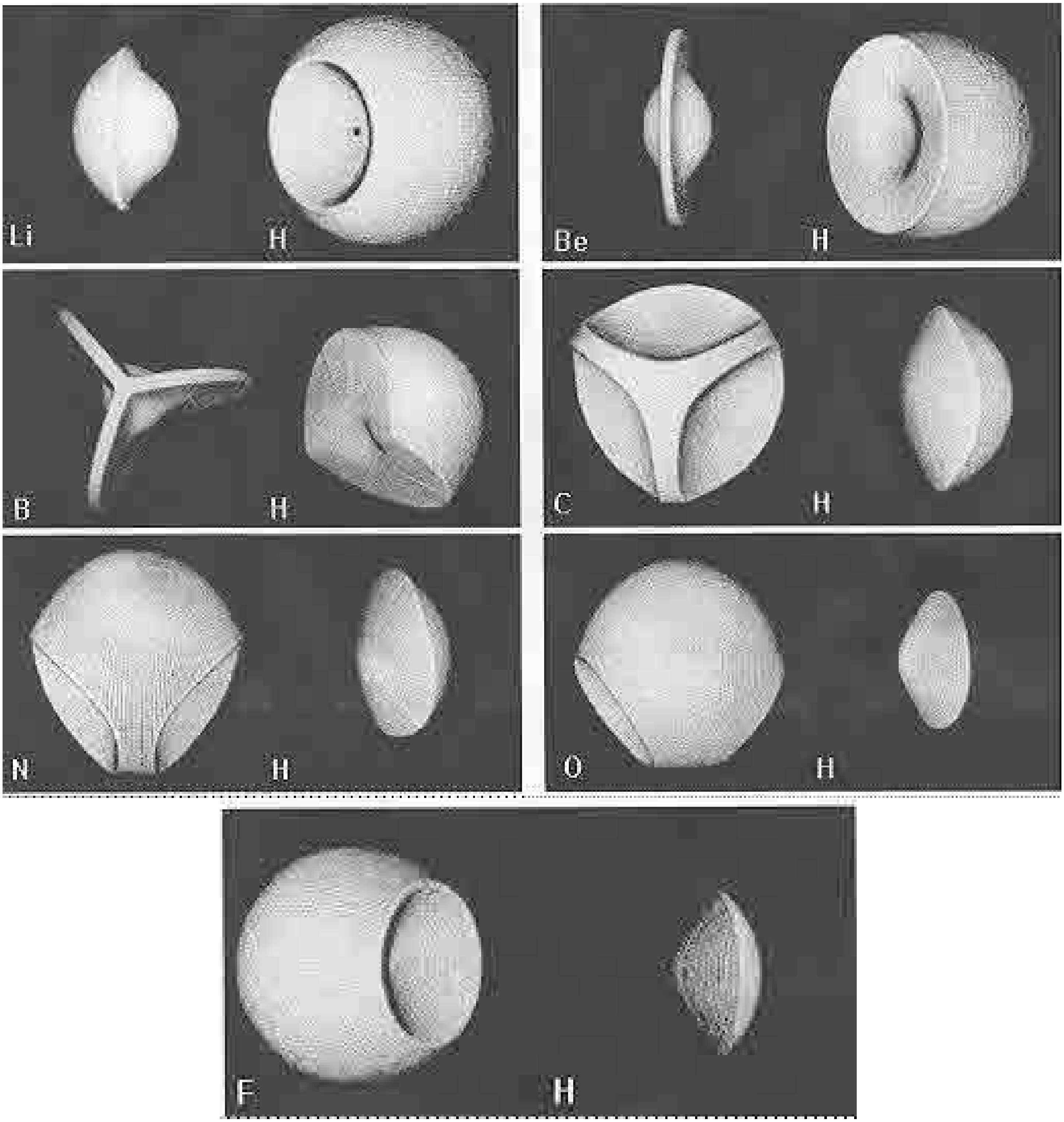
- In AIM theory an atom is defined as the union of a nucleus and the atomic basin that the nucleus dominates as an attractor of gradient paths.

- An atom in a molecule is defined by that portion of space bounded by its interatomic surfaces, except on an open side where it extends to infinity.



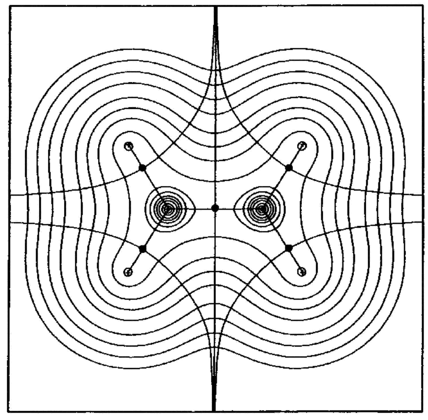
Shape of a sulfur atom in SCl_2 (IAS = interatomic surface, BCP = bond critical point). Open end is shown to ρ = 0.001 au.

AIM Depictions of Atoms in Period 2 Hydrides



Source: www.chemistry.mcmasters.ca/faculty/bader/aim/aim_3.html

AIM Definition of Bond

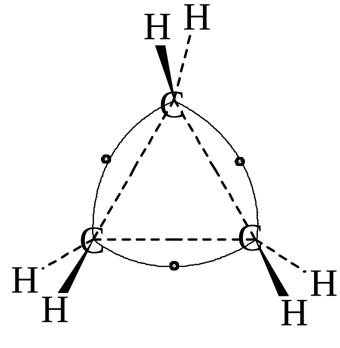


- ✔ The pair of gradient paths that originate at a bond critical point and terminate at two individual atoms is called an *atomic interaction line.*
  - Every pair of nuclei that have a common interatomic surface have an atomic interaction line connecting them.
  - For a molecule at equilibrium, an atomic interaction line is called a *bond path*.

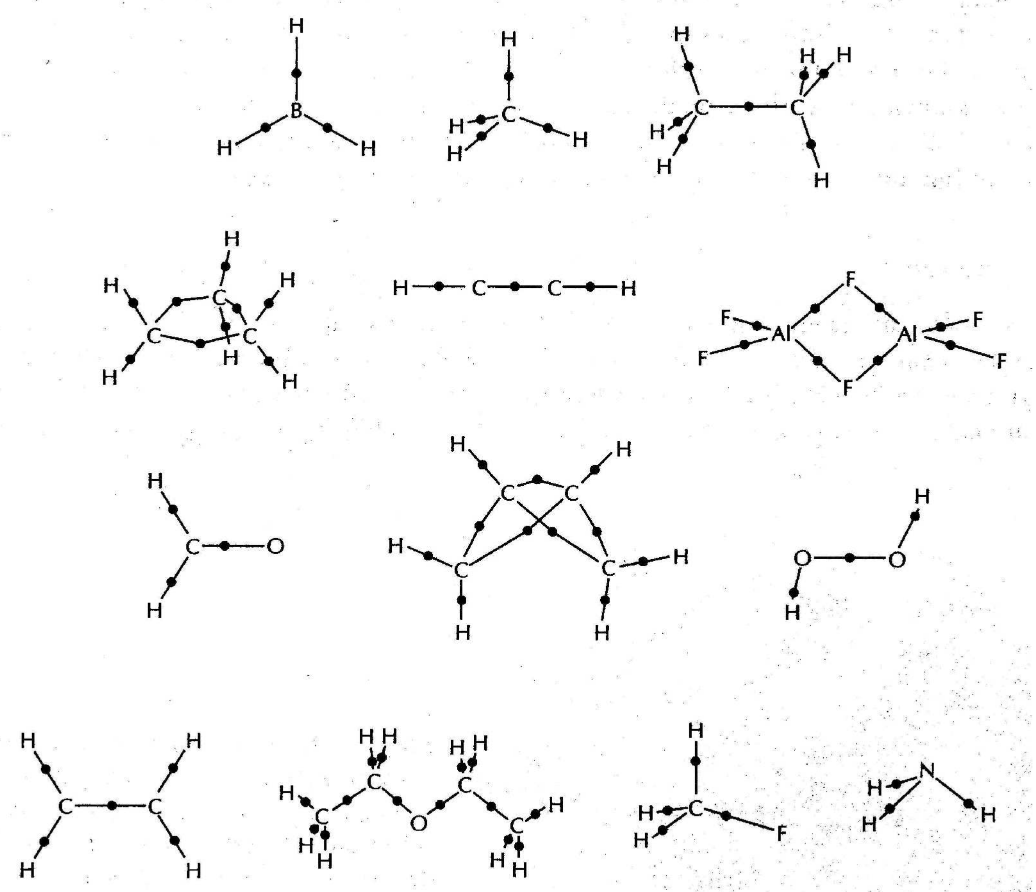
A bond path is the AIM definition of a bond.

- ✔ A bond path exists between atoms that have covalent bonds, ionic bonds, or have weak bonds such as hydrogen bonding or very weak donor-acceptor bonds (e.g., $F_3B{\cdot}CO$).

- ✔ Bond paths are usually straight lines, but in small ring structures they may curve outward.



Molecular Graphs



✔ Although these conform to our usual understanding of molecular shapes and bond linkages, these are not Lewis structures.

✔ Lewis notions of double, single, and triple bonds have no equivalent in AIM theory.

✔ Molecular graphs show where bonds exist, as indicated by the presence of bond paths with bond critical points between the linked nuclei.