AIM Theory

- ✔ The theory of atoms in molecules (AIM) is a method of analyzing the electron density distribution (ρ, rho), providing a detailed picture of how atoms exist in molecules and how they are bonded together.

- ✔ AIM analysis makes use of *ab initio* calculations of ρ in most cases, although x-ray data are sometimes used.

- ✔ The importance of ρ to an understanding of bonding is a consequence of the Hellmann-Feynman theorem, independently discovered by Hans Hellman[1] and Richard Feynman[2] in the 1930s.

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[1]H. Hellmann, *Einfürung in die Quantenchemie*, Franz Deuticke, Leipzig, **1937**, p. 285.

[2]R. P. Feynman, *Phys. Rev.*, **1939**, *56*, 340.

Hellmann-Feynman Theorem

☞ The force acting on each nucleus in a molecule is exactly that calculated by the principles of classical electrostatic theory from the charges and positions of the other nuclei and of the electrons.[3]

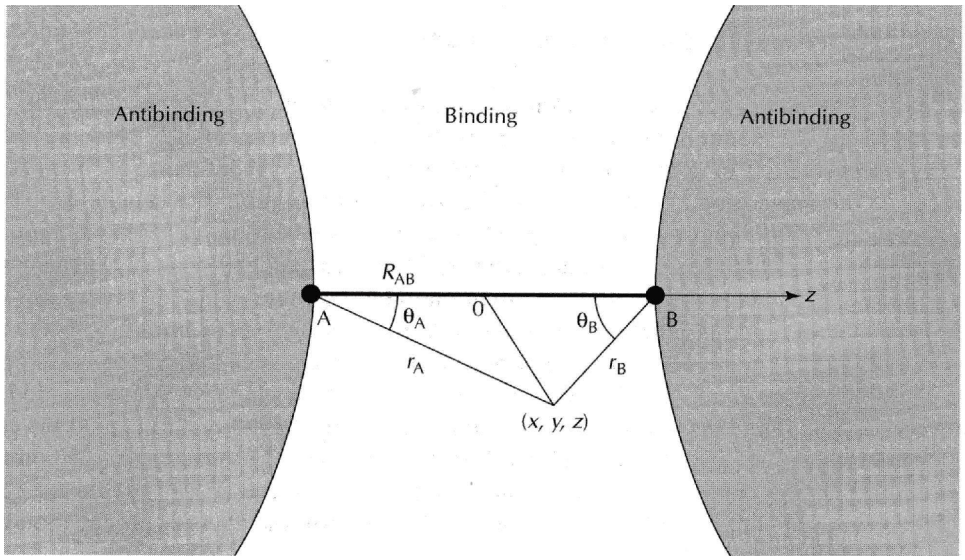
✔ The only forces operating in a molecule are electrostatic forces arising from repulsions between nuclei and attractions between nuclei and electrons.

✔ The electrons have the spatial distribution given by ρ, calculated from $\psi\psi^*$.

✔ At the equilibrium position of a stable molecule the resulting attractive and repulsive forces acting on each nucleus vanish (i.e., cancel exactly).

[3]Linus Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithica, NY, 3rd ed., **1960**, p. 21.

Diatomic Case

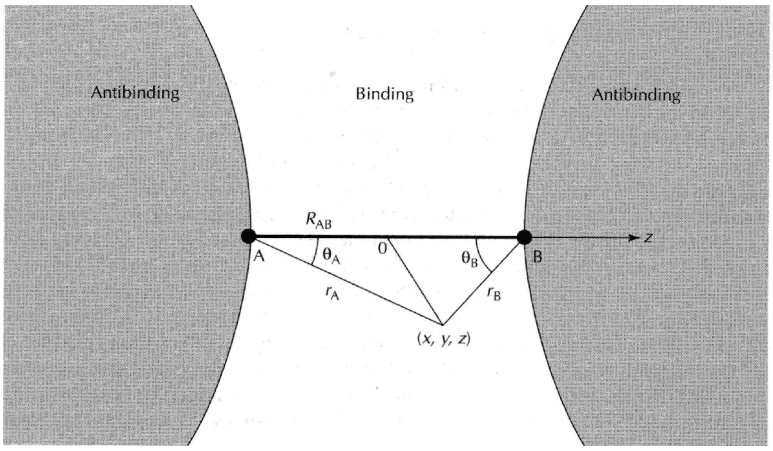


✔ Force acting on nucleus A along the internuclear axis, z, is given by

$$F_A = Z_A e^2 \int \rho(\mathbf{r}) \frac{\cos\theta_A}{r_A^2} - \frac{Z_A Z_B e^2}{R_{AB}^2} \, d\tau$$

Z_A, Z_B	nuclear charges on A and B
e	unit charge
θ_A	angle between position vector **r** and z
r_A	distance from A to point **r**(x,y,z)
R_{AB}	internuclear distance between A and B

Binding and Antibinding Regions



✔ A diatomic molecule can be partitioned into a binding region and an antibinding region, separated by two surfaces of revolution given by the function *B*:

$$B(Z_A, Z_B, \boldsymbol{r}) = Z_A \frac{\cos\theta_A}{r_A^2} + Z_B \frac{\cos\theta_B}{r_B^2}$$

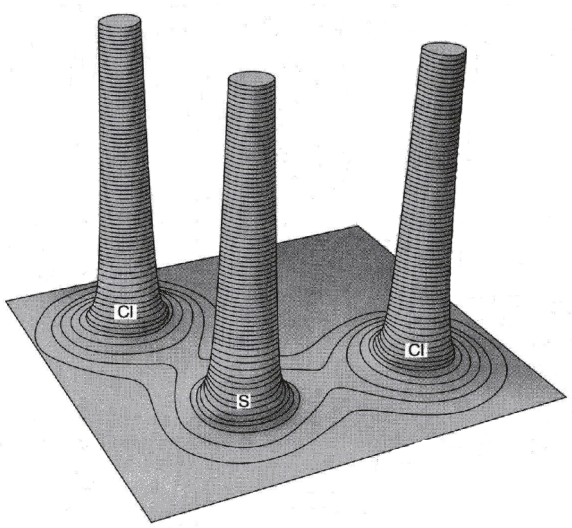
✔ An element of electronic charge on either surface separating the binding and antibinding regions exerts no force on the nuclei.

✔ An element of electronic charge in the space where $B(Z_A,Z_B,\mathbf{r}) > 0$ (binding region) draws the two nuclei together.

✔ An element of electronic charge in the space where $B(Z_A,Z_B,\mathbf{r}) < 0$ (antibinding region) attracts one nucleus more strongly than the other, drawing the two apart.

☞ A stable molecule at equilibrium can exist only if the attractive force from the binding region balances *both* the nuclear repulsive force *and* the repulsive force due to charge in the antibinding zone.

Representing Electron Density
Relief Map of SCl_2 in Molecular Plane



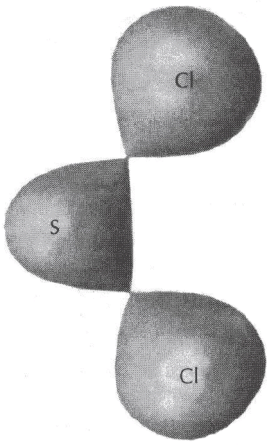
✔ Electron density is highest at the nuclei (here truncated at ~15 au)[4]

✔ This kind of mapping obscures the small but important differences in electron density between the nuclei.

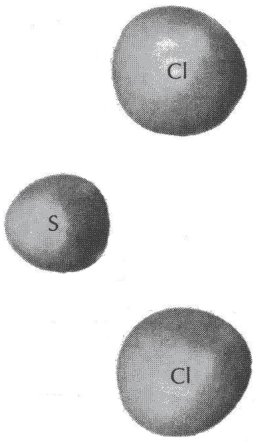
[4]Atomic unit (au) of charge density is the unit charge (e = 1.6011 x 10^{-19} C) per Bohr radius (a_o = 5.2918 x 10^{-11} m) cubed, e/a_o^3, equal to 1.0812 x 10^{12} C·m^3.

Representing Electron Density
Constant Electron Density Envelopes for SCl_2

ρ = 0.001 au



ρ = 0.133 au



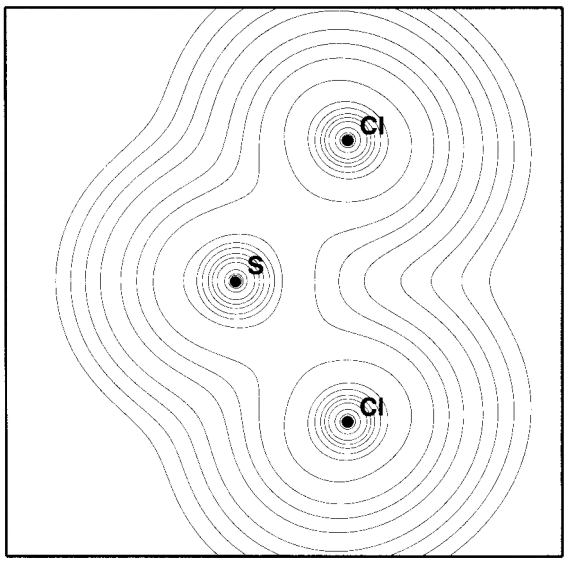
ρ = 0.200 au

✔ Envelope for ρ = 0.001 au is the practical limit of the molecule, essentially the van der Waals surface, containing ~98% of the total electron density.

✔ Envelope for ρ = 0.133 au shows minima between nuclei where envelopes just touch, called *bond critical points*.

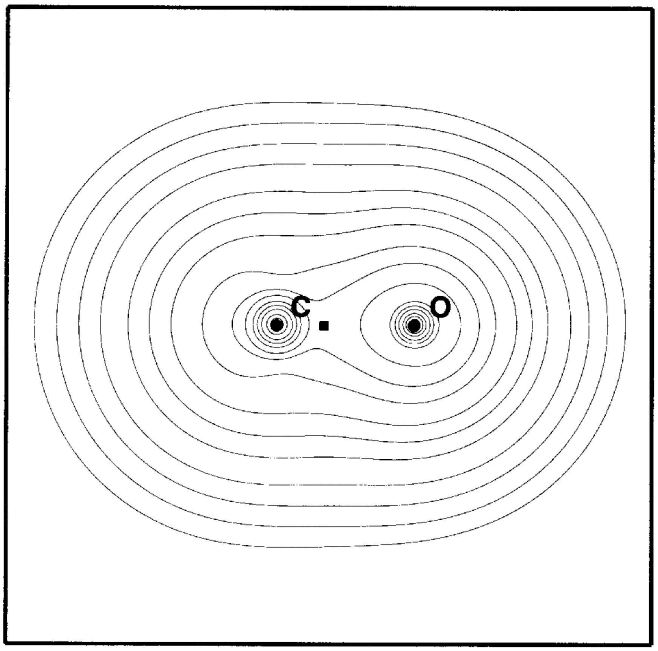
✔ Envelope for ρ = 0.200 au shows high localized electron density around each nucleus.

Representing Electron Density
Contour Map of SCl_2

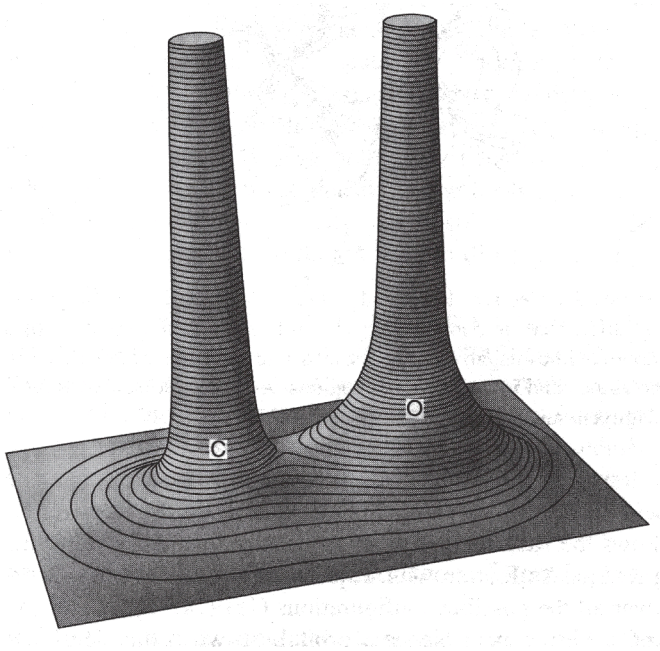


- ✔ Outer contour shows $\rho = 0.001$
- ✔ Next contour lines increase in the pattern 2×10^n, 4×10^n, 8×10^n, where $n =$ -3, -2, -1, 0, 1, 2.

Variation in Electron Density



CO contour map



CO relief map

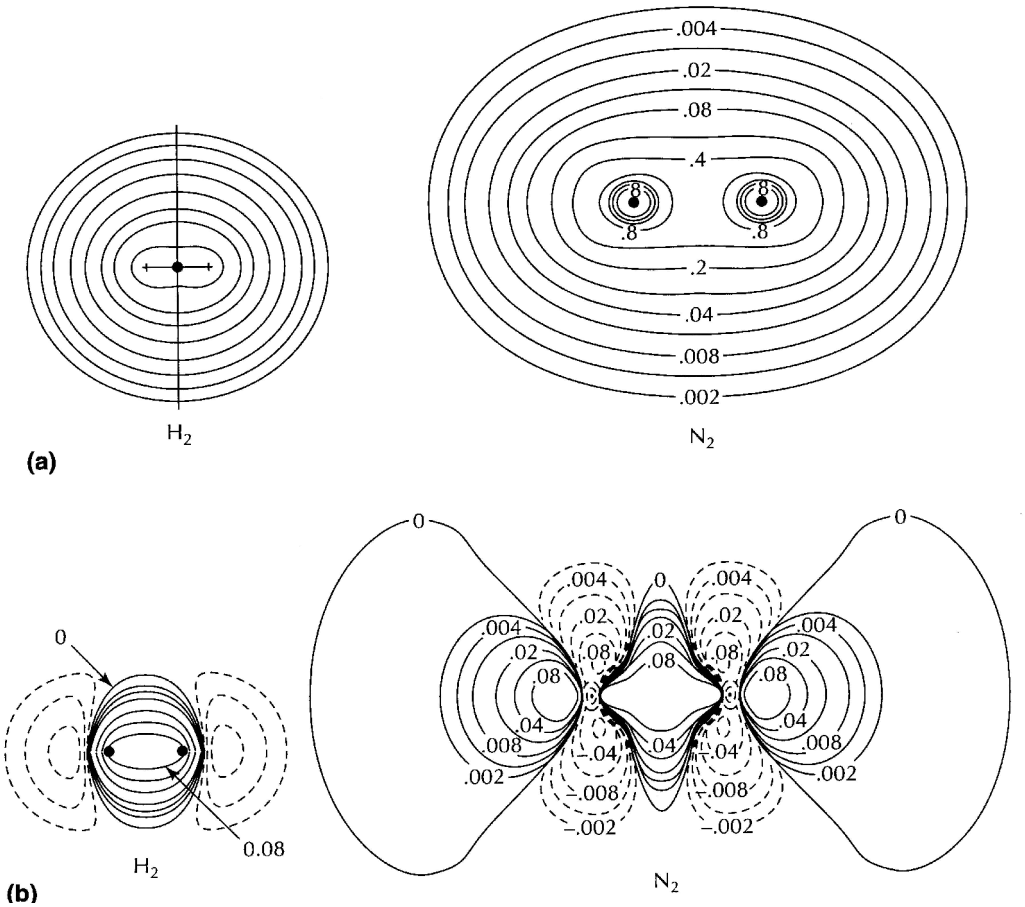
- ✔ Electron density is highest at the nuclei.
- ✔ Electron density decreases less rapidly along the internuclear axis than in any other direction from each nucleus.
- ✔ In the contour map there is a minimum (■) along the internuclear axis, closer to C, which corresponds to a low point along the ridge between the nuclei in the relief map.
- ✔ The internuclear axis is a line along which electron density is higher than in any other direction.

Standard Deformation Density

☞ Standard deformation density seeks to show areas of electron build-up and electron diminution in a molecule relative to the electron densities of the neutral atoms:

$$\Delta\rho(\mathbf{r}) = \rho_{\text{mol}}(\mathbf{r}) - \rho_{\text{atom}}(\mathbf{r})$$

✔ In maps of $\Delta\rho(\mathbf{r})$, regions with greater electron density than the standard are shown with solid lines, and regions of lesser electron density than the standard are shown with dotted lines.



✔ H_2 shows build-up between nuclei only due to bonding electron density.

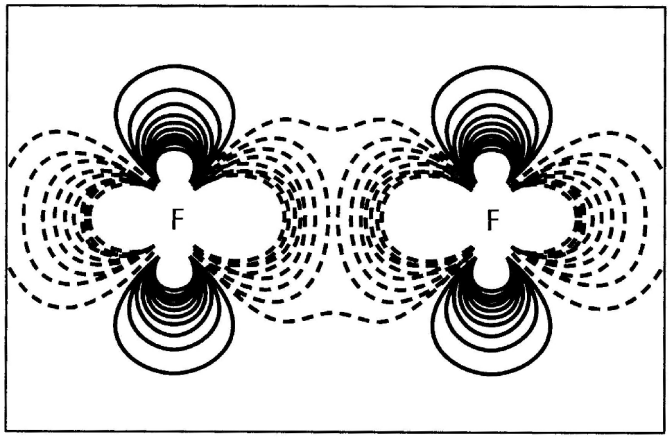
✔ N_2 shows build-up from both bonding and lone-pair electron density.

Problems with Standard Deformation Density

✔ Choice of the electronic configuration of the neutral atom can lead to bizarre results.

✔ If atomic F is taken as the average of all three $1s^2 2s^2 2p^5$ configurations, the reference has 5/3 = 1.66 electrons per valence *p* orbital along the internuclear axis, *z*.

- This suggests a charge loss between the nuclei.



✔ If atomic F is taken as $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^1$, then the expected build-up along the *z* axis between the nuclei results.