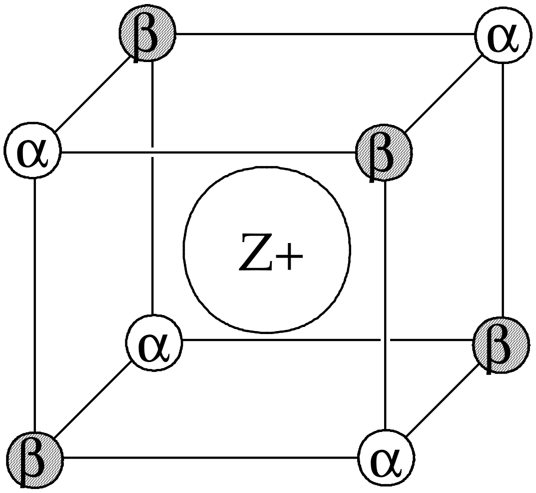
Electrons in a Free Atom or Monatomic Ion

- ✔ All electrons in the valence shell of a free atom or monatomic ion are completely delocalized, occupying the same spherical domain.

- ✔ Same-spin electrons are kept apart by the Pauli principle and to a lesser extent electrostatic repulsions, resulting in an average relative orientation that defines a tetrahedron.

- ✔ The tetrahedron of same-spin electrons in a free atom has no preferred orientation, so the overall density distribution is spherical.

- ✔ Both α and β electrons behave the same way, but each unoriented tetrahedron is kept apart by electrostatic repulsions, resulting in an unoriented cubic preferred relative geometry, again resulting in a spherical distribution.



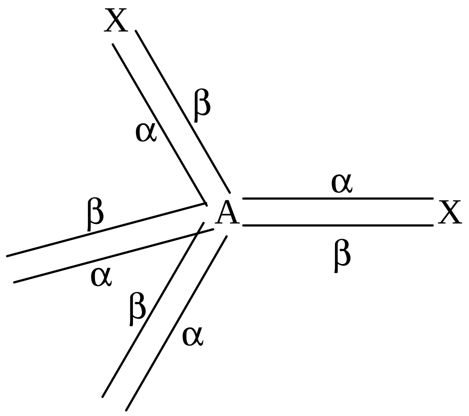
L and the VSEPR Model

✔ In a molecule, the nuclei of the ligand atoms attract electrons in the valence shell of the central atom to the bond region.

✔ By the Pauli principle the tetrahedral arrangement of four same-spin electrons is maintained, but in the presence of ligands it may adopt a specific orientation.

✔ Tetrahedra of α and β electrons under the influence of ligands are not prevented by the Pauli principle from occupying the same regions of space and so are brought into the same regions along the bond lines.

✔ The presence of ligand nuclei creates regions of enhanced electron density in a tetrahedral arrangement in both the bonding regions and nonbonding regions.

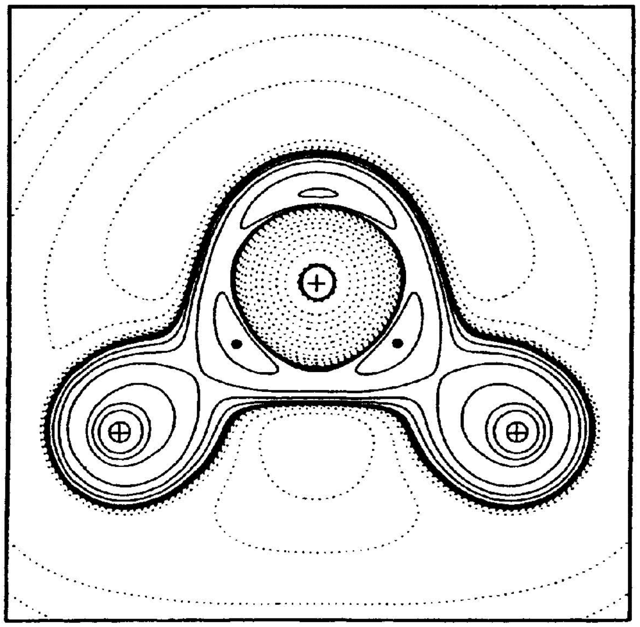


✔ Localizaion of bonding and nonbonding electrons by ligands results in charge concentrations evident in plots of *L* as regions where $L > 0$.

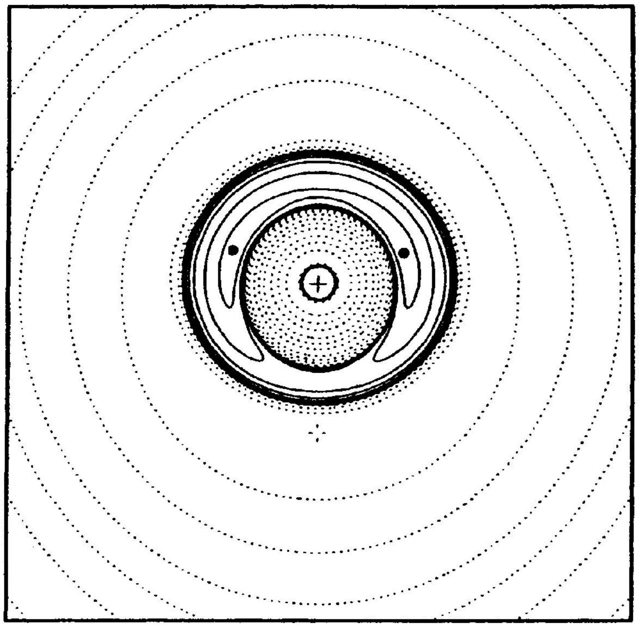
✔ Regions where $L > 0$ indicate concentrations of α and β electrons, a pair of opposite-spin electrons.

☞ The Laplacian of ρ provides a physical justification for the domains of the VSEPR model.

H_2O



L contour of H_2O in molecular plane



L contour of H_2O perpendicular to molecular plane

✔ Four maxima about O in an approximately tetrahedral arrangement.

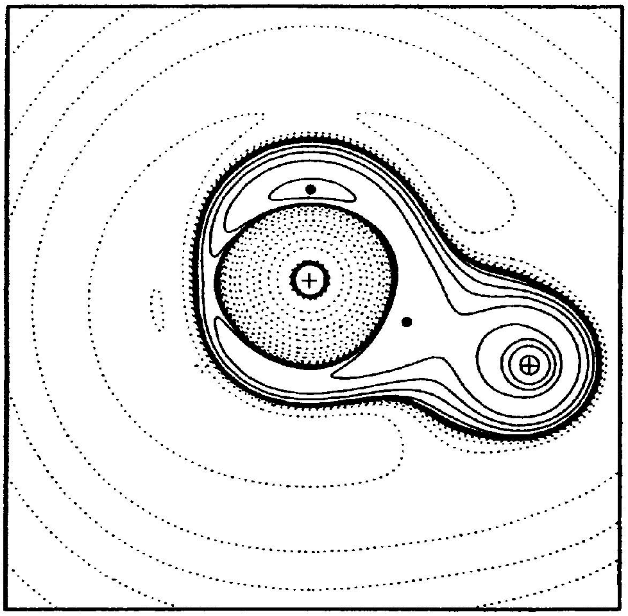
✔ Two bonding VSCCs, joined together, with continuous contours about O–H bond lines, consistent with covalent bonds.

✔ Apparent third maximum in the in-plane map is a saddle point between nonbonding VSCCs.

✔ Two nonbonding VSCC apparent in perpendicular projection with 138° angle between maxima.

☞ *L* contours consistent with VSEPR expectations.

NH_3



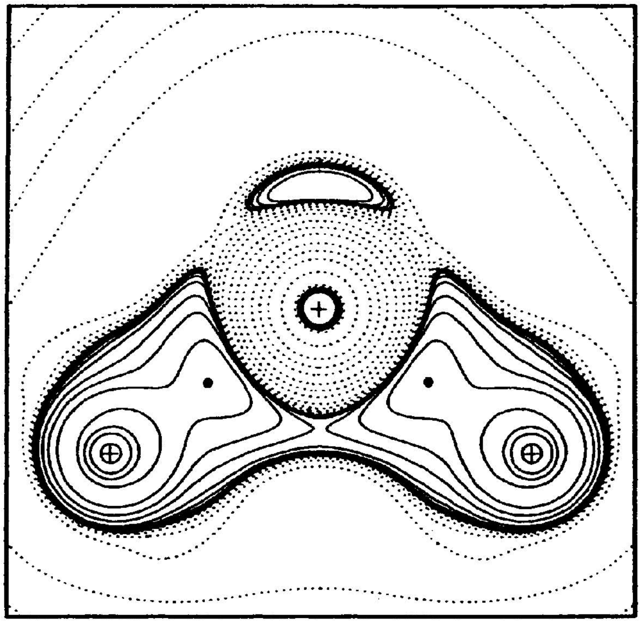
L contour of NH_3 in σ_v plane

✔ Three bonding VSCCs (one shown) and one nonbonding VSCC in an approximately tetrahedral arrangement, as predicted by VSEPR.

✔ Continuous contours consistent with covalent bonding.

✔ Apparent maximum in lower left is saddle point between two bonding VSCCs.

CH_4



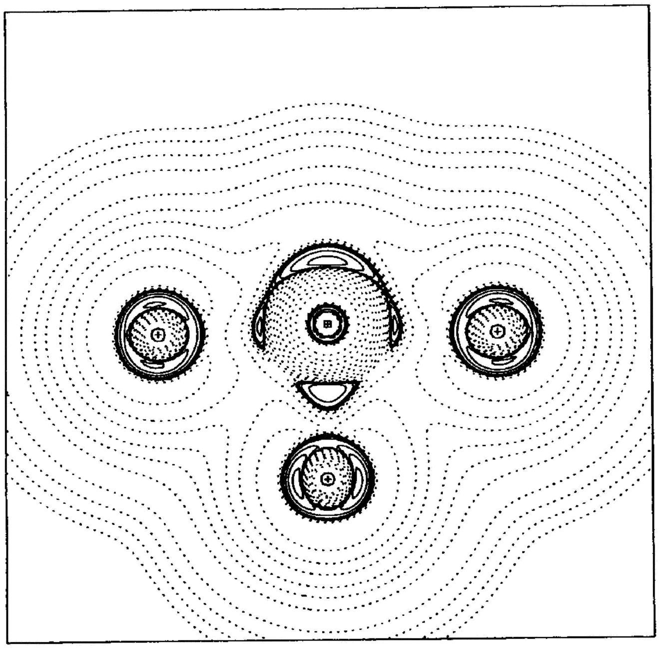
CH_4 in one H-C-H plane

✔ Tetrahedrally oriented VSCCs, as expected.

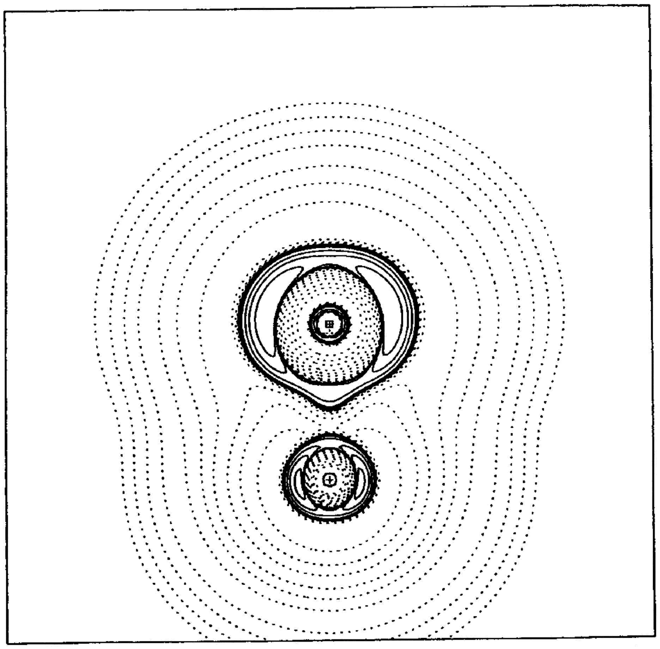
✔ Continuous contours consistent with covalent bonding.

✔ Apparent maximum on top is a saddle point between bonding VSCCs above and below the plane of the projections.

ClF_3 - AX_3E_2 (*tbp* domain geometry)



L contour of ClF_3 in molecular plane



L contour of ClF_3 in plane perpendicular to molecular plane

✔ Three bonding VSCCs in T-shape and two nonbonding VSCCs perpendicular to the molecular plane, consistent with overall *tbp* domain structure.

✔ Apparent maximum on top in molecular plane projection is saddle point between nonbonding VSCCs.

VSCCs and Domains

- ✔ There is not always a one-to-one correspondence between the number of VSCCs and the number of domains.

- ✔ An atom's valence shell is defined by a region of charge concentration followed by a region of charge depletion on the outside.

- ✔ When two atoms' valance shells overlap in bond formation, their regions of charge depletion always overlap, but their regions of charge concentration may or may not overlap.

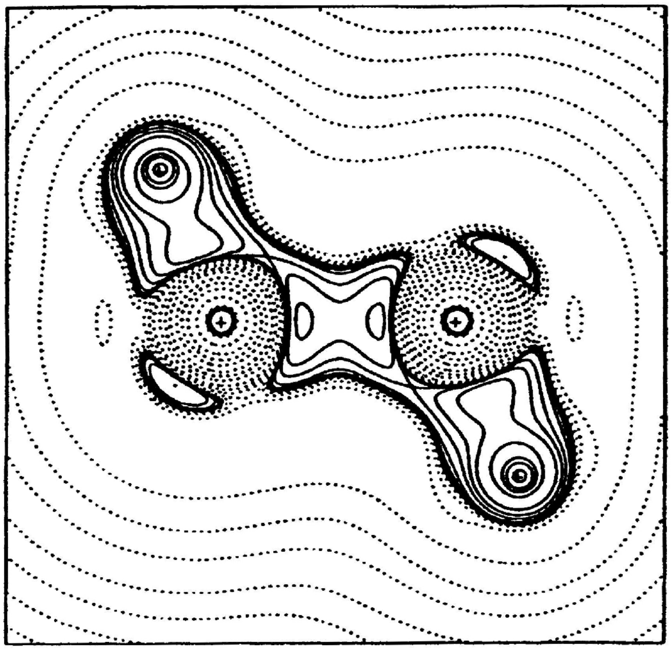
- ✔ Depending on the extent of overlap, each atom may show a VSCC, only one atom may show a VSCC, or neither atom may show a VSCC.

- ✔ With two atoms of very different electronegativity, electron density from the less electronegative atom is essentially transferred to the more electronegative atom (ionic bonding), and no VSCC is apparent along the bond line.

- ✔ Nonbonding electrons are always observed as nonbonding VSCCs of one atom.

Pure Covalent Bonds

- ✔ In a strong, short, predominantly covalent bond between two atoms of identical or nearly identical electronegativity, the two atomic VSCC merge to give a single region of bonding charge concentration, usually with two maxima.



L contour of C_2H_6 in one σ_v plane

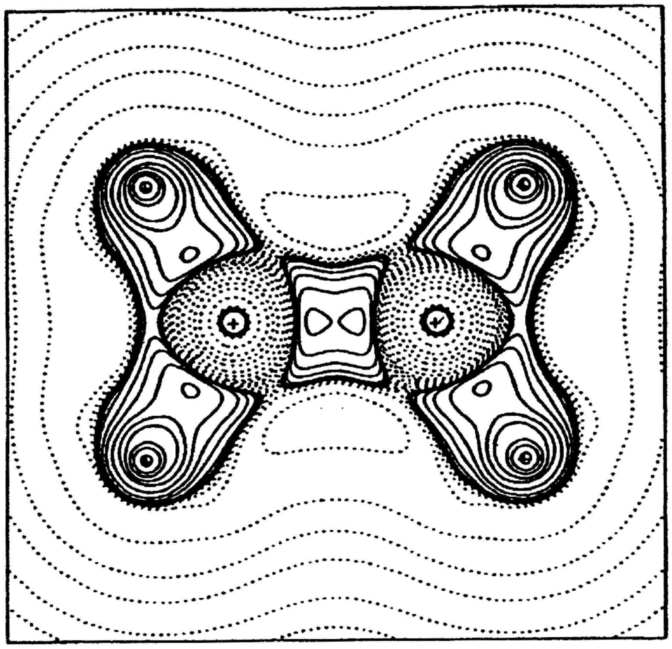
- ✔ In C_2H_6, the C–C bond line shows one region of bonding charge concentration with two maxima.

- ✔ The two maxima lie equidistant on both sides of the bond critical point (BCP) minimum at the center of the bond line.

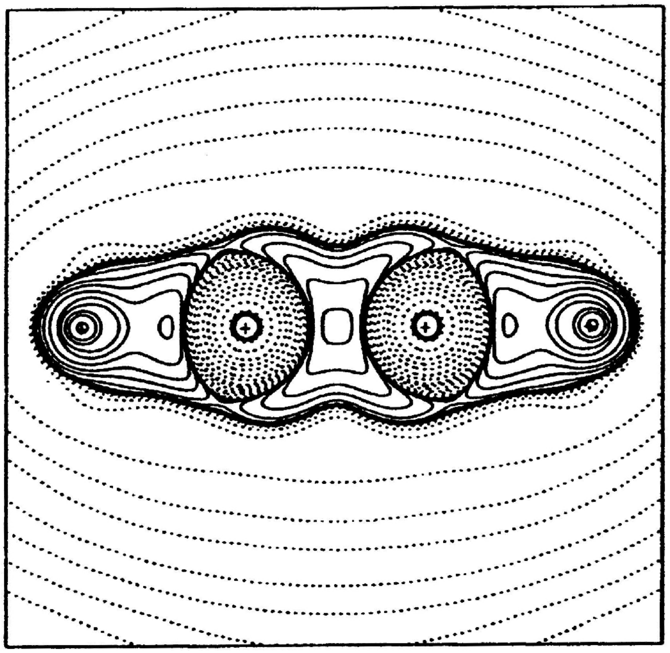
Multiple Bonds

✔ Although the Lewis model of X=X and X≡X double and triple bonds assumes two and three pairs, respectively, there is only one region along the bond path where VSCCs may occur.

✔ There is no correlation between the number of pairs involved in the bond and the number of VSCCs along the bond line.



L contour of C_2H_4



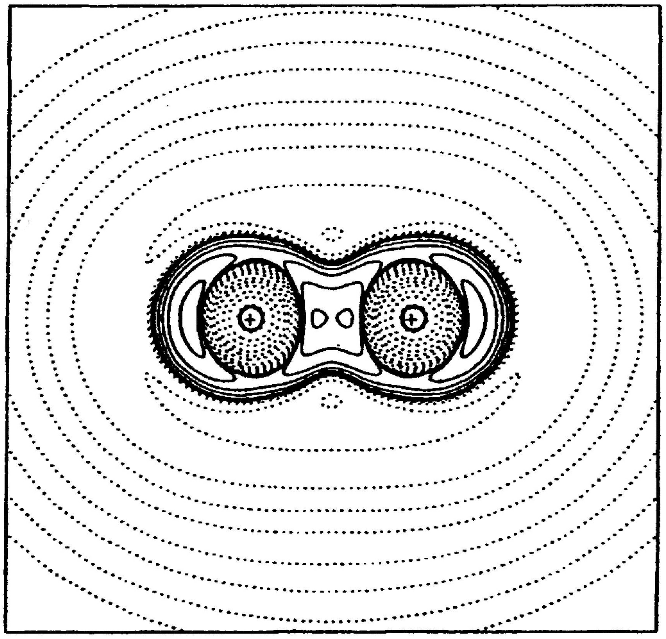
L contour C_2H_2

✔ C_2H_4 has two VSCCs along the bond line, but C_2H_2 has only one.

✔ Note that in C_2H_6, C_2H_4, and C_2H_2, the C–H bonds show one VSCC on the carbon for each bond.

✔ Hydrogen’s valence shell is also its core electron density, so any A–H bond has a maximum at the H nucleus.

N_2



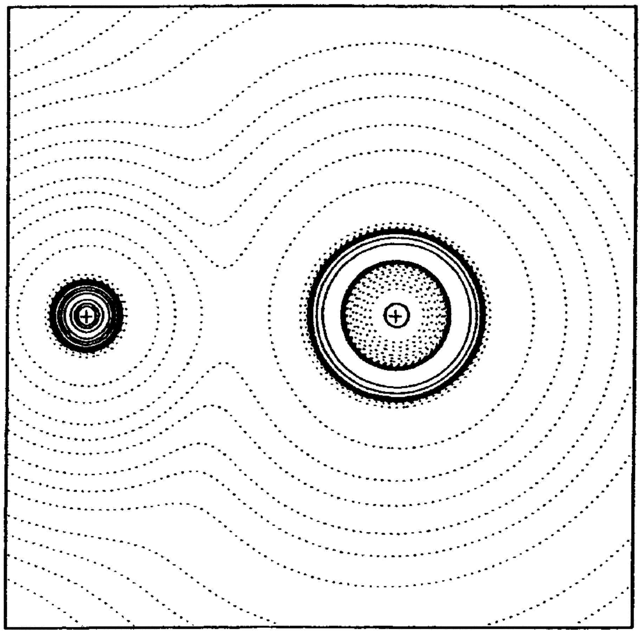
L contour of N_2

✔ N≡N bond shows two VSCCs, one on each N.

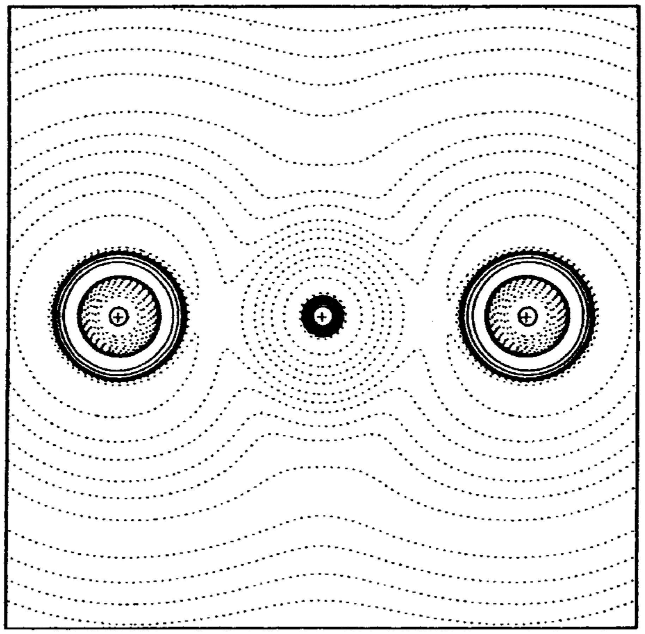
✔ Maxima on the outer ends are lone pairs on each nitrogen.

$$:N\equiv N:$$

Predominantly Ionic Molecules: LiF and BeF_2



L contour of LiF



L contour of BeF_2

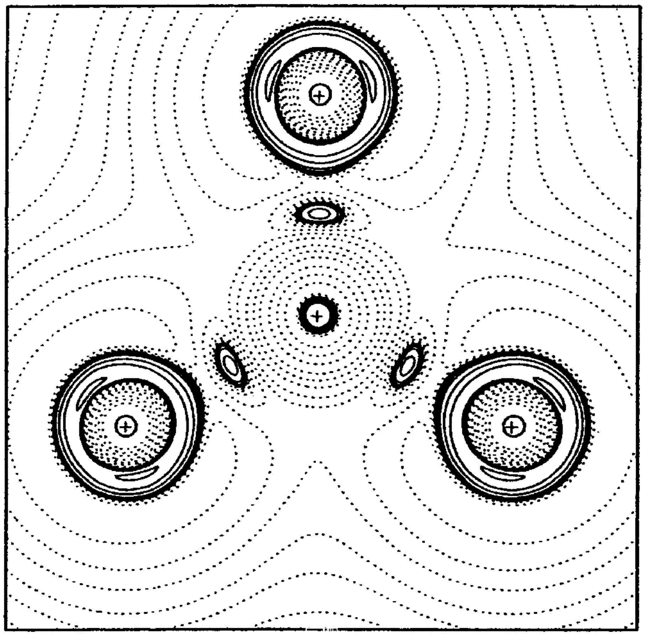
- ✔ Both Li and Be have essentially lost their valence electron densities to fluorine (i.e., ionic bonding).

- ✔ There is no localized bonding VSCC on either Li or Be, just maxima from their core electron densities.

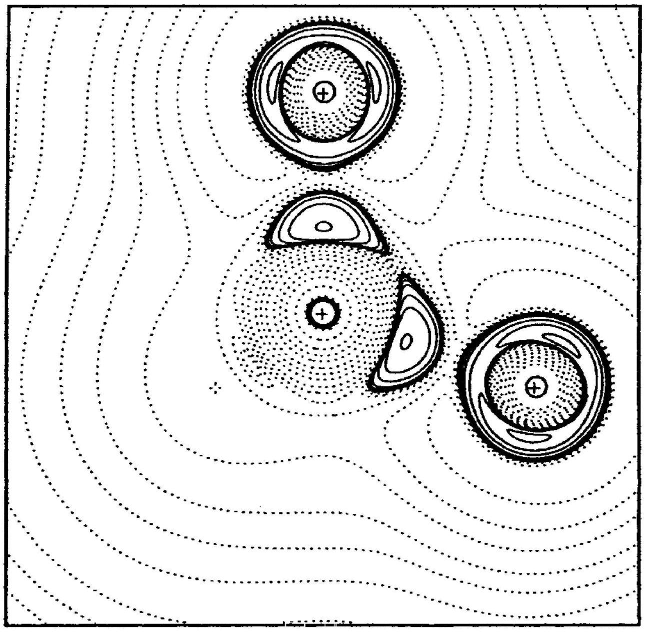
- ✔ Spherical distribution about fluorine in LiF indicates essentially ionic F^-.

- ✔ Fluorine in BeF_2 shows only slight distortion from spherical distribution, indicating that here, too, it is nearly F^-.

Slightly More Covalent Molecules: BF_3 and CF_4



L contour of BF_3



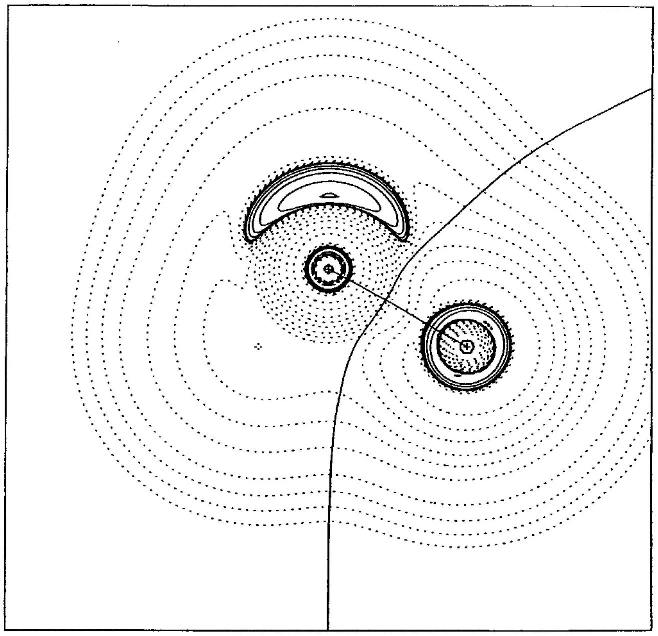
L contour of CF_4 in one σ_d plane

- ✔ As the central atom becomes more electronegative (B < C), the A–F bond becomes shorter and more covalent.

- ✔ From BF_3 to CF_4 increasingly prominent bonding VSCCs appear on the central atom.

- ✔ From, BF_3 to CF_4 the fluorine ligands are increasingly polarized, and an increasingly prominent torus of nonbonding electron density becomes evident.

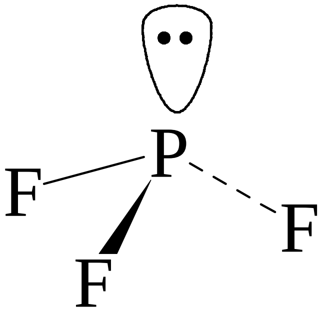
PF_3



L contour of PF_3 in one σ_v plane

✔ Lack of bonding VSCC suggest essentially ionic P–F bond, consistent with the large difference in electronegativity ($\chi_P = 2.1$, $\chi_F = 4.1$) and AIM calculated charges (P, +2.28; F, –0.76) .

✔ Although much of phosphorous's valence shell density has been transferred to fluorine, the two nonbonding electrons remain in the phosphorous valence shell and appear as a nonbonding VSCC, consistent with the VSEPR model.



Summary

- ✔ The number and geometry of lone pairs about a central atom predicted by VSEPR is always observed as corresponding nonbonding VSCCs in the *L* plot.

- ✔ Lone pairs of singly bonded monatomic ligands are not localized into pairs, but rather form a torus of electron density about the ligand nucleus, consistent with VSEPR prediction.

- ✔ In contrast to VSEPR, which assumes a single bonding domain for each bond, there may be:

    - A single bonding maximum in the VSCC of the more electronegative atom.

    - Two bonding maxima, one in each atom's VSCC.

    - One or two maxima within a single shared VSCC in short covalent bonds.

    - No bonding maxima in the case of predominantly ionic bonds.

Reconsidering the Concept of Electron Pair Localization
Free Atoms and Cores of Bonded Atoms

- ✔ Electrons in the core are fully localized into spherical shells but not into opposite-spin pairs.

- ✔ In an isolated atom, valence electrons are also localized into spherical shells but not into opposite-spin pairs.

- ✔ The Laplacian shows each spherical shell has a region of charge concentration and an outer region of charge depletion.

- ✔ There are no Lewis pairs or electron pair domains in an inner shell.

- ✔ The domain of each electron is spherical and full delocalized through the shell.

Reconsidering the Concept of Electron Pair Localization
Atoms in Molecules

✔ In molecules, the valence shells of atoms are generally distorted from spherical.

✔ As maps of *L* show, the valence shell charge concentration may develop maxima surrounded by regions of enhanced charge concentration in bonding and nonbonding regions.

✔ Regions of charge concentration have enhanced probability of finding both an α-spin and a β-spin electron, approximating pair formation, but there are no isolated electron pairs in an atom or molecule.

☞ There are no real electron pairs “occupying the same orbital”!

✔ The assumed electron pair domains of VSEPR are not finite regions of space, but only regions of charge concentration that have enhaced probability for both α-spin and a β-spin electrons as a result of the Pauli principle and to a lesser extent electrostatic repulsions.

✔ The concepts of a Lewis pair or a VSEPR electron domain are only approximate but useful models for the actual charge concentrations