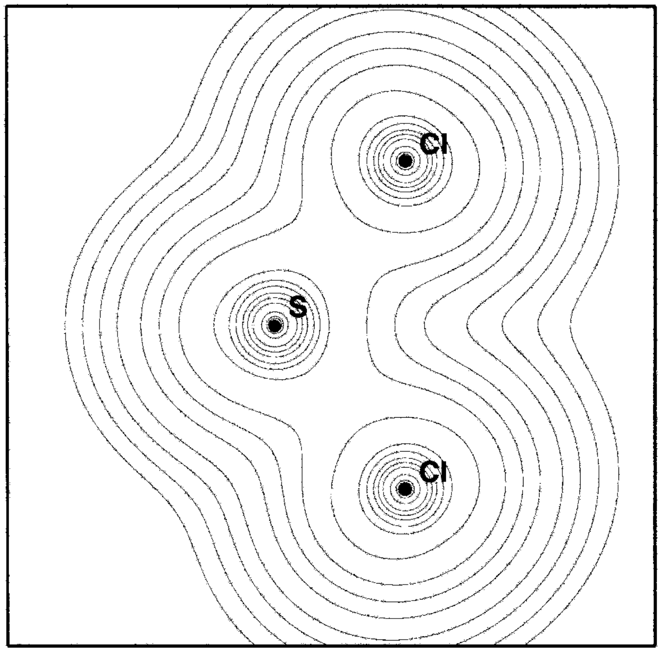
Looking for Non-bonding Pairs

✔ A ligand nucleus can cause an electron of each spin to become localized in the region around the bond line, corresponding to the Lewis idea of a bond pair.

✔ Consistent with VSEPR theory and the Pauli Principle, localization of bonding electrons may result in non-bonding electrons becoming localized, too, creating the Lewis equivalent of lone pairs.

✔ These lone pairs should appear as bulges in the contour maps of ρ, but often the concentration is not easily discerned.

Lone pairs? ➜



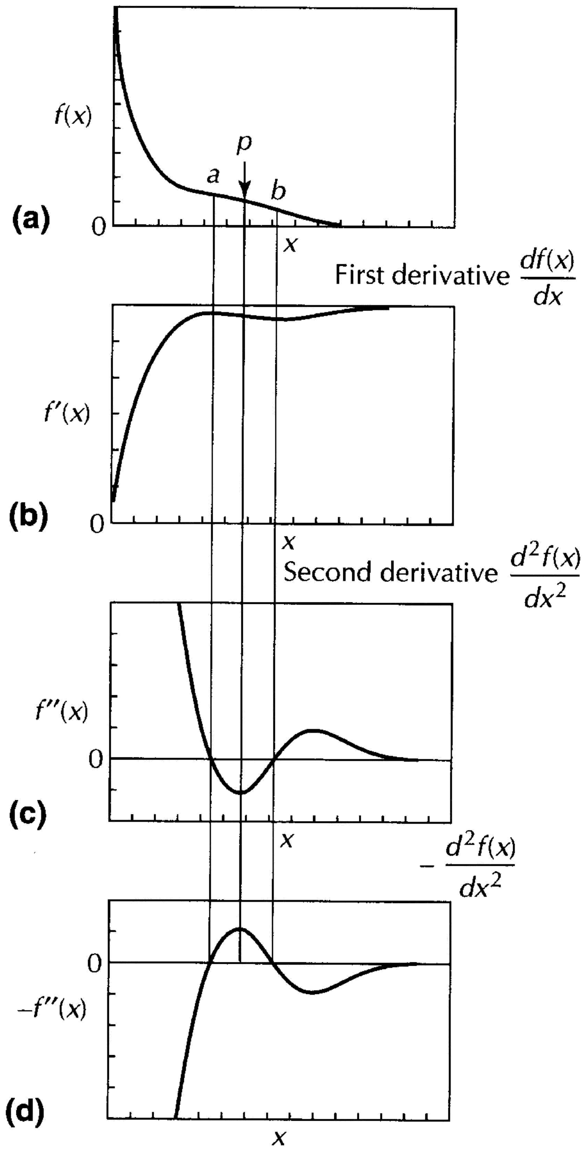
☞ A different mapping technique is needed to magnify the subtle differences that mark the existence of localized non-bonding electrons (“lone pairs”).

Using the Second Derivative to Amplify Differences

✔ A first derivative of a monotonically decreasing function is everywhere negative but shows an inflection for any localized maximum (function concentration).

✔ The second derivative passes through zero at the function's inflection points and has a minimum at the function's localized maximum.

✔ If the negative of the second derivative is used, there will be a maximum wherever the function itself has a concentration.



$f(x) = 8 \exp(-7x) + \exp[-10(x - 0.5)^2]$

The Laplacian Function, *L*

✔ The second derivative of the electron density field, called the Laplacian, can be used to show where ρ is locally concentrated or depleted.

☞ The Laplacian of the electron density, $\nabla^2\rho$, is defined by

$$\nabla^2\rho = \left(\frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2} \right) \rho$$

✔ $\nabla^2\rho$ has a minimum wherever ρ is concentrated and a maximum wherever ρ is depleted.

☞ To conform with our ideas of electron concentration and depletion, the function *L* is defined as

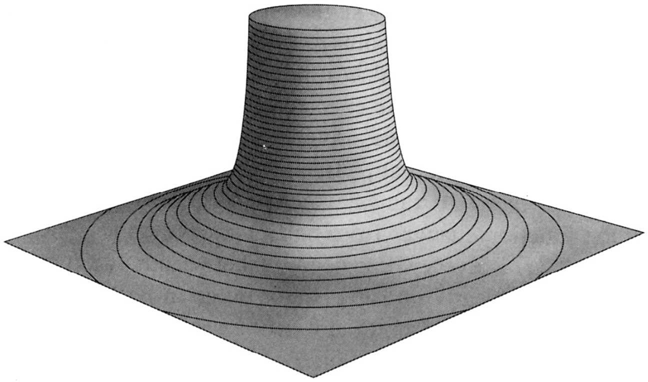
$$L = -\nabla^2\rho$$

✔ Reference to “the Laplacian” in discussions of electron density should be understood to mean *L*, which is actually the negative of the Laplacian.

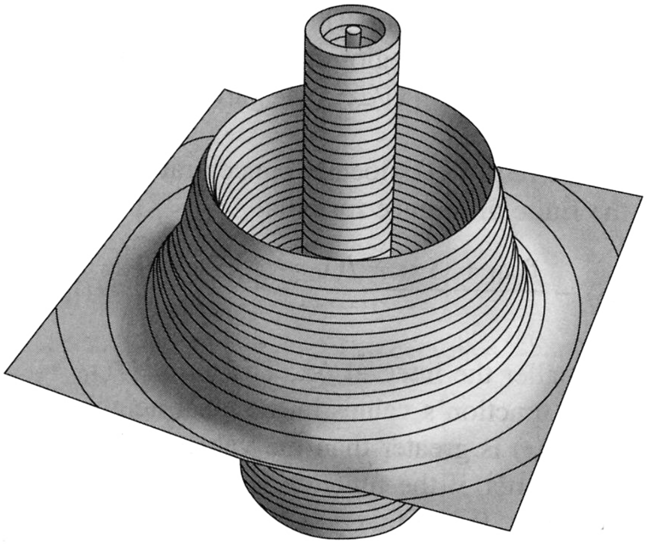
L of Isolated Atoms
Electron Density Distribution of Ar

✔ Any isolated atom has a spherical electron density distribution.

✔ Relief map of ρ shows a continuous falling off from the maximum at the nucleus.

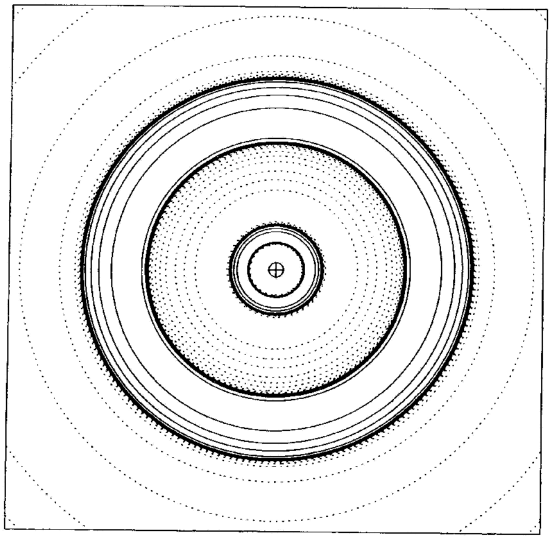


✔ Relief map of L shows maxima and minima corresponding to K, L, and M shells (i.e., n = 1, 2, 3).



Valence Shell Charge Concentration (VSCC)

✔ In discussing atoms in molecules, the atom’s outer-most charge concentration (valence shell) is most important (e.g., *M* shell in Ar).



Contour map of *L* for Ar

☞ An atom’s valence shell is defined by an outer sphere of charge concentration and a more extensive sphere of charge depletion.

✔ In a molecule, an atom’s inner charge distribution remains essentially spherical.

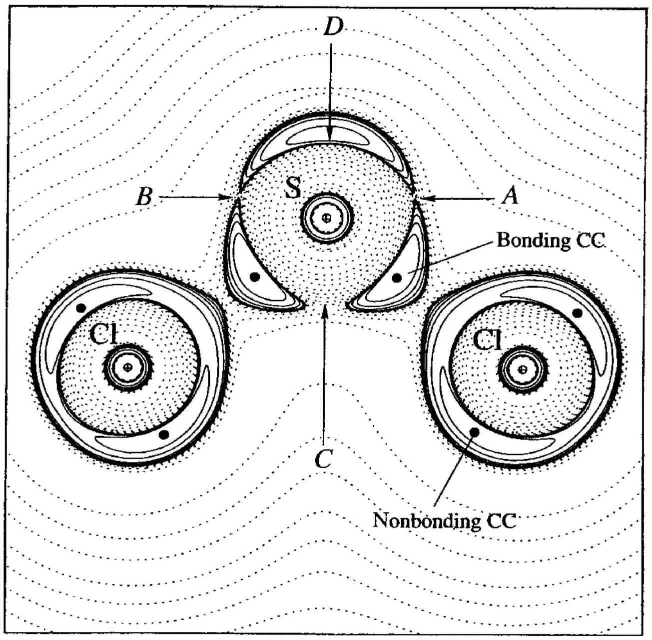
✔ In a molecule an atom’s VSCC is always distorted from a spherical shape.

- With polar ligands it may be broken up into separate charge distributions.
- In highly polar molecules it may disappear.

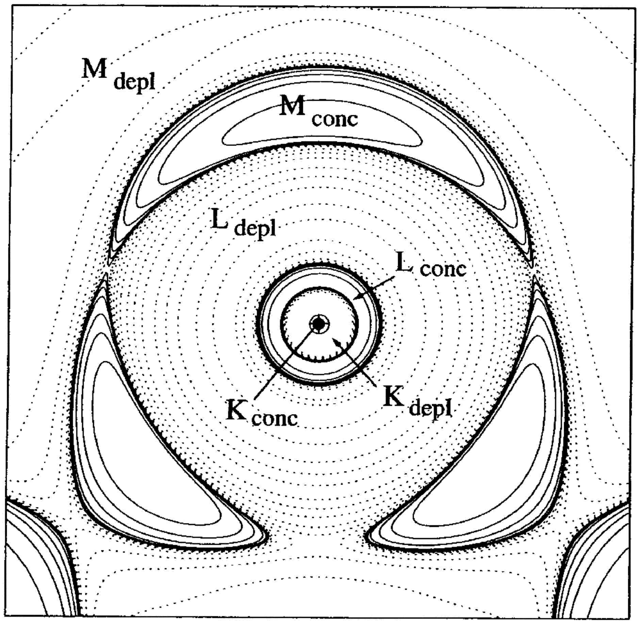
✔ In molecules an atom’s VSCC may show maxima along the bond lines, called bonding charge concentrations (bonding CCs), and nonbonding charge concentrations (nonbonding CCs).

Contour Maps of *L* for SCl$_2$

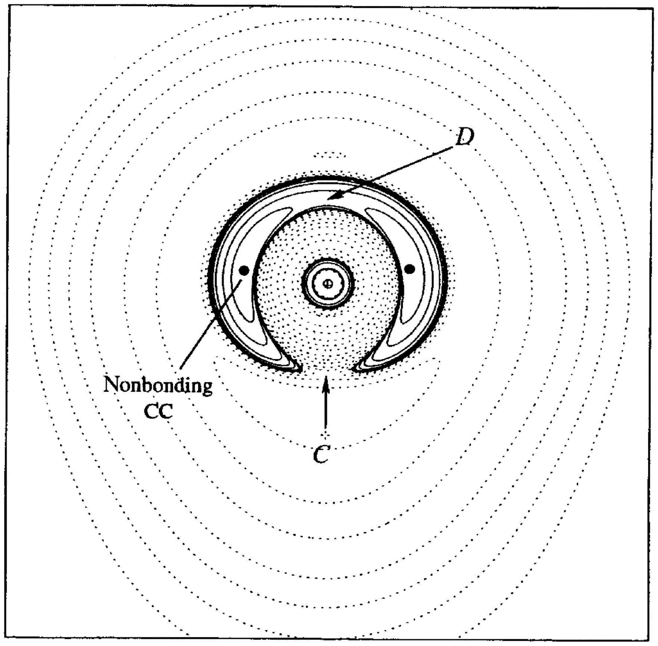
Legend: *A, B, C* – minima; *D* – saddle point between lone pair maxima;
K, L, M – shells of sulfur; CC – charge concentration



L in molecular plane (σ_v)



L of sulfur in molecular plane (σ_v)



L in σ_v' plane

Notes on SCl_2 Contour Plots of *L*

✔ Minima along S–Cl bond line mark the bond critical points.

✔ Minima A and B mark the separation of the bond VSCCs from the nonbonding VSCCs.

✔ Minimum C marks the separation between the two bonding VSCCs.

✔ D is a saddle point between the nonbonding VSCCs.

☞ The two bonding and two nonbonding VSCCs of the sulfur atom in SCl_2 have an approximately tetrahedral arrangement, consistent with the VSEPR model of SCl_2.

✔ The two apparent maxima on each Cl atom are points on a ring of maximum nonbonding charge concentration (a torus) of charge concentration about each Cl nucleus.

☞ The single bond region about each Cl atom *does not* orient the nonbonding charge distribution into a tetrahedral arrangement.