VSEPR Theory: A closer look at chlorine trifluoride, ClF3.

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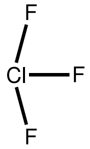
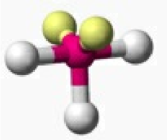
Valence shell electron pair repulsion theory is a simple way of rationalising the shapes of many compounds in which a main group element is surrounded by ligands. ClF3 is a good illustration of this theory.



The standard application of VSEPR theory to this molecule is as follows:

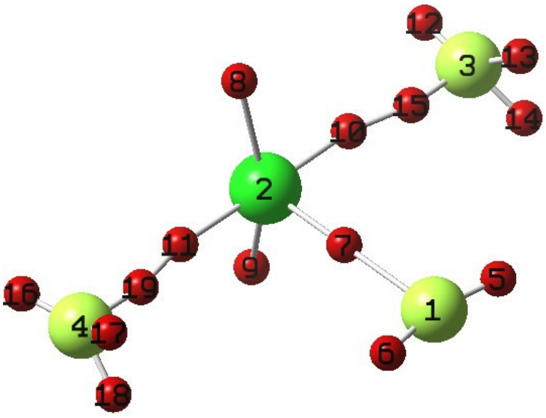
1. Central atom: chlorine
2. Valence electrons on central atom: 7
3. Three fluorine atoms contribute: 1 each
4. Total: **10** = **five electron pairs**.
5. The highest repulsion is between any two "lone electron pairs", resulting in these moving apart as far as possible
6. the next highest is between one lone pair and a bond pair
7. the lowest is between two bond pairs.

As applied to chlorine trifluoride, it results in a **trigonal bipyramidal** geometry for the shape-determining five electron pairs. One of the trigonal positions is occupied by the pair deriving from a Cl-F bond (F=white, Cl=red below). The other two trigonal positions are occupied by two sets of electron lone pairs (yellow below) at ≥ 120° (rule 5, but much more and the repulsions between the lone pair and the trigonal Cl-F bond would become too great, rule 6 above). The remaining two Cl-F bond pairs occupy the di-axial positions (rule 7 above).



The above at least is the standard "text-book" picture. Regular readers of this blog may have noted that I often like to question the text books. So here goes. My issue is with the above explanation, of five electron pairs all associated in some way with the central atom. An expanded octet in other words. Well, if you take a look at earlier blogs, you may have observed that this expanded octet is not real (IMHO). If it's not real, then we cannot be dealing with five electron pairs. Can VSEPR work with only eight electrons in this instance? And what are the coordinates of the so-called two "lone pairs": is the angle subtended at the Cl by them really trigonal (~120)?

I start with computing an accurate wavefunction, using the DFT-based ωB97XD/6-311++G(d,p)[1]. The electron count and the coordinates of the localised basins will be obtained using ELF (Electron localisation function).



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1. The electron basins are shown here as red spheres; 8 and 9 are the “lone pairs”, as it happens a very reasonable description since the populations for these are 2.07e. The 8-2-9 angle of 154° results from rule 5 above; lone pairs repel greatly. Indeed, one might almost describe 8 and 9 as being di-axial. In which case, the geometry is not that of a trigonal bipyramid but is closer to that of a **square pyramid**.
2. Basin 7 is a Cl-F bond, with a population of 0.87e, rather less than a “pair” (the Wiberg bond index is 0.82).
3. Basins 11+19 and 10+15 (similar basin splitting is observed for F2[2]) each total 0.91e; again less than a pair (Wiberg index 0.63). So the three Cl-F bonds are
4. Other features include *eg* the orientation of the “lone pairs” on fluorines 3 and 4, in which e.g. 16 is oriented anti-periplanar to the 2-1 bond. This is in fact an anomeric effect! An NBO analysis reveals E(2) between Lp16 and σ*2-1 to be 6.3 kcal/mol, a relatively weak but still a real anomeric interaction.
5. The total electron count for the ELF basins surrounding the central Cl is 6.84, not 10 as was implied in the simple argument set out above.

VS**EP**R theory is a highly simplified way of looking at the geometric origins of this odd little molecule; an ELF analysis likewise paints only a partial picture. Indeed, it seems doubtful that any simple way of regarding this species can ever be entirely adequate. But we should be mindful that the “EP” (electron pair) of VSEPR might itself be rather misleading in perpetuating the idea that such main group elements contain expanded octets. But the geometry of chlorine trifluoride makes sense without imposing 10 valence electrons on the chlorine after all!

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