A Simple Electrostatic Critique of VSEPR

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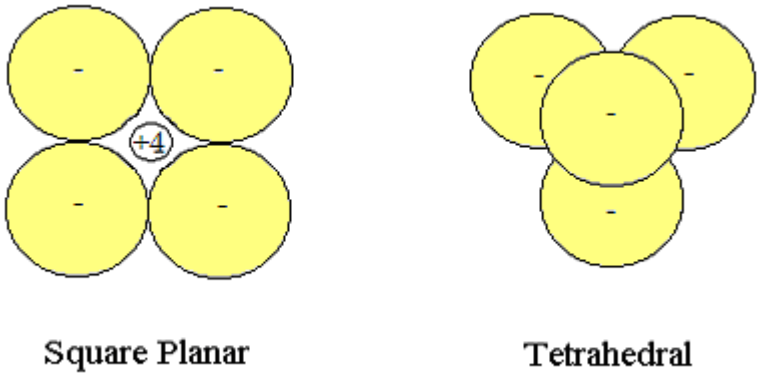
In a previous tutorial [1] it was shown that the reason methane is tetrahedral (T_d) rather than square planar (D_{4h}) is because electron-nucleus attractions are greater for the tetrahedral geometry. VSEPR teaches (incorrectly) that minimization of electron-electron potential energy drives molecular geometry. However, the previous variational calculation showed that electron-electron repulsion is actually higher in T_d methane than it is in the D_{4h} molecule.

In what follows a simple electrostatic calculation will be presented which reaches the same conclusion as the more elaborate and rigorous variational calculation based on Henry Bent's [2] Tangent Spheres Model (TSM) of chemical bonding and molecular geometry. This calculation was suggested to the author in a private communication from Henry Bent.

A simple ionic model is proposed for the bonding in methane. The +4 carbon kernel (nucleus and nonvalence electrons) is treated as a point charge which interacts electrostatically with four unpolarized hydride anions of unit diameter in either a square planar or tetrahedral arrangement. In tetrahedral methane the +4 kernel occupies the tetrahedral hole and is not visible in the diagram shown below.



Rudimentary geometrical considerations provide the necessary molecular parameters in the following table.

molecular parameter	D_{4h}	T_d
hydride-hydride distance	4 @ 1 and 2 @ $\sqrt{2}$	6 @ 1
hydride-nucleus distance	4 @ $\sqrt{2}/2$	4 @ $\sqrt{(3/8)}$

From an electrostatic perspective a hydride anion is equivalent to an electron. Therefore, the calculation of the potential energy will be expressed in terms of electron-electron potential energy and electron-nucleus potential energy. Using the molecular parameters listed in the table above we calculate the potential energy contributions for both geometries as follows.

Square Planar Methane

$$V_{ee} = 4\frac{(-1)(-1)}{1} + 2\frac{(-1)(-1)}{\sqrt{2}} = 5.41$$

$$V_{en} = 4\frac{(-1)(+4)}{\sqrt{2}/2} = -22.63$$

Tetrahedral Methane

$$V_{ee} = 6\frac{(-1)(-1)}{1} = 6.00$$

$$V_{en} = 4\frac{(-1)(+4)}{\sqrt{3/8}} = -26.13$$

These results are summarized in the following table.

Energy Contribution	D_{4h}	T_d
V_{ee}	5.41	6.00
V_{en}	-22.63	-26.13
V_{tot}	-17.22	-20.13

The results of this simple electrostatic calculation contradict the VSEPR model in two significant ways:

1. Electron-electron repulsions are greater for tetrahedral geometry than they are for square planar geometry.
2. T_d is favored over D_{4h} because of electron-nucleus attractions. In other words, electron-nuclear attractions are the most important energy contribution in determining molecular geometry.

The latter conclusion should not be surprising. There are four types of energy contributions in a molecule under the Born-Oppenheimer approximation: (1) electron kinetic energy; (2) electron-nucleus potential energy; (3) electron-electron potential energy; (4) nucleus-nucleus potential energy. Electron-nucleus potential energy is the only attractive term, and electron-electron potential energy is the smallest of the "repulsive" terms. Clearly electron-nucleus attraction is the single most important term in determining molecular geometry.

Furthermore, this guarantees that electron-electron potential energy will track in the opposite direction. Electron domains get closer to nuclei in two ways: by adopting a close-packed geometry (T_d versus D_{4h})

and by shrinking in size. Both lead to larger electron-electron potential energy and lower (more negative) electron-nucleus potential energy.

For the reasons enumerated above, chemical educators should recall VSEPR. It is not a valid model for molecular geometry and takes up space in textbooks that would be better devoted to viable quantum mechanical models of molecular geometry such as TSM [1, 2] or molecular orbital theory. Even in those textbooks in which it is juxtaposed with more credible models it distracts attention from them because of its specious predictive methodology.

1. Rioux, F. http://www.users.csbsju.edu/~frioux/vsepr/NVSEPR.htm
2. Bent, H. A. *J. Chem. Educ.* **40**, 446-452 (1963).