

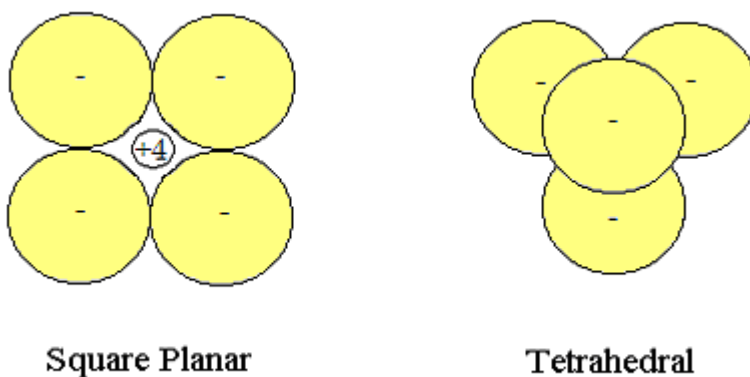
## A Simple Electrostatic Critique of VSEPR

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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 <sub>4h</sub> | T <sub>d</sub> |
|---------------------|-----------------|----------------|
| V <sub>ee</sub>     | 5.41            | 6.00           |
| V <sub>en</sub>     | -22.63          | -26.13         |
| V <sub>tot</sub>    | -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<sub>d</sub> is favored over D<sub>4h</sub> 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<sub>d</sub> versus D<sub>4h</sub>)

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).