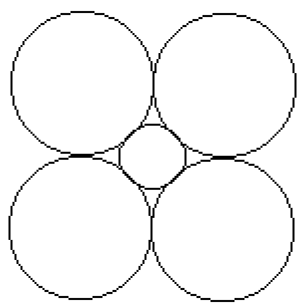
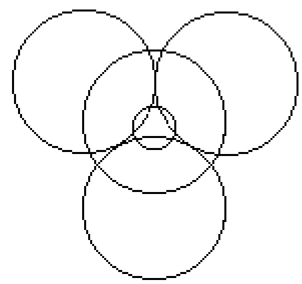
Tangent Spheres Critique of VSEPR for CH_4

This analysis uses Henry Bent's Valence Spheres Model (VSM) to analyse the VSEPR claim that the reason tetrahedral geometry is preferred over square planar for four pairs of electron is because tetrahedral geometry gives the pairs more space and, therefore, reduces electron-electron replusions. The calculation is for methane, CH_4. The VSM calculation tells a different story. The electron pairs are actually smaller in the tetrahedral configuration than they are in the square planar arrangement. This means that the electrons are closer in the tetrahedral geometry. Furthermore the real driving force for this geometry appears to be electron-nuclear attraction and not electron-electron repulsion, as VSEPR theory teaches. The VSM calculations show that inter-pair electron-electron repulsion actually increases from square planar geometry to tetrahedral geometry.



Square Planar



Tetrahedral

Square Planar Geometry

The energy expression below includes contributions involving only the valence electrons. The nucleus and the core electrons are treated as a plus 4 point charge located at the center of the square plane.

EnergyContribution	SquarePlanarGeometry
ElectronKineticEnergy	$8 \cdot \frac{9}{8 \cdot R^2}$
IntraPairElectronRepulsion	$4 \cdot \frac{6}{5 \cdot R}$
InterPairElectronRepulsion	$4 \cdot \frac{2 \cdot 2}{2 \cdot R} + 2 \cdot \frac{2 \cdot 2}{2 \cdot \sqrt{2} \cdot R}$
HH − NuclearRepulsion	$4 \cdot \frac{1 \cdot 1}{2 \cdot R} + 2 \cdot \frac{1 \cdot 1}{2 \cdot \sqrt{2} \cdot R}$
CH − NuclearRepulsion	$4 \cdot \frac{1 \cdot Z}{\sqrt{2} \cdot R}$
ElectronCarbonKernelAttraction	$8 \cdot \frac{-1 \cdot Z}{\sqrt{2} \cdot R}$
MolecularElectronHydrogenAttraction	$\frac{-8}{R} - \frac{8}{2 \cdot \sqrt{2} \cdot R}$
AtomicElectronHydrogenAttraction	$-8 \cdot \frac{3}{2 \cdot R}$

Kernel charge: $Z := 4$ The energy as a function of R is shown below:

$$E(R) := 8\cdot\frac{9}{8\cdot R^2} + 4\cdot\frac{6}{5\cdot R} + 4\cdot\frac{2\cdot 2}{2\cdot R} + 2\cdot\frac{2\cdot 2}{2\cdot\sqrt{2}\cdot R} - 4\cdot\frac{2\cdot Z}{\sqrt{2}\cdot R} - 8\cdot\frac{3}{2\cdot R} + \frac{4}{2\cdot R} + \frac{2}{2\cdot\sqrt{2}\cdot R} + 4\cdot\frac{Z}{\sqrt{2}\cdot R} - \frac{8}{R} - \frac{4}{\sqrt{2}\cdot R}$$

Minimize the energy with respect to the electron-pair radius, R.

$R := .2$ Given $\frac{d}{dR}E(R) = 0$ $R := \text{Find}(R)$ $R = 1.139$

Display the ground state energy: $E(R) = -6.94$

Factor the ground state energy into its kinetic and electrostatic contributions. The calculation satisfies the virial theorem.

$T(R) := \frac{9}{R^2}$ $T(R) = 6.94$ $V(R) := E(R) - T(R)$ $V(R) = -13.88$

Further break down the potential energy into intra-pair electron-electron potential energy, inter-pair electron-electron potential energy, and electron-nucleus potential energy.

Intra-pair Vee: $\frac{24}{5\cdot R} = 4.215$ Inter-pair Vee: $\frac{8}{R} + \frac{4}{\sqrt{2}\cdot R} = 9.509$

Electron-nucleus potential energy: $-\frac{8\cdot Z}{\sqrt{2}\cdot R} - 8\cdot\frac{3}{2\cdot R} - \frac{8}{R} - \frac{4}{\sqrt{2}\cdot R} = -39.917$

Electron-carbon nucleus: $-\frac{8\cdot Z}{\sqrt{2}\cdot R} = -19.87$ Electron-hydrogen nucleus,atomic: $-8\cdot\frac{3}{2\cdot R} = -10.538$

Electron-hydrogen nucleus, molecular: $-\frac{8}{R} - \frac{4}{\sqrt{2}\cdot R} = -9.509$

Nuclear-nuclear potential energy: $\frac{4}{2\cdot R} + \frac{2}{2\cdot\sqrt{2}\cdot R} + 4\cdot\frac{Z}{\sqrt{2}\cdot R} = 12.312$

H-H repulsion: $\frac{4}{2\cdot R} + \frac{2}{2\cdot\sqrt{2}\cdot R} = 2.377$ C-H repulsion: $4\cdot\frac{Z}{\sqrt{2}\cdot R} = 9.935$

Tetrahedral Geometry

The energy expression below includes contributions involving only the valence electrons. The nucleus and the core electrons are treated as a plus 4 point charge located at the center of the square plane.

EnergyContribution	TetrahedralGeometry
ElectronKineticEnergy	$8 \cdot \frac{9}{8 \cdot R^2}$
IntraPairElectronRepulsion	$4 \cdot \frac{6}{5 \cdot R}$
InterPairElectronRepulsion	$6 \cdot \frac{2 \cdot 2}{2 \cdot R}$
HH − NuclearRepulsion	$6 \cdot \frac{1 \cdot 1}{2 \cdot R}$
CH − NuclearRepulsion	$4 \cdot \frac{1 \cdot Z}{1.2247 \cdot R}$
ElectronCarbonKernelAttraction	$8 \cdot \frac{-1 \cdot Z}{1.2247 \cdot R}$
MolecularElectronHydrogenAttraction	$24 \cdot \frac{-1 \cdot 1}{2 \cdot R}$
AtomicElectronHydrogenAttraction	$-8 \cdot \frac{3}{2 \cdot R}$

Energy as a function of R:

$$E(R) := 8 \cdot \frac{9}{8 \cdot R^2} + 4 \cdot \frac{6}{5 \cdot R} + 6 \cdot \frac{2 \cdot 2}{2 \cdot R} + 6 \cdot \frac{1 \cdot 1}{2 \cdot R} + 4 \cdot \frac{1 \cdot Z}{1.2247 \cdot R} + 8 \cdot \frac{-1 \cdot Z}{1.2247 \cdot R} + 24 \cdot \frac{-1 \cdot 1}{2 \cdot R} - 8 \cdot \frac{3}{2 \cdot R}$$

Minimize the energy with respect to the electron-pair radius, R.

$R := .2$ Given $\frac{d}{dR}E(R) = 0$ $R := \text{Find}(R)$ $R = 1.043$

Display the ground state energy: $E(R) = -8.279$

Factor the ground state energy into its kinetic and electrostatic contributions.

$T(R) := \frac{9}{R^2}$ $T(R) = 8.279$ $V(R) := E(R) - T(R)$ $V(R) = -16.559$

Further break down the potential energy into electron-electron potential energy and electron-nucleus potential energy.

Intra-pair Vee: $\frac{24}{5 \cdot R} = 4.604$ Inter-pair Vee: $\frac{12}{R} = 11.51$

Electron-nucleus potential energy: $-\frac{8\cdot Z}{1.2247\cdot R} - 8\cdot\frac{3}{2\cdot R} - 6\cdot\frac{2}{R} = -48.08$

Electron-carbon nucleus: $-\frac{8\cdot Z}{1.2247\cdot R} = -25.061$ Electron-hydrogen nucleus, atomic: $-8\cdot\frac{3}{2\cdot R} = -11.51$

Electron-hydrogen nucleus, molecuar: $-6\cdot\frac{2}{R} = -11.51$

Nuclear-nuclear potential energy: $6\cdot\frac{1}{2\cdot R} + 4\cdot\frac{Z}{1.2247\cdot R} = 15.408$

H-H repulsion: $6\cdot\frac{1}{2\cdot R} = 2.877$ C-H repulsion: $4\cdot\frac{Z}{1.2247\cdot R} = 12.531$

Summary

The summary below shows that according to the Valence Spheres Model the reason methane adopts the tetrahedral geometry rather than square planar is due to the enhanced electron-nuclear attraction of the tetrahedral geometry. That electron-nuclear interaction should be the driving force for molecular geometry should not be surprizing: it is the only attractive energy term and it is by far the largest.

By comparison all the "repulsive" terms (kinetic energy, electron-electron and nuclear-nuclear potential energy) are actually greater in the tetrahedral arrangement. But they are overwhelmed by the electron-nuclear attraction.

Methane	SquarePlanar	Tetrahedral	Difference
ElectronKineticEnergy	6.94	8.28	1.34
Total − ElectronElectronRepulsion	13.73	16.11	2.38
IntraPairElectronRepulsion	4.22	4.60	0.38
InterPairElectronRepulsion	9.51	11.51	2.00
Total − NuclearNuclearRepulsion	12.31	15.41	3.10
HH − NuclearRepulsion	2.38	2.88	2.60
CH − NuclearRepulsion	9.94	12.53	2.60
Total − ElectronNuclearAttraction	−39.92	−48.08	−8.16
ElectronCarbonAttraction	−19.87	−25.06	−5.19
MolecularElectronHydrogenAttraction	−9.51	−11.51	−2.00
AtomicElectronHydrogenAttraction	−10.54	−11.51	−0.97
Total − Energy	−6.94	−8.28	−1.34
ValenceSphereRadius	1.14	1.04	−0.10