3.012 Fund of Mat Sci: Bonding – Lecture 10

MOLECULES FROM ATOMS

Image of a journal article removed for copyright reasons.
See Slater, J. C., and G. F. Koster. "Simplified LCAO Method for the Periodic Potential Problem." *Physical Review* 94, no. 6 (1954).

Homework for Mon Oct 17

- Study: 25.2, 25.4, 24.4, 24.6

Last time:

1. Variational principle
2. Application to the hydrogen atom
3. LCAO – optimize the coefficients
4. Hydrogen molecular ion

Energy of a Molecule

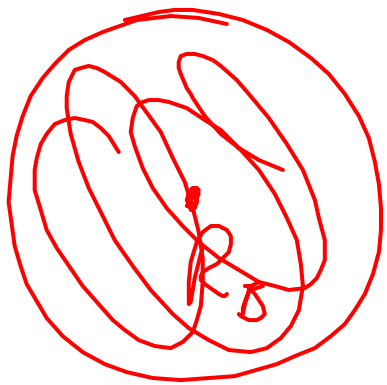
$$E = T_e + V_{e-N} + V_{e-e} + V_{N-N}$$

Linear Combination of Atomic Orbitals

- Trial wavefunction is a linear combination of atomic orbitals – the variational parameters are the coefficients:

$$\Psi_{trial} = c_1 \Psi_{1s}\left(\vec{r} - \vec{R}_A\right) + c_2 \Psi_{1s}\left(\vec{r} - \vec{R}_B\right)$$

$$\frac{\langle \Psi | H | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$



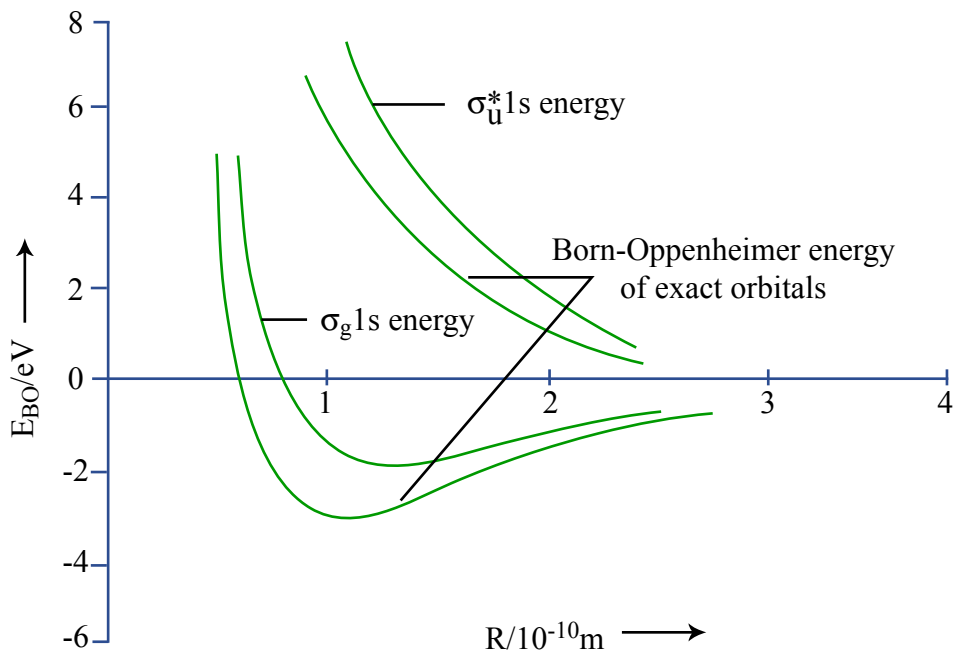
Formation of a Bonding Orbital

See animation at
http://winter.group.shef.ac.uk/orbitron/MOs/H2/1s1s-sigma/index.html

Formation of an Antibonding Orbital

See animation at
http://winter.group.shef.ac.uk/orbitron/MOs/H2/1s1s-sigma-star/index.html

Bonding and Antibonding (II)



Orbital Energies for the σ_g 1s and σ_u^* 1s LCAO Molecular Orbitals.

Figure by MIT OCW.

Many-Atoms Hamiltonian

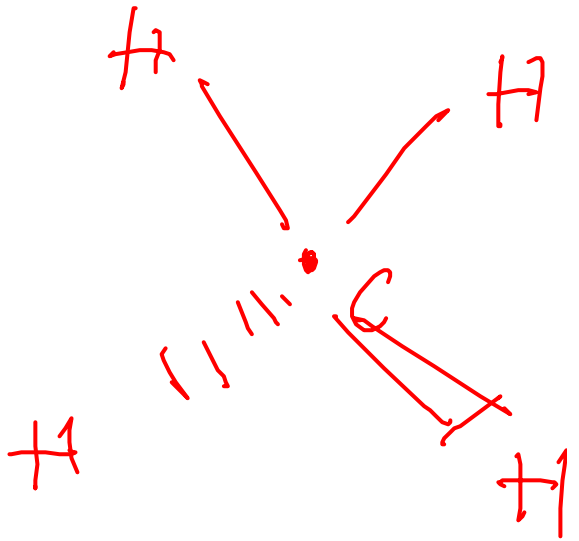
$$\hat{H} = \hat{T}_e + \hat{V}_{e-N} + \hat{V}_{e-e} + V_{N-N}$$

$$\hat{T}_e = -\frac{1}{2}\sum_i \nabla_i^2 \qquad \hat{V}_{e-N} = -\sum_i \sum_I \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} \qquad \hat{V}_{e-e} = \sum_i \sum_{j>i} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

$$-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{\hbar^2}{2m}\nabla_3^2 \cdots$$

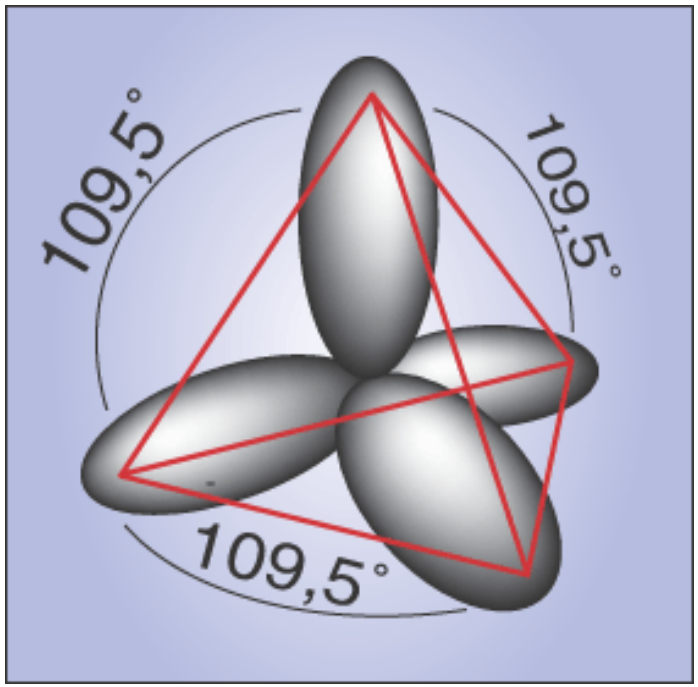
$$\sum_{i,j} -\frac{1}{4\pi\varepsilon_0}\frac{Z_j}{|\vec{r}_i - \vec{R}_j|} \qquad \sum_{i,j} \frac{1}{4\pi\varepsilon_0}\frac{1}{|\vec{r}_i - \vec{r}_j|}$$

Molecular Orbitals From Atomic Orbitals



$$\Psi_{trial} = c_1\Psi_{1s,H_a} + c_2\Psi_{1s,H_b} + c_3\Psi_{1s,H_c} + c_4\Psi_{1s,H_d}$$
$$+ c_5\Psi_{2s,C} + c_6\Psi_{2p_x,C} + c_7\Psi_{2p_y,C} + c_8\Psi_{2p_z,C}$$

sp^3 hybridization



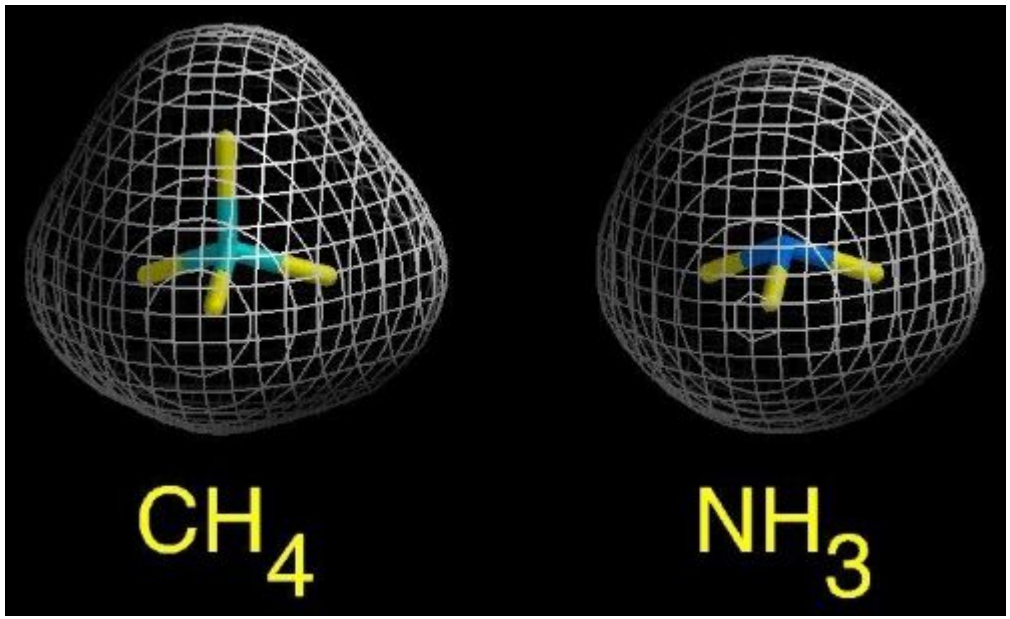
sp^3 Hypbridization. Source: Wikipedia.

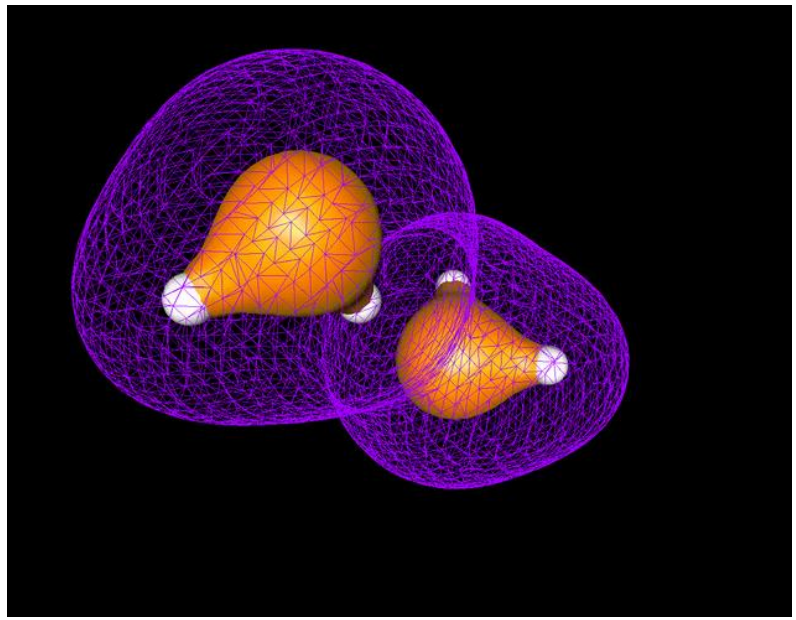
Diagram of s and p orbitals combining to create sp^3 hybridization removed for copyright reasons.
See p. 440, figure 12-5 in Petrucci, R. H., W. S. Harwood, and F. G. Herring. *General Chemistry: Principles and Modern Applications*. 8th ed. Upper Saddle River, NJ: Prentice Hall, 2002.

sp^3 hybridization

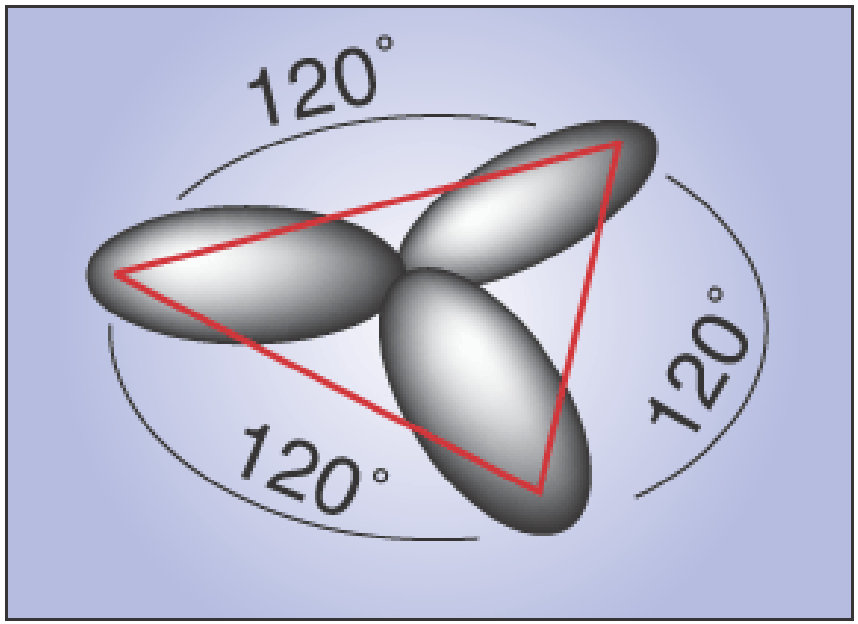
Images of sp^3 hybridization in CH_4 and NH_3 removed for copyright reasons.
See pp. 441-442, figures 12-6 and 12-7 in Petrucci, R. H., W. S. Harwood, and F. G. Herring. *General Chemistry: Principles and Modern Applications*. 8th ed. Upper Saddle River, NJ: Prentice Hall, 2002.

Great gases and liquids…





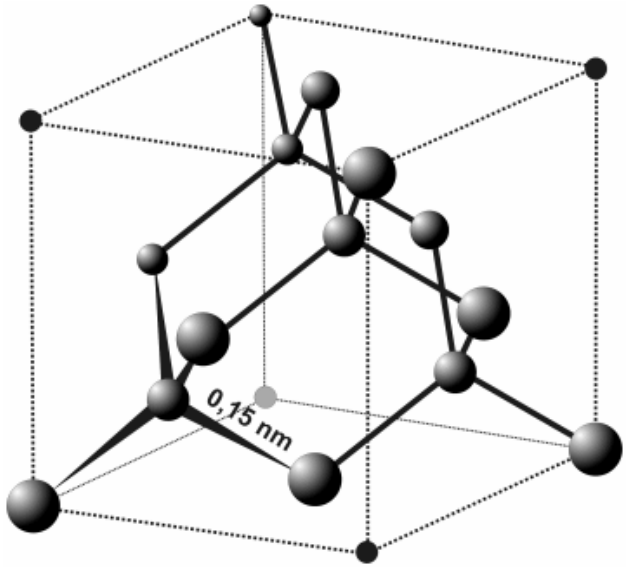
sp^2 hybridization

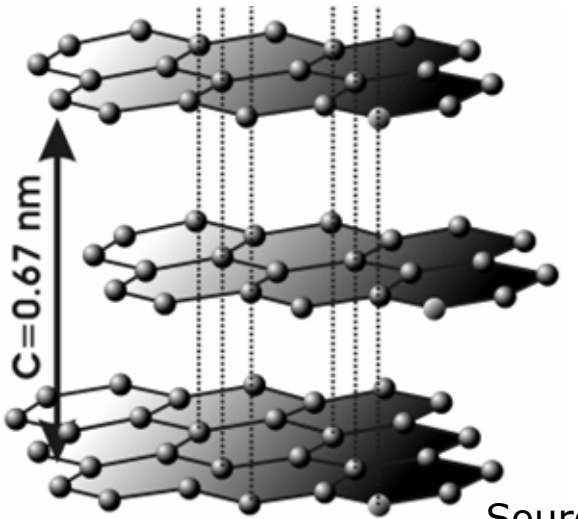


sp^2 Hypbridization. Source: Wikipedia.

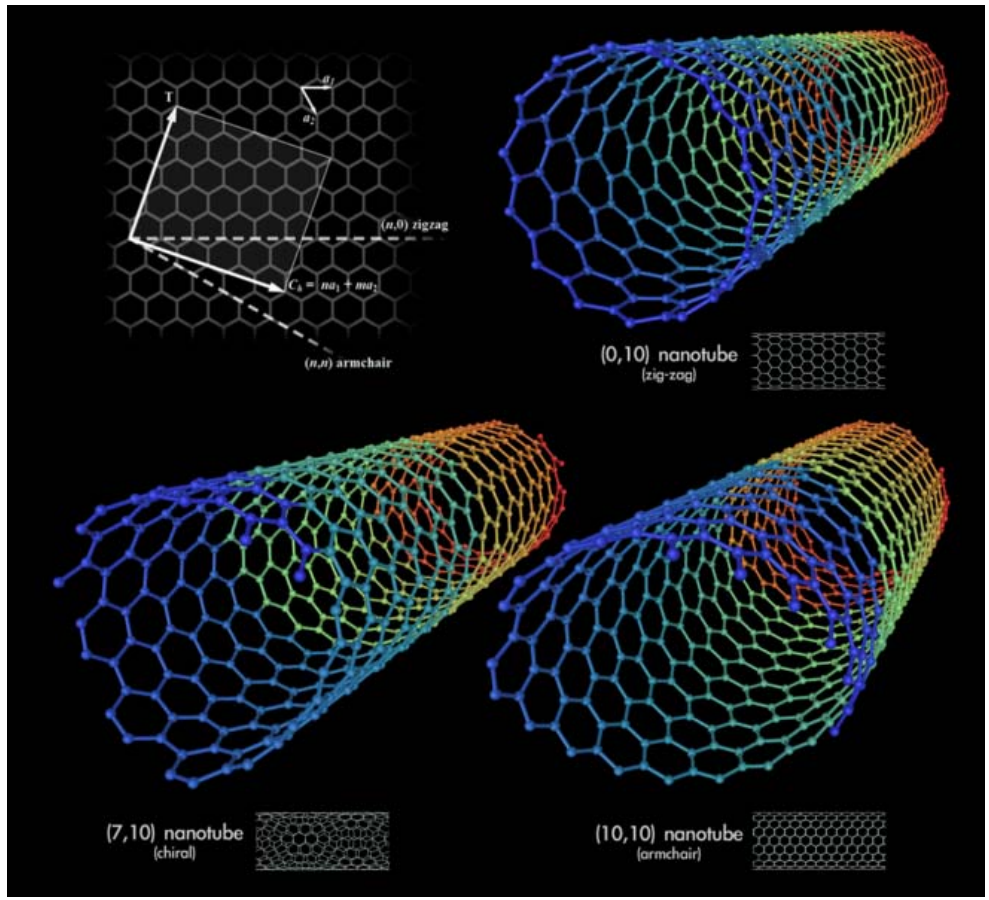
Diagram of s and p orbitals combining to create sp^2 hybridization removed for copyright reasons.
See p. 442, figure 12-8 in Petrucci, R. H., W. S. Harwood, and F. G. Herring. *General Chemistry: Principles and Modern Applications*. 8th ed. Upper Saddle River, NJ: Prentice Hall, 2002.

Carbon Compounds





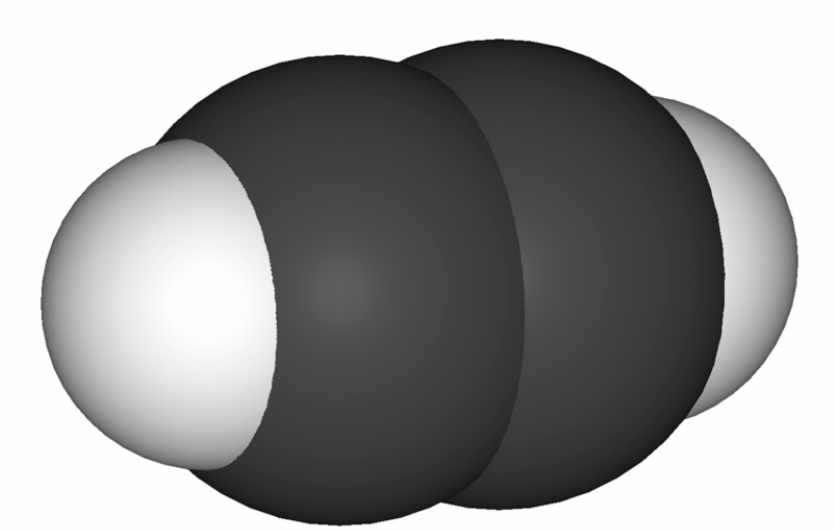
Source: Wikipedia



sp hybridization

Diagram of s and p orbitals combining to create sp hybridization removed for copyright reasons.
See p. 443, figure 12-9 in Petrucci, R. H., W. S. Harwood, and F. G. Herring. *General Chemistry: Principles and Modern Applications*. 8th ed. Upper Saddle River, NJ: Prentice Hall, 2002.

Ethyne (Acetylene)



$$H-C\equiv C-H$$

Source: Wikipedia

Diagram of the formation of σ and π bonds in ethyne removed for copyright reasons.

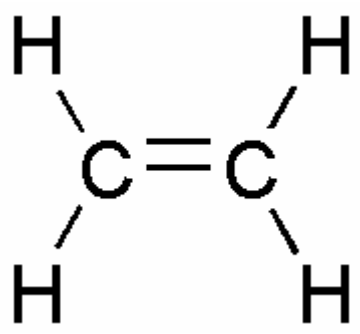
Formation of a σ Bonding Orbital

See animation at
http://winter.group.shef.ac.uk/orbitron/MOs/N2/2pz2pz-sigma/index.html

Formation of a π Bonding Orbital

See animation at
http://winter.group.shef.ac.uk/orbitron/MOs/N2/2px2px-pi/index.html

Ethene (Ethylene)



Source: Wikipedia

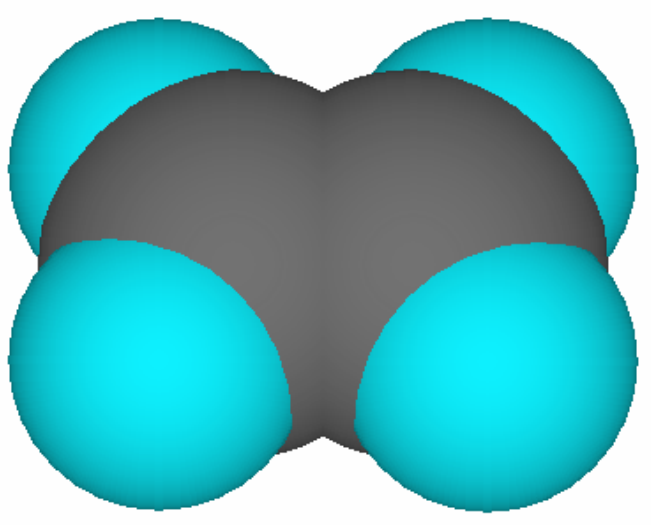
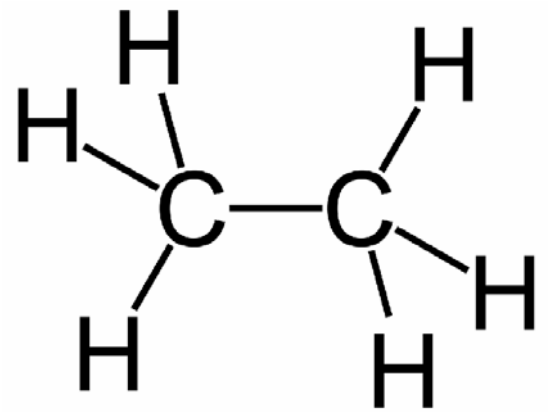


Diagram of the formation of σ and π bonds in ethene removed for copyright reasons.

Ethane (saturated)



Source: Wikipedia

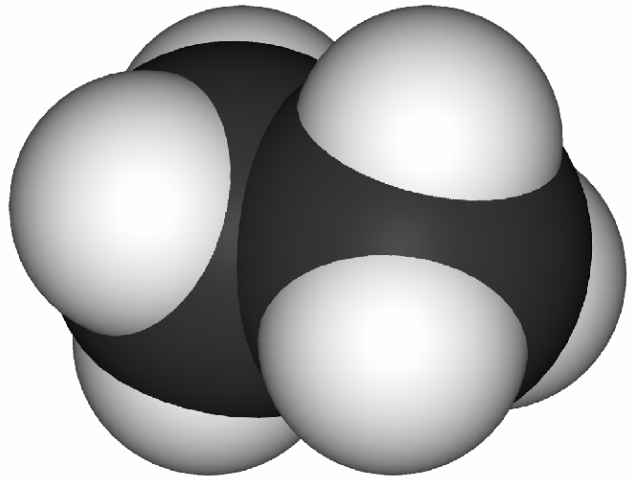


Diagram of ethane removed for copyright reasons. See Goodman et al., Nature (2001).

Bond Lengths and Bond Energies

Tables of Average Bond Lengths and Average Bond Energies removed for copyright reasons.
See p. 420, table 11.2, and p. 422, table 11.3, in Petrucci, R. H., W. S. Harwood, and F. G. Herring. *General Chemistry: Principles and Modern Applications*. 8th ed. Upper Saddle River, NJ: Prentice Hall, 2002.