Chemical Bonds

Vibrations, translation, and rotation

Mass-spring model for n atoms with $3n$ degrees of freedom

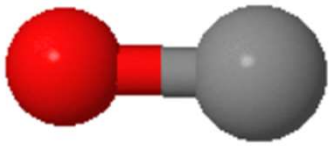
$$
\begin{aligned}
m_1 \frac{d^2 u_1}{dt^2} &= k_{12}(u_2 - u_1) + k_{13}(u_3 - u_1) + \cdots + k_{1,3n}(u_{3n} - u_1) \\
m_1 \frac{d^2 u_2}{dt^2} &= k_{12}(u_1 - u_2) + k_{23}(u_3 - u_2) + \cdots + k_{2,3n}(u_{3n} - u_2) \\
m_1 \frac{d^2 u_3}{dt^2} &= k_{13}(u_1 - u_3) + k_{23}(u_2 - u_3) + \cdots + k_{3,3n}(u_{3n} - u_3) \\
m_2 \frac{d^2 u_4}{dt^2} &= k_{12}(u_1 - u_4) + k_{23}(u_2 - u_4) + \cdots + k_{4,3n}(u_{3n} - u_4) \\
m_2 \frac{d^2 u_5}{dt^2} &= k_{12}(u_1 - u_5) + k_{23}(u_2 - u_5) + \cdots + k_{5,3n}(u_{3n} - u_5) \\
m_2 \frac{d^2 u_6}{dt^2} &= k_{12}(u_1 - u_6) + k_{23}(u_2 - u_6) + \cdots + k_{6,3n}(u_{3n} - u_6) \\
&\vdots \\
m_n \frac{d^2 u_{3n-2}}{dt^2} &= k_{1,3n-2}(u_1 - u_{3n-2}) + k_{2,3n-2}(u_2 - u_{3n-2}) + \cdots + k_{3n-2,3n}(u_{3n} - u_{3n-2}) \\
m_n \frac{d^2 u_{3n-1}}{dt^2} &= k_{1,3n-1}(u_1 - u_{3n-1}) + k_{2,3n-1}(u_2 - u_{3n-1}) + \cdots + k_{3n-1,3n}(u_{3n} - u_{3n-1}) \\
m_n \frac{d^2 u_{3n}}{dt^2} &= k_{1,3n}(u_1 - u_{3n}) + k_{2,3n}(u_2 - u_{3n}) + \cdots + k_{3n-1,3n}(u_{3n-1} - u_{3n})
\end{aligned}
$$

Vibrations, translation, and rotation for a diatomic molecule

eigenvectors

$$\begin{pmatrix} \frac{1}{6} & -\frac{1}{6} & 0 & 0 & 0 & 0 \\ -\frac{1}{8} & \frac{1}{8} & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

$v_1 = \left(-\frac{4}{3}, 1, 0, 0, 0, 0\right)$	$\lambda_1 = \frac{7}{24}$
$v_2 = (0, 0, 0, 0, 0, 1)$	$\lambda_2 = 0$
$v_3 = (0, 0, 0, 0, 1, 0)$	$\lambda_3 = 0$
$v_4 = (0, 0, 0, 1, 0, 0)$	$\lambda_4 = 0$
$v_5 = (0, 0, 1, 0, 0, 0)$	$\lambda_5 = 0$
$v_6 = (1, 1, 0, 0, 0, 0)$	$\lambda_6 = 0$



Eigen modes for CO

Vibrations, translation, and rotation

N atoms in a molecule

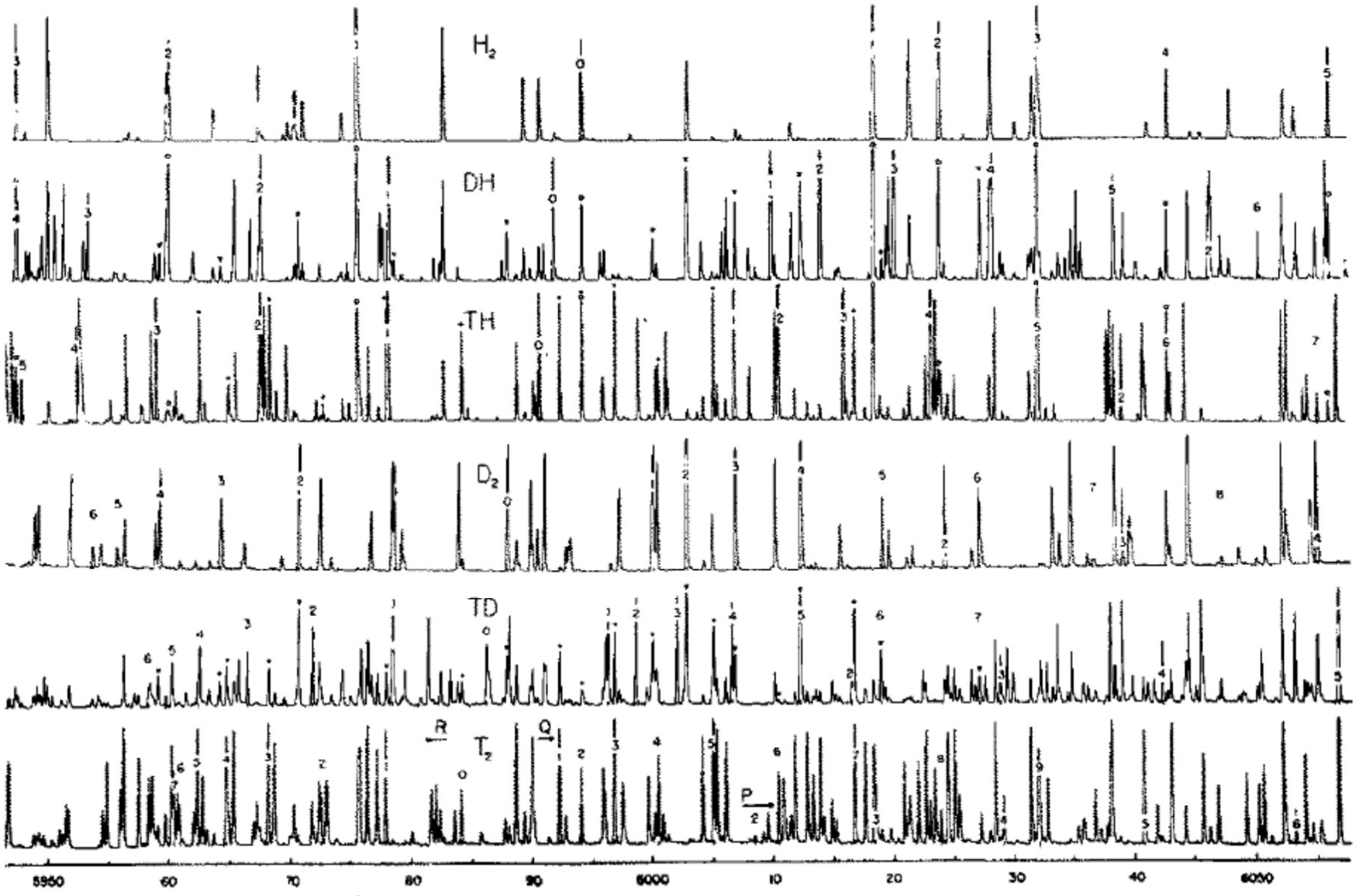
$3N$ degrees of freedom

3 translational degrees of freedom

Linear molecule: 2 rotational, $3N$-5 vibrational degrees of freedom

Nonlinear molecule: 3 rotational, $3N$-6 vibrational degrees of freedom

Emission spectra



Dieke, Journal of Molecular Spectroscopy 2, p. 494 (1958)

Transition rates

$$H = H_0 + H_1$$

We know the eigenstates of H_0 = molecule + EM waves
$|\, i >$ is the initial state, $|\, f >$ is the final state.

H_1 is the perturbation that couples the molecular states to the EM waves.

Fermi's golden rule: $$\Gamma_{i\to f} = \frac{2\pi}{\hbar}|\langle f|H_1|i\rangle|^2\delta(E_f - E_i)$$

Often you can show $|\langle f|H_1|i\rangle| = 0$ by symmetry $\Longrightarrow$ Forbidden transition

Chemical bonds

Ionic bonds
Covalent bonds
Metallic bonds
Bond potentials
Polar bonds
σ - bonds
π - bonds
double bonds
triple bonds

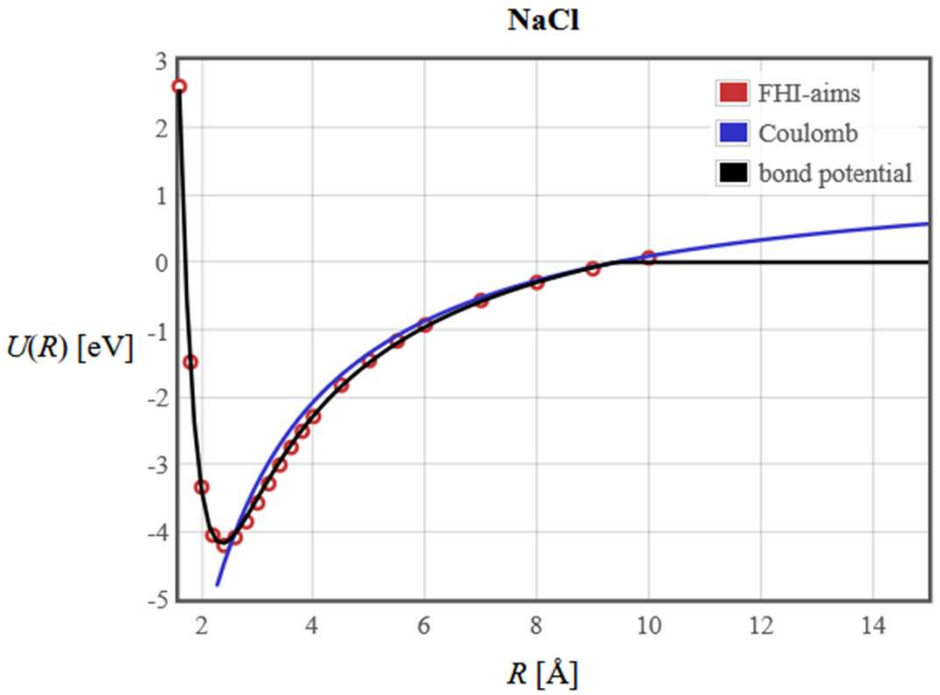
Ionic bond

Coulomb force: $$F = \frac{e^2}{4\pi\varepsilon_0 r^2}$$

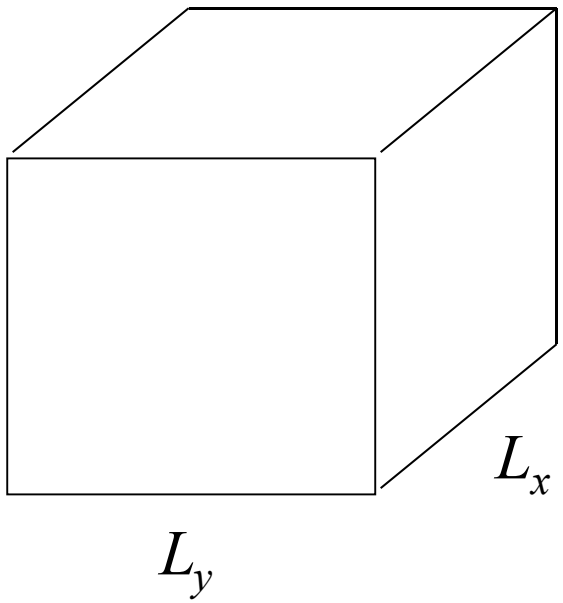
Energy needed to separate charges e and $-e$

$$E = \int \vec{F} \cdot d\vec{r} = \int_{0.2\text{ nm}}^{\infty} \frac{-e^2}{4\pi\varepsilon_0 r^2} dr = 7\text{ eV}$$

Ionic bonds are a few eV



Covalent bond: Square well potential



$$V = \begin{cases} 0 & \text{inside the cube} \\ \infty & \text{outside the cube} \end{cases}$$

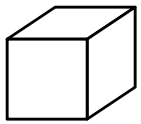
$$-\frac{\hbar^2}{2m}\nabla^2\Psi = E\Psi$$

$$\Psi = \frac{2\sqrt{2}}{\sqrt{L_x L_y L_z}} \sin\frac{n_x \pi x}{L_x} \sin\frac{n_y \pi y}{L_y} \sin\frac{n_z \pi z}{L_z} \qquad n_x, n_x, n_x = 1, 2, 3\cdots$$

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$

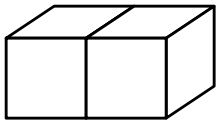
Covalent bond

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$



Energy of a particle confined to a cube $L \times L \times L$

$$E = \frac{3h^2}{8mL^2} = \frac{12h^2}{32mL^2}$$



Energy of a particle confined to a cube $L \times L \times 2L$

$$E = \frac{9h^2}{32mL^2}$$

Decrease in energy:

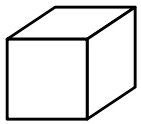
$$E = 2 \times \frac{3h^2}{32mL^2} = \frac{3h^2}{16mL^2}$$

Two electrons

For $L = 0.2$ nm $\quad \Delta E = 14$ eV

Covalent bond

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$



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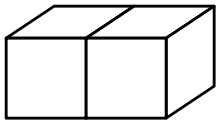

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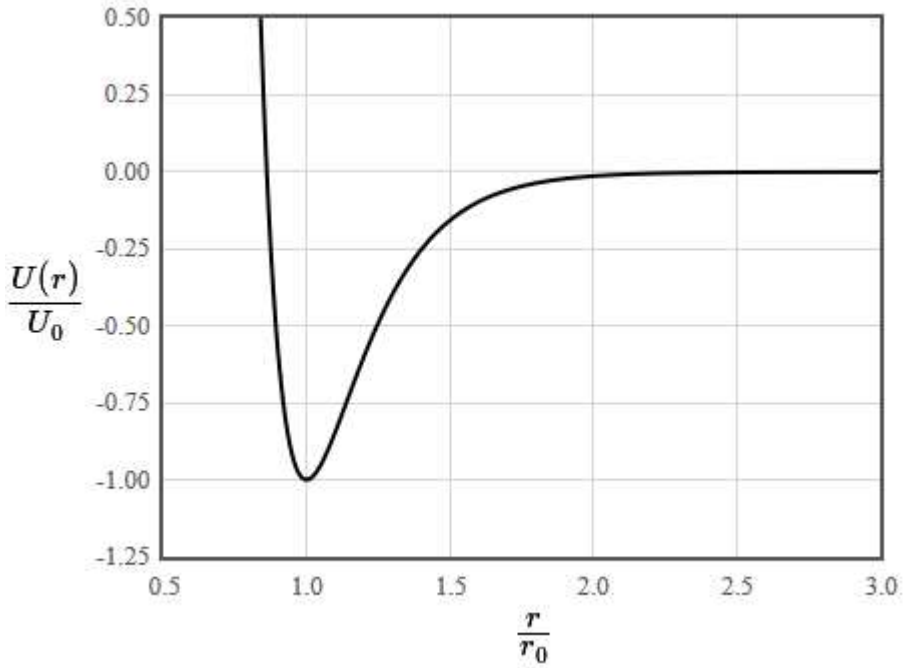
Two electrons

For $L = 0.2$ nm $\quad \Delta E = 14$ eV

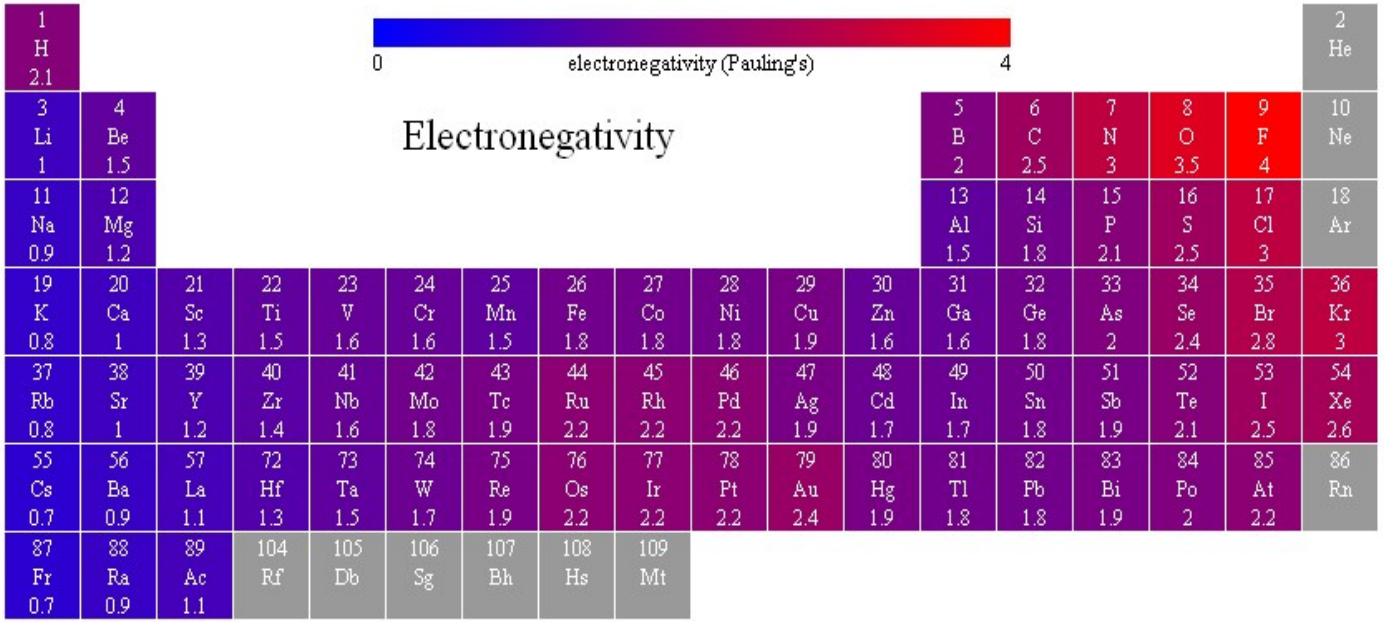
Morse potential (covalent)

$$U(r) = U_0 \left(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)} \right)$$



Polar bonds

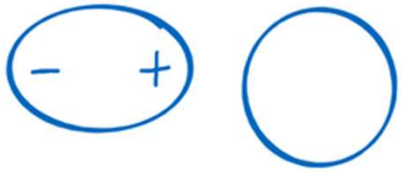
Partly covalent and partly ionic. The more electronegative element will have more negative charge.



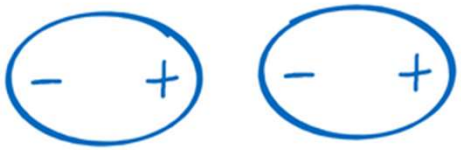
http://www.webelements.com/ http://www.chemicalelements.com/ http://www.chemicool.com/

Van der Waals bond

Two neutral atoms.



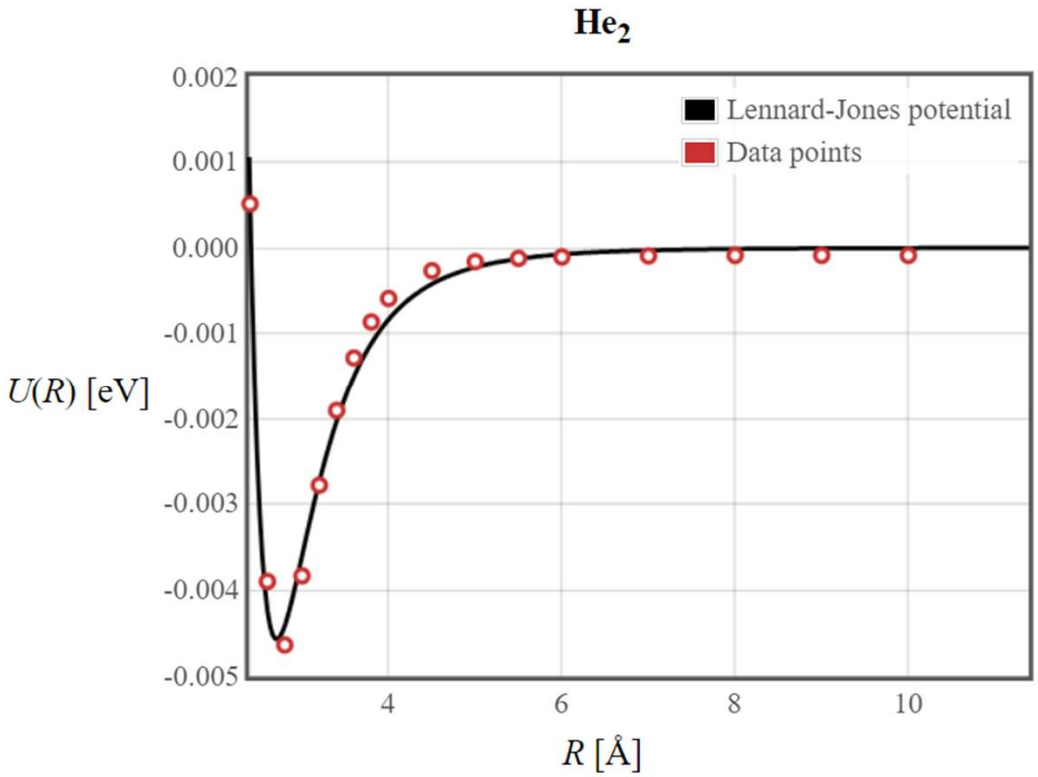
A charge fluctation creates a dipole.



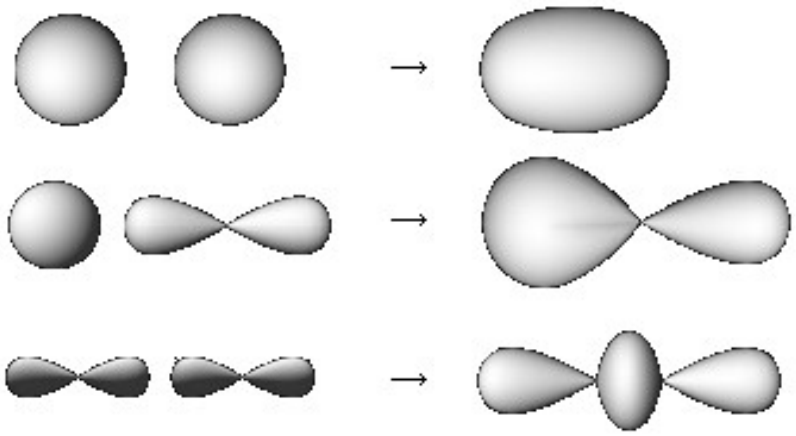
The dipole induces a dipole on the other atom.

Lennard - Jones (van der Waals)

$$U(R) = 4\epsilon\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$$



Sigma bonds



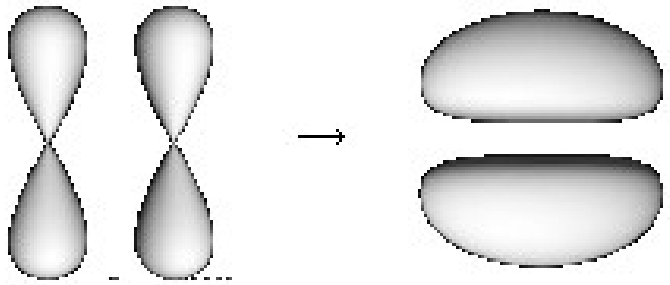
Sigma bond between two s orbitals

Sigma bond between s and p orbitals

Sigma bond between two p orbitals

The angular momentum of a sigma orbital around the interatomic axis is zero. A molecule can twist around a sigma bond.

Pi bonds



Pi bond between two p orbitals

There is an energy barrier for rotation around a Pi bond.

Single bond / double bond / triple bonds

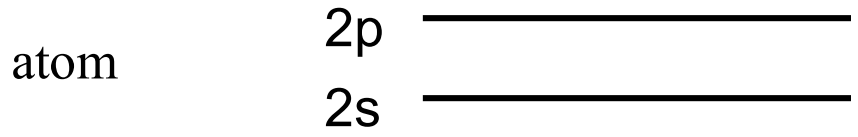
Single bond : Two electrons are shared, sigma bond

Double bond : Four electrons are shared, sigma bond + pi bond

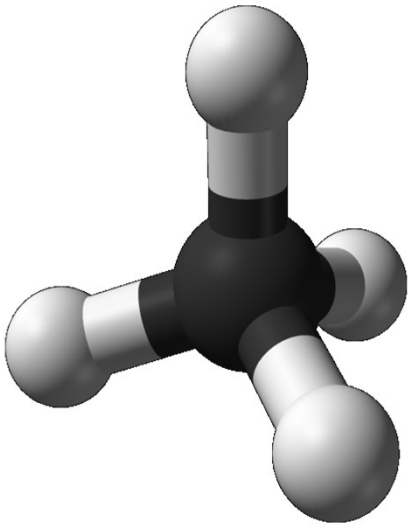
Triple bond : Six electrons are shared, sigma bond + 2 pi bonds

Hybrid orbitals

isolated carbon atom



In molecules, carbon forms sp, sp^2, and sp^3 orbitals.



$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{\frac{3}{2}}\left(2-\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}$$

$$\psi_{2px} = \frac{x}{\sqrt{32\pi a_0^5}}e^{-r/2a_0}$$

$$\psi_{2py} = \frac{y}{\sqrt{32\pi a_0^5}}e^{-r/2a_0}$$

$$\psi_{2pz} = \frac{z}{\sqrt{32\pi a_0^5}}e^{-r/2a_0}$$

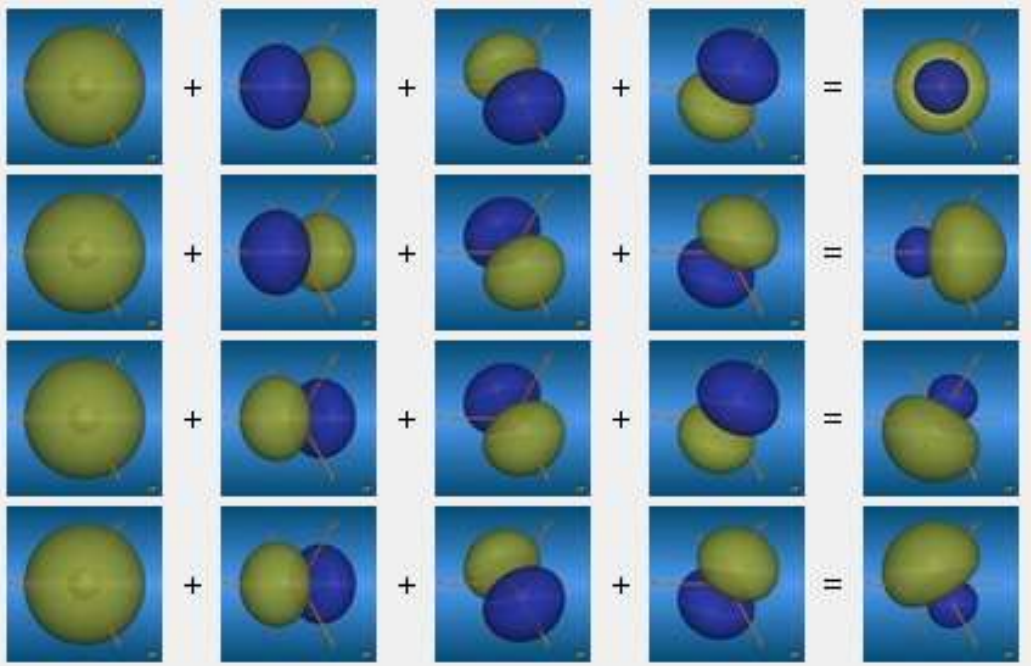
sp^3 hybrid orbitals

$1/\sqrt{4}\,\varphi_{2s} + 1/\sqrt{4}\,\varphi_{2p_x} + 1/\sqrt{4}\,\varphi_{2p_y} + 1/\sqrt{4}\,\varphi_{2p_z}$

$1/\sqrt{4}\,\varphi_{2s} + 1/\sqrt{4}\,\varphi_{2p_x} - 1/\sqrt{4}\,\varphi_{2p_y} - 1/\sqrt{4}\,\varphi_{2p_z}$

$1/\sqrt{4}\,\varphi_{2s} - 1/\sqrt{4}\,\varphi_{2p_x} - 1/\sqrt{4}\,\varphi_{2p_y} + 1/\sqrt{4}\,\varphi_{2p_z}$

$1/\sqrt{4}\,\varphi_{2s} - 1/\sqrt{4}\,\varphi_{2p_x} + 1/\sqrt{4}\,\varphi_{2p_y} - 1/\sqrt{4}\,\varphi_{2p_z}$



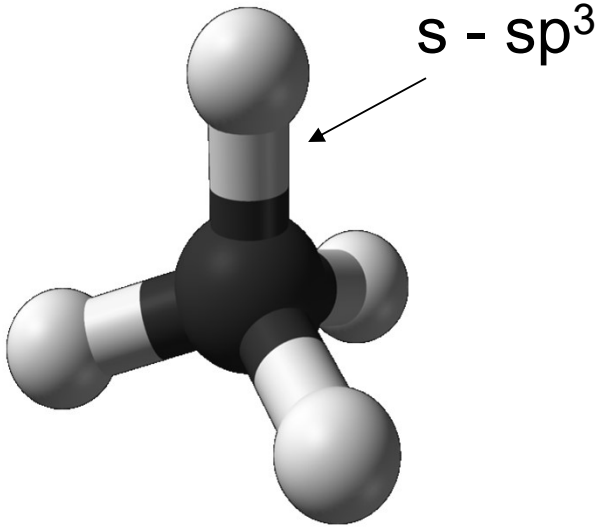
sp^3 hybrid orbitals 109^o

$$\psi_1 = \frac{1}{2}\left(\phi_{2s} + \phi_{2p_x} + \phi_{2p_y} + \phi_{2p_z}\right)$$

$$\psi_2 = \frac{1}{2}\left(\phi_{2s} + \phi_{2p_x} - \phi_{2p_y} - \phi_{2p_z}\right)$$

$$\psi_3 = \frac{1}{2}\left(\phi_{2s} - \phi_{2p_x} + \phi_{2p_y} - \phi_{2p_z}\right)$$

$$\psi_4 = \frac{1}{2}\left(\phi_{2s} - \phi_{2p_x} - \phi_{2p_y} + \phi_{2p_z}\right)$$



diamond, silicon

sp^2 hybrid orbitals 120°

The four orbitals are sp^2,sp^2, sp^2, p

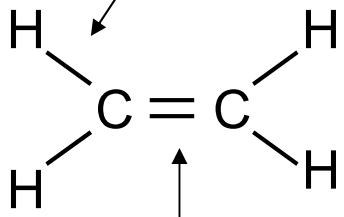
$$\psi_1 = \frac{1}{\sqrt{3}}\left(\phi_{2s} + \sqrt{2}\phi_{2p_x}\right)$$

$$\psi_2 = \frac{1}{\sqrt{3}}\phi_{2s} - \frac{1}{\sqrt{6}}\phi_{2p_x} + \frac{1}{\sqrt{2}}\phi_{2p_y}$$

$$\psi_3 = \frac{1}{\sqrt{3}}\phi_{2s} - \frac{1}{\sqrt{6}}\phi_{2p_x} - \frac{1}{\sqrt{2}}\phi_{2p_y}$$

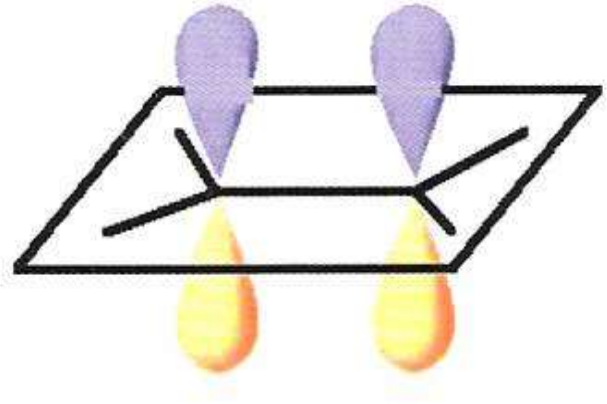
$$\psi_4 = \phi_{2p_z}$$

s - sp^2

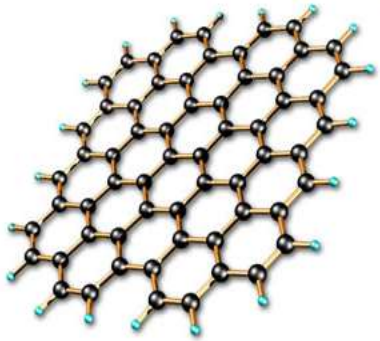


ethene

sp^2 - sp^2, p-p



Graphene

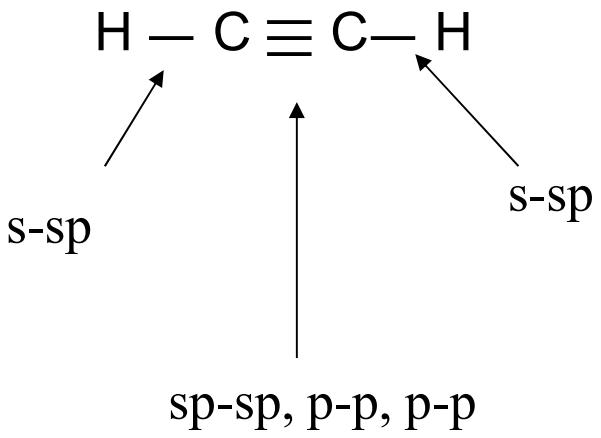


sp hybrid orbitals

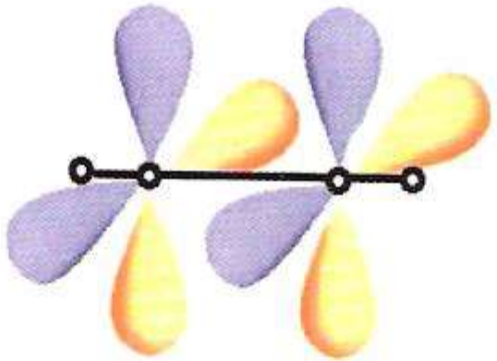
The four orbitals are sp, sp, p, p

$$\psi_1 = \frac{1}{\sqrt{2}}(\phi_{2s} + \phi_{2p_x}) \qquad \psi_2 = \frac{1}{\sqrt{2}}(\phi_{2s} - \phi_{2p_x})$$

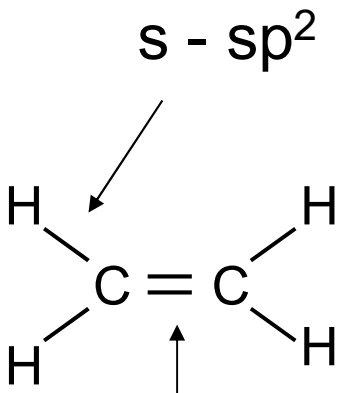
$$\psi_3 = \phi_{2p_y} \qquad \psi_4 = \phi_{2p_z}$$



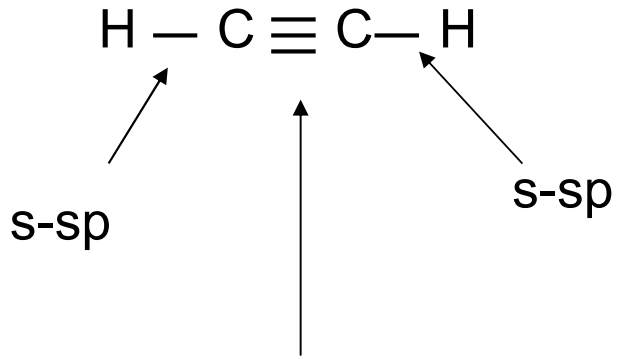
acetylene



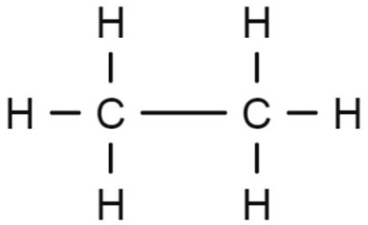
Examples of bonds



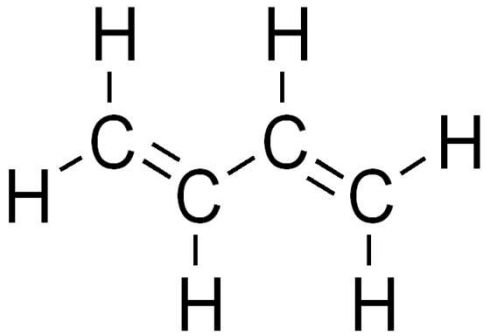
ethene



acetylene

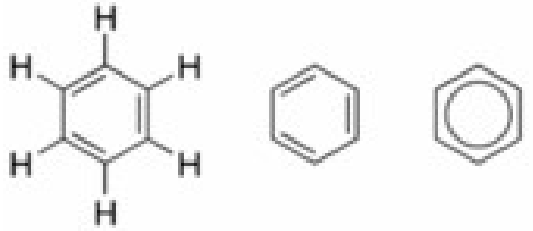


ethane



butadiene

benzene



better described by molecular orbitals than by bonds

Symmetries

Molecules can be classified by their symmetries. The eigenfunctions of the Hamiltonian will also be eigenfunctions of the symmetry operators.

Symmetries belong to a group. for $A, B \in G, AB \in G$

Symmetry @ Otterbein

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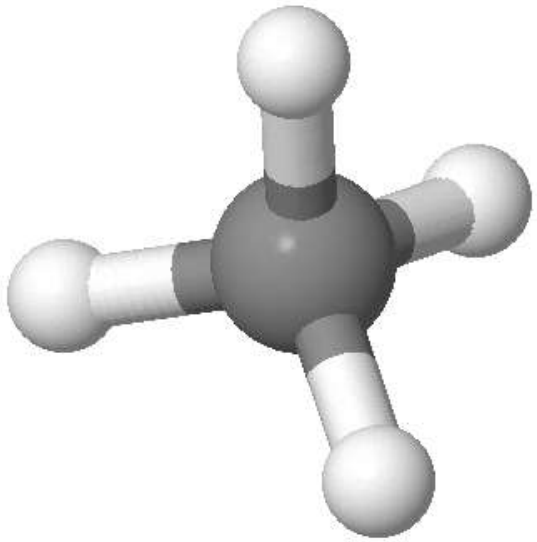


Point Group = T_d

Jmol

Element	Operation	Element	Operation
Show All Proper		*Show All Planes*	
C_3 axis	Rotate	plane (σ_d)	Reflect
C_3 axis	Rotate	plane (σ_d)	Reflect
C_3 axis	Rotate	plane (σ_d)	Reflect
C_3 axis	Rotate	plane (σ_d)	Reflect
C_2 axis	Rotate	plane (σ_d)	Reflect
C_2 axis	Rotate	plane (σ_d)	Reflect
C_2 axis	Rotate		
S_4 axis	Rotate		
S_4 axis	Rotate		
S_4 axis	Rotate		

https://symotter.org/tutorial/intro

Point symmetries

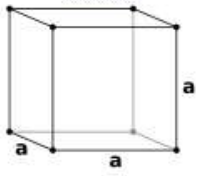
If one point remains fixed during transformation, symmetries can be represented by 3×3 matrices.

$AB \in G$ for $A, B \in G$

Rotation about the x axis by angle α:

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\alpha & \sin\alpha \\ 0 & -\sin\alpha & \cos\alpha \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

The 32 Crystal Classes

Crystal system	Crystal Class	International symbol	Schoenflies symbol	Space groups	2-fold axes	3-fold axes	4-fold axes	6-fold axes	mirror planes	inversion	Examples	Number of symmetry elements
Cubic 	tetrahedral	23	T	195-199	3	4	-	-	-	n		12
	diploidal	$m3$	T_h	200-206	3	4	-	-	3	y		24
	gyroidal	432	O	207-214	6	4	3	-	-	n		24
	hextetrahedral	$\bar{4}3m$	T_d	215-220	3	4	-	-	6	n	216: Zincblende, ZnS, GaAs, GaP, InAs, SiC	24
	hexoctahedral	$m3m$	O_h	221-230	6	4	3	-	9	y	221: CsCl, cubic perovskite 225: fcc, Al, Cu, Ni, Ag, Pt, Au, Pb, γ-Fe, NaCl 227: diamond, C, Si, Ge, α-Sn, spinel 229: bcc, Na, K, Cr, α-Fe, β-Ti, Nb, Mo, Ta	48

http://lamp.tu-graz.ac.at/~hadley/ss2/crystalphysics/crystalclasses/crystalclasses.html