5. Molecules

March 20, 2018

Every property of a molecule can be calculated using quantum mechanics.

$$H_{\mathrm{mp}} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \sum_a \frac{\hbar^2}{2m_a} \nabla_a^2 - \sum_{a,i} \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_a|} + \sum_{i<j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|} + \sum_{a<b} \frac{Z_a Z_b e^2}{4\pi\epsilon_0 |\vec{r}_a - \vec{r}_b|}$$

Make some approximations.

$$H_{\mathrm{red}} = -\sum_i \frac{\hbar^2}{2m_e} \nabla_i^2 - \cancel{\sum_a \frac{\hbar^2}{2m_a} \nabla_a^2} - \sum_{a,i} \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_a|} + \cancel{\sum_{i<j} \frac{e^2}{4\pi\epsilon_0 |\vec{r}_i - \vec{r}_j|}} + \sum_{a<b} \frac{Z_a Z_b e^2}{4\pi\epsilon_0 |\vec{r}_a - \vec{r}_b|}.$$

$$H_{\mathrm{red}}(\vec{r}_1, \vec{r}_1, \cdots, \vec{r}_N) = H_{\mathrm{mo}}(\vec{r}_1) + H_{\mathrm{mo}}(\vec{r}_2) + \cdots + H_{\mathrm{mo}}(\vec{r}_N).$$

$$\Psi_{\mathrm{red}}(\vec{r}_1, \vec{r}_1, \cdots, \vec{r}_N) = |\psi_{\mathrm{mo}}(\vec{r}_1)\psi_{\mathrm{mo}}(\vec{r}_2)\cdots\psi_{\mathrm{mo}}(\vec{r}_N)\rangle.$$

Molecular orbital Hamiltonian: $\qquad H_{\mathrm{mo}} = -\frac{\hbar^2}{2m_e} \nabla^2 - \sum_a \frac{Z_a e^2}{4\pi\epsilon_0 |\vec{r} - \vec{r}_a|}.$

The exact solution to H_{red} can be constructed from the solutions to H_{mo}.

$$H_{\mathrm{mo}} = -\frac{\hbar^2}{2m_e}\nabla^2 - \sum_a \frac{Z_a e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_a|}.$$

The molecular orbitals are constructed using LCAO.

$$\psi_{\mathrm{mo}}(\vec{r}) = \sum_a \sum_{ao} c_{ao,a}\phi_{ao}^{Z_a}(\vec{r} - \vec{r}_a).$$

Substitute into $H_{\mathrm{mo}}\psi_{\mathrm{mo}} = E\psi_{\mathrm{mo}}$, construct the Roothaan equations.

The many electron wavefunction is constructed as a Slater determinant.

$$\Psi(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) \approx |\psi_{\mathrm{mo1}}\uparrow(\vec{r}_1), \psi_{\mathrm{mo2}}\uparrow(\vec{r}_2), \cdots, \psi_{\mathrm{moN}}\uparrow(\vec{r}_N)\rangle.$$

This is an exact solution to H_{red} and an approximate solution to H_{mp}.

The energy is calculated including the electron-electron interactions.

$$E = \frac{\langle\Psi|H_{mp}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$$
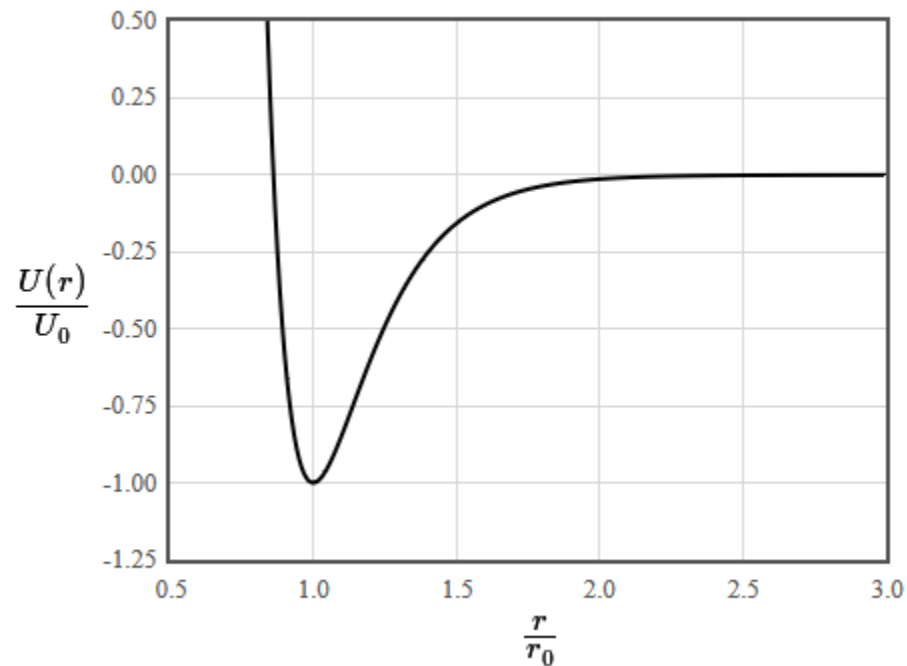
Bond potentials

Morse (covalent)

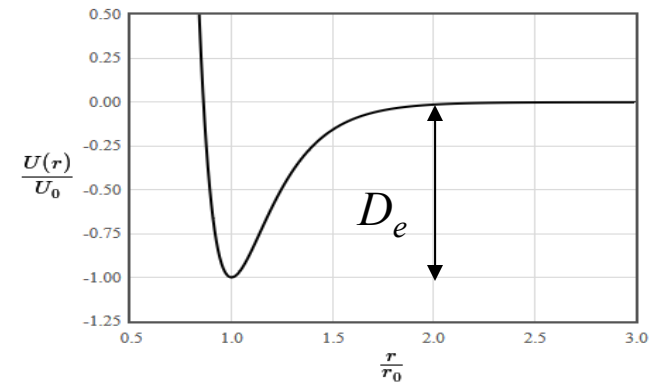$$U(r) = U_0 \left(e^{-2a(r-r_0)} - 2e^{-a(r-r_0)} \right)$$

Lennard - Jones (van der Waals)

$$U(r) = 4\varepsilon \left(\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^{6} \right)$$

Born-Oppenheimer Approximation (part 2)

Use the electronic energy as the potential for the nuclei

For H_2, the Hamiltonian for the protons is

$$H\Psi(\vec{r}_A,\vec{r}_B) = \frac{-\hbar^2}{2m_p}\left(\nabla_A^2 + \nabla_B^2\right)\Psi(\vec{r}_A,\vec{r}_B) + E_{elec}\left(r_{AB}\right)\Psi(\vec{r}_A,\vec{r}_B)$$
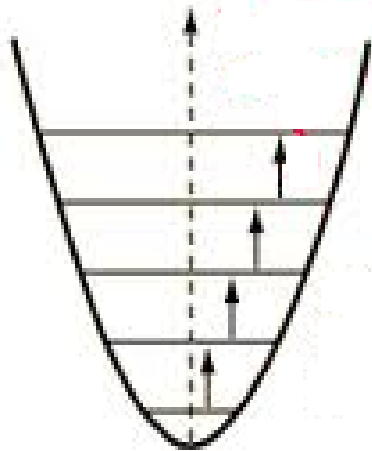
go to center of mass and relative coordinates

$$\vec{R} = \frac{\vec{R}_A + \vec{R}_B}{2} \qquad \vec{r} = \frac{\vec{R}_A - \vec{R}_B}{2}$$

$$H = H_R + H_r = -\frac{\hbar^2}{4m_p}\nabla_R^2 - \frac{\hbar^2}{2\mu}\nabla_r^2 + E_{elec}\left(r\right) \qquad \mu = \left[\frac{1}{m_A} + \frac{1}{m_B}\right]^{-1}$$
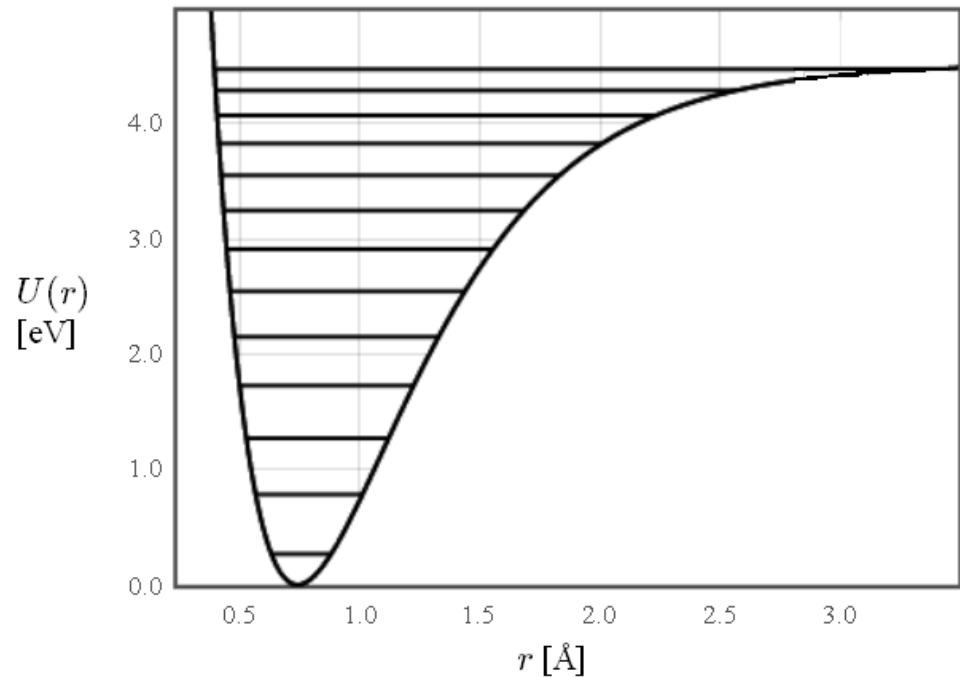
Vibrational energy levels

harmonic oscillator

Morse

$$E = \hbar \omega_0 \left(n + \tfrac{1}{2} \right)$$

$$\omega = \sqrt{\frac{k_{eff}}{\mu}} = \sqrt{\frac{2U_0 a^2}{\mu}}$$

$$U(r) \approx U_0 a^2 \left(r - r_0 \right)^2 + \cdots$$

$$\approx \frac{k_{eff}}{2} \left(r - r_0 \right)^2 + \cdots$$

Energy levels of the Morse potential

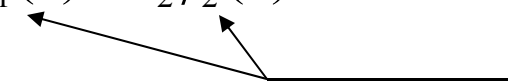$$H = -\frac{\hbar^2}{2\mu}\nabla^2 + U_{Morse}(r)$$

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

Look for a solution in terms of the harmonic oscillator wave functions

$$\psi_{LCHM}(r) = c_0\phi_0(r) + c_1\phi_1(r) + c_2\phi_2(r) + \cdots$$

Harmonic oscillator eigen functions

$$H_{Morse}\psi_{LCHM} = E\psi_{LCHM}$$

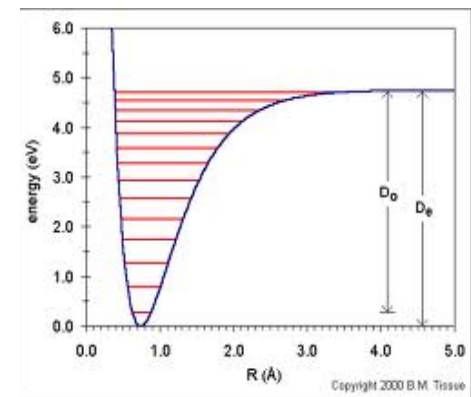$$\langle\phi_0|H_{Morse}|\psi_{LCHM}\rangle = E\langle\phi_0|\psi_{LCHM}\rangle$$

$$c_0\langle\phi_0|H_{Morse}|\phi_0\rangle + c_1\langle\phi_0|H_{Morse}|\phi_1\rangle + \cdots = Ec_0\langle\phi_0|\phi_0\rangle + Ec_0\langle\phi_0|\phi_1\rangle + \cdots$$

$$c_0\langle\phi_j|H_{Morse}|\phi_0\rangle + c_1\langle\phi_j|H_{Morse}|\phi_1\rangle + \cdots = Ec_j$$

Energy levels of the Morse potential

This results in the following matrix equation

$$\begin{bmatrix} \langle H_{00} \rangle & \langle H_{01} \rangle & \langle H_{02} \rangle \\ \langle H_{10} \rangle & \langle H_{11} \rangle & \langle H_{12} \rangle \\ \langle H_{20} \rangle & \langle H_{21} \rangle & \langle H_{22} \rangle \end{bmatrix} \begin{bmatrix} c_0 \\ c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} c_0 \\ c_1 \\ c_2 \end{bmatrix}$$

$$\langle H_{ij} \rangle = \langle \phi_i | H_{Morse} | \phi_j \rangle$$

Normalized harmonic oscillator wave functions

The eigen values of this matrix are the energy levels of the Morse potential

Vibrations, translation, and rotation

$3n$ 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

Vibrations, translation, and rotation

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

$$m_1 \frac{d^2 u_1}{dt^2} = k_{12}(u_2 - u_1) + k_{13}(u_3 - u_1) + \cdots + k_{1,3n}(u_{3n} - u_1)$$

$$m_1 \frac{d^2 u_2}{dt^2} = k_{12}(u_1 - u_2) + k_{23}(u_3 - u_2) + \cdots + k_{2,3n}(u_{3n} - u_2)$$

$$m_1 \frac{d^2 u_3}{dt^2} = k_{13}(u_1 - u_3) + k_{23}(u_2 - u_3) + \cdots + k_{3,3n}(u_{3n} - u_3)$$

$$m_2 \frac{d^2 u_4}{dt^2} = k_{12}(u_1 - u_4) + k_{23}(u_2 - u_4) + \cdots + k_{4,3n}(u_{3n} - u_4)$$

$$m_2 \frac{d^2 u_5}{dt^2} = k_{12}(u_1 - u_5) + k_{23}(u_2 - u_5) + \cdots + k_{5,3n}(u_{3n} - u_5)$$

$$m_2 \frac{d^2 u_6}{dt^2} = k_{12}(u_1 - u_6) + k_{23}(u_2 - u_6) + \cdots + k_{6,3n}(u_{3n} - u_6)$$

$$\vdots$$

$$m_n \frac{d^2 u_{3n-2}}{dt^2} = k_{1,3n-2}(u_1 - u_{3n-2}) + k_{2,3n-2}(u_2 - u_{3n-2}) + \cdots + k_{3n-2,3n}(u_{3n} - u_{3n-2})$$

$$m_n \frac{d^2 u_{3n-1}}{dt^2} = k_{1,3n-1}(u_1 - u_{3n-1}) + k_{2,3n-1}(u_2 - u_{3n-1}) + \cdots + k_{3n-1,3n}(u_{3n} - u_{3n-1})$$

$$m_n \frac{d^2 u_{3n}}{dt^2} = k_{1,3n}(u_1 - u_{3n}) + k_{2,3n}(u_2 - u_{3n}) + \cdots + k_{3n-1,3n}(u_{3n-1} - u_{3n})$$
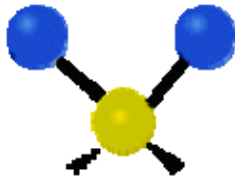
Vibrations, translation, and rotation

For a normal mode solution, all of the atoms move with the same frequency $u_p = A_p e^{i\omega t}$, where A_p is the amplitude of displacement $p = 1, 2, \cdots, 3n$.

$$
\begin{bmatrix}
\displaystyle\sum_{p\neq 1} \frac{k_{1p}}{m_1} & -\dfrac{k_{12}}{m_1} & -\dfrac{k_{13}}{m_1} & \cdots & -\dfrac{k_{1,3n}}{m_1} \\[2em]
-\dfrac{k_{21}}{m_1} & \displaystyle\sum_{p\neq 2} \frac{k_{2p}}{m_1} & -\dfrac{k_{23}}{m_1} & \cdots & -\dfrac{k_{2,3n}}{m_1} \\[2em]
-\dfrac{k_{31}}{m_1} & -\dfrac{k_{32}}{m_1} & \displaystyle\sum_{p\neq 3} \frac{k_{3p}}{m_1} & \cdots & -\dfrac{k_{3,3n}}{m_1} \\[2em]
\vdots & & & & \\[1em]
-\dfrac{k_{1,3n-2}}{m_n} & \cdots & \displaystyle\sum_{p\neq 3n-2} \frac{k_{p,3n-2}}{m_n} & -\dfrac{k_{3n-1,3n-2}}{m_n} & -\dfrac{k_{3n,3n-2}}{m_n} \\[2em]
-\dfrac{k_{1,3n-1}}{m_n} & \cdots & -\dfrac{k_{3n-2,3n-1}}{m_n} & \displaystyle\sum_{p\neq 3n-1} \frac{k_{p,3n-1}}{m_n} & -\dfrac{k_{3n,3n-1}}{m_n} \\[2em]
-\dfrac{k_{1,3n}}{m_n} & \cdots & -\dfrac{k_{3n-2,3n}}{m_n} & -\dfrac{k_{3n-1,3n}}{m_n} & \displaystyle\sum_{p\neq 3n} \frac{k_{p,3n}}{m_n}
\end{bmatrix}
\begin{bmatrix}
A_1 \\ A_2 \\ A_3 \\ \vdots \\ A_{3n-1} \\ A_{3n-2} \\ A_{3n}
\end{bmatrix}
= \omega^2
\begin{bmatrix}
A_1 \\ A_2 \\ A_3 \\ \vdots \\ A_{3n-1} \\ A_{3n-2} \\ A_{3n}
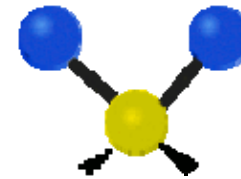\end{bmatrix}
$$

$3n$ elements $\downarrow$

The three fundamental vibrations of the water molecule

ν_1, O-H symmetric stretching
3657 cm^{-1} (2.734 μm)
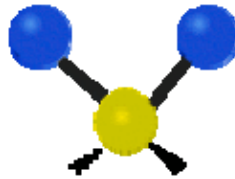
ν_2, H-O-H bending
1595 cm^{-1} (6.269 μm)

ν_3, O-H asymmetric stretching
3756 cm^{-1} (2.662 μm)

$3n$ - 3 translational - 3 rotational = 3 vibrational normal modes

Molecular rotations

In the first approximation, consider the molecules as rigid and calculate the moment of inertia (Trägheitsmoment).

The energy levels for a rigid rotator are

$$E_\ell = \frac{\hbar^2}{2I}\ell(\ell+1) \qquad\qquad \ell = 0,1,2,\cdots$$

Moment of inertia (Trägheitsmoment)

$$I = \sum_i m_i r_i^2$$

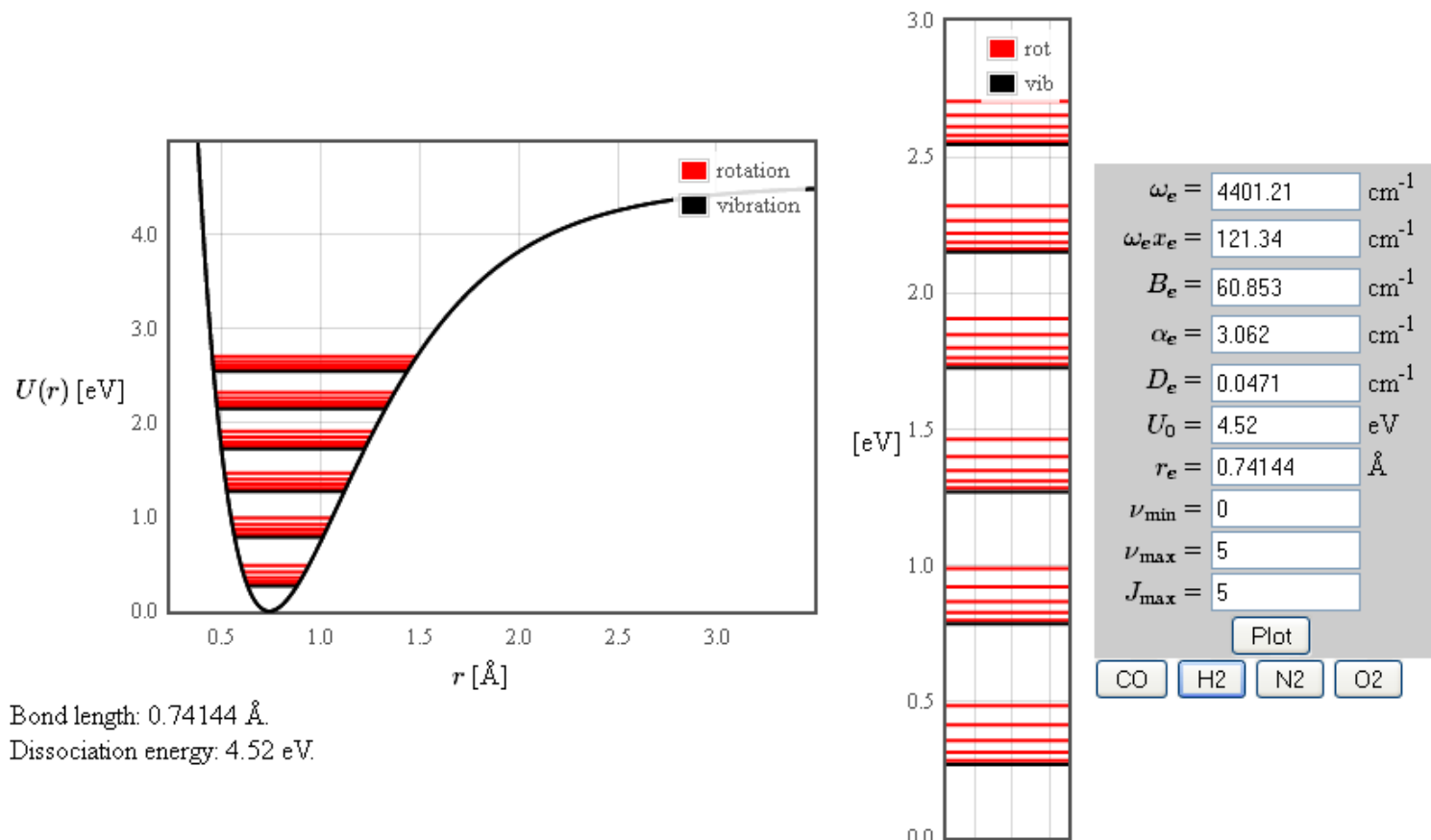# Rotational and vibrational energy levels of diatomic molecules

The rotational and vibrational energy levels of diatomic molecules can be approximated as,

$$E_{\text{vib}} = hc\omega_e(\nu + 1/2) - hc\omega_e x_e(\nu + 1/2)^2,$$

$$E_{\text{rot}} = hc(B_e - \alpha_e(\nu + 1/2))J(J+1) + D_e(J(J+1))^2),$$

where ω_e, x_e, B_e, α_e, and D_e are specroscopic constants. The quantum numbers ν and J can take on integer values, $\nu, J = 0, 1, 2, \cdots$. Here h is Planck's constant and c is the speed of light in vacuum. The units of all of the spectroscopic constants are cm^{-1} except for x_e which is unitless. The rotational and vibrational energy levels $E_{\nu J} = E_{\text{vib}} + E_{\text{rot}}$ are plotted in the bond potential on the left. An enlargement of the energy level spacing is shown on the right.

Vibration-rotation energy levels of H$_2$

Bond length: 0.74144 Å.
Dissociation energy: 4.52 eV.

$\omega_e = $ 4401.21 cm^{-1}
$\omega_e x_e = $ 121.34 cm^{-1}
$B_e = $ 60.853 cm^{-1}
$\alpha_e = $ 3.062 cm^{-1}
$D_e = $ 0.0471 cm^{-1}
$U_0 = $ 4.52 eV
$r_e = $ 0.74144 Å
$\nu_{\min} = $ 0
$\nu_{\max} = $ 5
$J_{\max} = $ 5

Plot

CO   H2   N2   O2

Excited electrical states

The bonding between atoms and the effective spring constants change when a molecule enters an excited electronic state. The vibrational and rotational modes have to be recalculated.
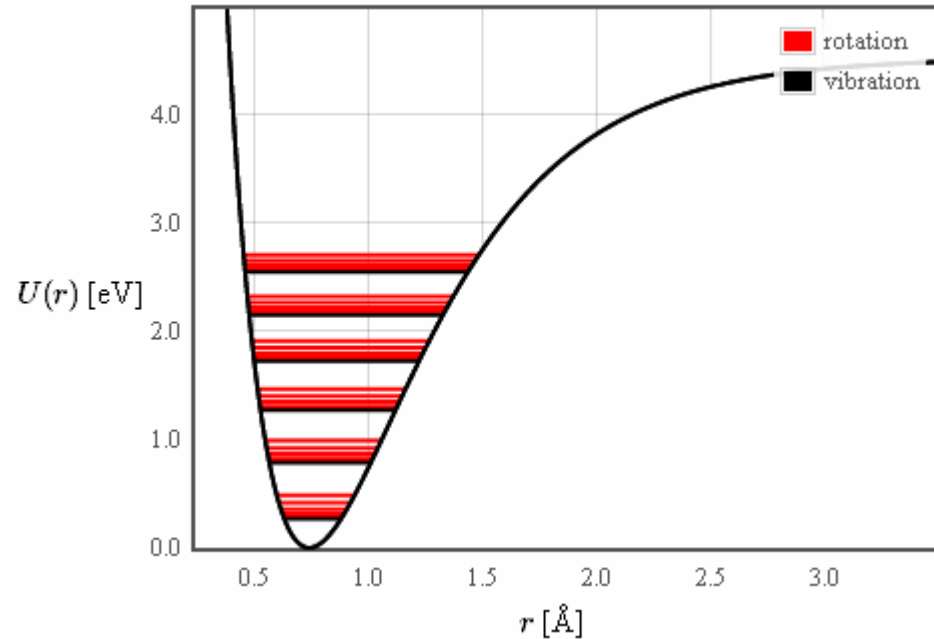
"Molecular spectroscopy is the study of absorption of light by molecules. In the gas phase at low pressures, molecules exhibit absorption in narrow lines which are very characteristic of the molecule as well as the temperature and pressure of its environment. In the microwave and long-wavelength infrared regions of the spectrum, these lines are due to quantized rotational motion of the molecule. At shorter wavelengths similar lines are due to quantized vibration and electronic motion as well as rotational motion. The precise frequencies of these lines can be fit to quantum mechanical models which can be used both to determine the structure of the molecule and to predict the frequencies and intensities of other lines. Because this absorption is so characteristic, it is very valuable for detecting molecules in the Earth's stratosphere, planetary atmospheres, and even the interstellar medium."

http://spec.jpl.nasa.gov/

Molecular Spectroscopy
Jet Propulsion Laboratory
California Institute of Technology

Catalog Directory

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    ID Name        # lines Ver.  Catalog    Documentation
  1001 H-atom           1  1   c001001.cat pdf or Tex format
  2001 D-atom           1  1   c002001.cat pdf or Tex format
  3001 HD               1  2   c003001.cat pdf or Tex format
  4001 H2D+            32  2*  c004001.cat pdf or Tex format
  7001 Li-6-H          51  2*  c007001.cat pdf or Tex format
  8001 LiH             53  2*  c008001.cat pdf or Tex format
  8002 Li-6-D          80  1   c008002.cat pdf or Tex format
  9001 LiD             90  1   c009001.cat pdf or Tex format
 12001 C-atom           2  2   c012001.cat pdf or Tex format
 13001 C-13-atom        7  2   c013001.cat pdf or Tex format
 13002 CH             508  2*  c013002.cat pdf or Tex format
 13003 CH+              9  2   c013003.cat pdf or Tex format
 14001 N-atom           2  1   c014001.cat pdf or Tex format
 14002 N-atom-D-st      6  3   c014002.cat pdf or Tex format
 14003 13CH           648  1*  c014003.cat pdf or Tex format
 14004 CD             188  1*  c014004.cat pdf or Tex format
 15001 NH            1416  1*  c015001.cat pdf or Tex format
 16001 O-atom           2  2   c016001.cat pdf or Tex format
 17001 OH            3153  5*  c017001.cat pdf or Tex format
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 17004 NH3-v2        4198  5*  c017004.cat pdf or Tex format
 18001 OD            9351  2   c018001.cat pdf or Tex format
 18002 N-15-H3        235  2   c018002.cat pdf or Tex format
 18003 H2O           1376  6*  c018003.cat pdf or Tex format
 18004 NH2D          5036  1   c018004.cat pdf or Tex format
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 18006 13CH3D         143  1*  c018006.cat pdf or Tex format
 18007 17OH         46769  1*  c018007.cat pdf or Tex format
 19001 HO-18         3159  3   c019001.cat pdf or Tex format
 19002 HDO           1401  3   c019002.cat pdf or Tex format
 19003 H2O-17         404  1   c019003.cat pdf or Tex format
 19004 H3O+           304  3*  c019004.cat pdf or Tex format
 19005 H3O+ v1,v3,v  1973  2*  c019005.cat pdf or Tex format
 19006 17OD        113226  1*  c019006.cat pdf or Tex format
 20001 D2O           1137  2   c020001.cat pdf or Tex format
 20002 HF               8  1   c020002.cat pdf or Tex format
 20003 H2O-18         726  1   c020003.cat pdf or Tex format
 20004 18OD          3632  1*  c020004.cat pdf or Tex format
 21001 HDO-18         952  1   c021001.cat pdf or Tex format
 21002 DF              20  1   c021002.cat pdf or Tex format
 25001 CCH            114  1   c025001.cat pdf or Tex format
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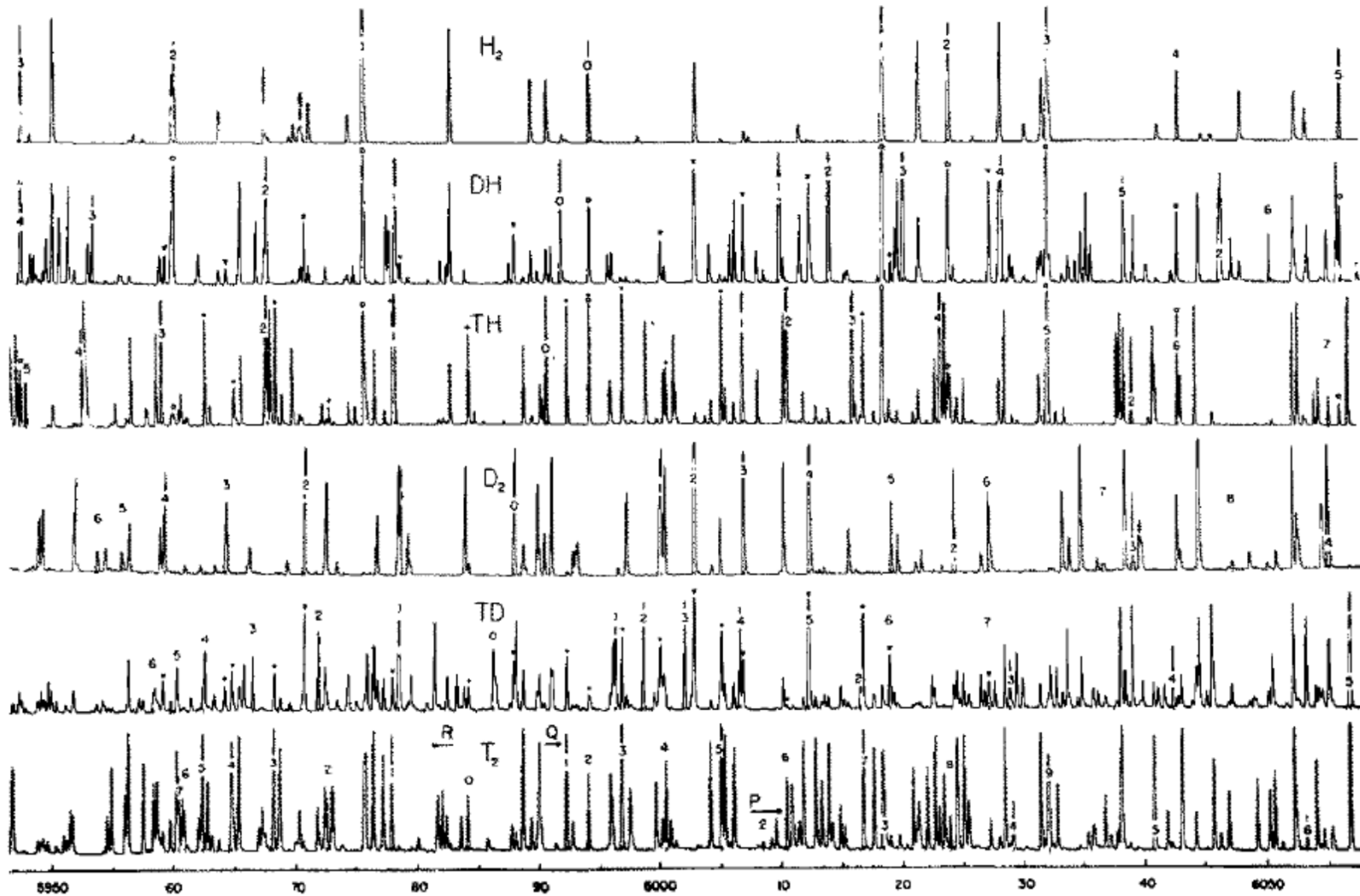
IR absorption spectrum
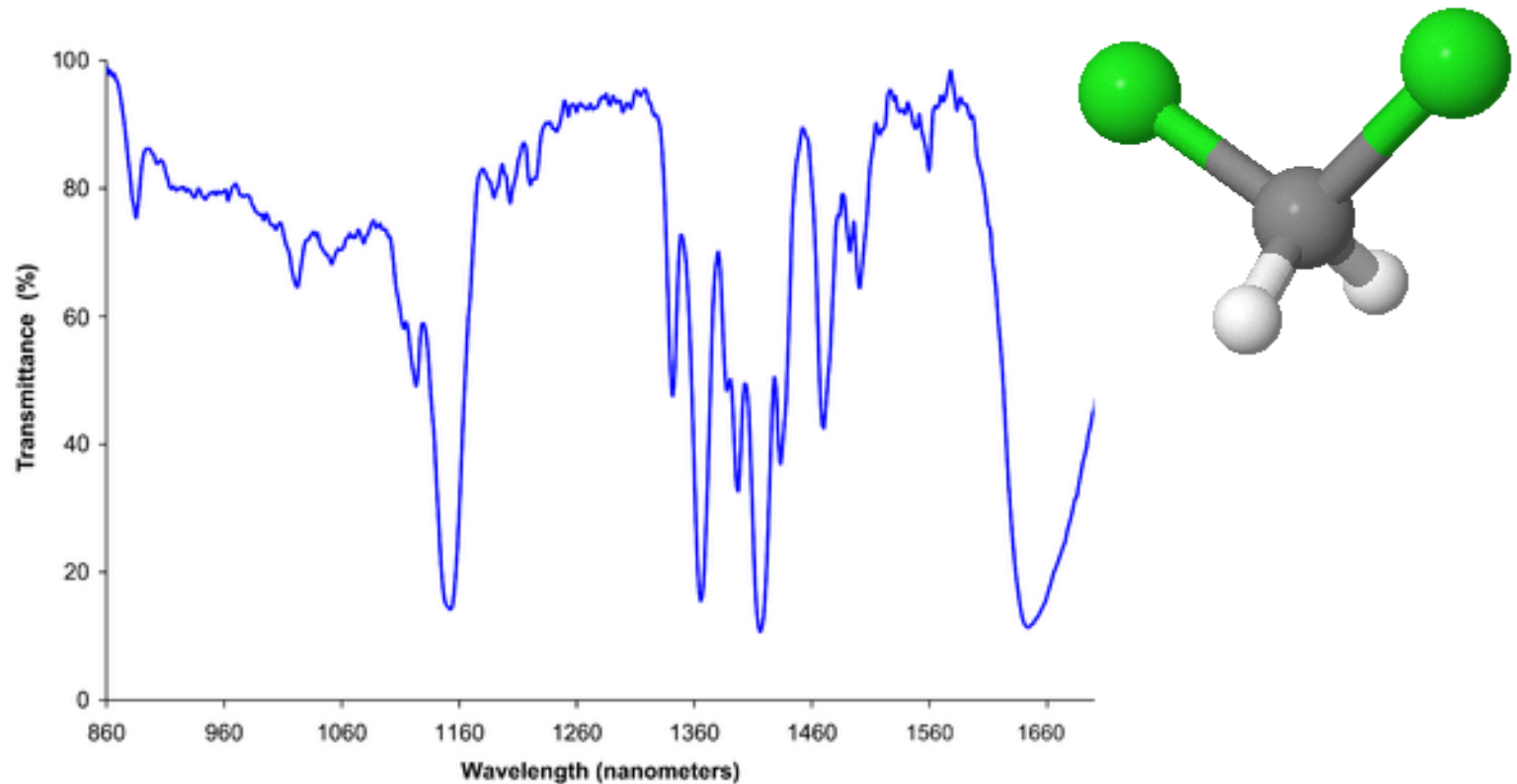
Near IR absorption spectrum of dichloromethane .

Emission spectra

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

Chemical bonds

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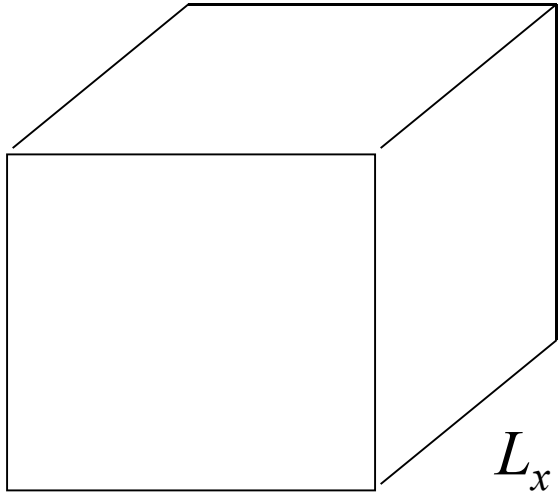double bonds
triple bonds

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

L_z

L_x

L_y

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

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

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

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

Covalent bond

$$E_{n_x n_y n_z} = \frac{\hbar^2 \pi^2}{2m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$$
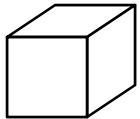
Energy of a particle confined to a cube $L \times L \times L$

$$E = \frac{3h^2}{8mL^2} = \frac{12h^2}{32mL^2}$$
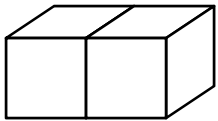
Energy of a particle confined to a cube $L \times L \times 2L$

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

Decrease in energy:

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

Two electrons

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

Polar bonds

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

electronegativity (Pauling's)

Electronegativity

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
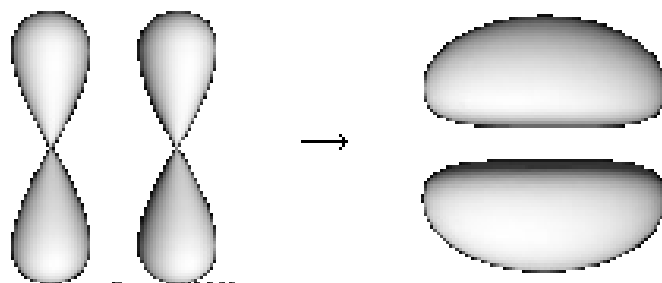
Pi bond between two p orbitals

A molecule cannot twist around a Pi bond.

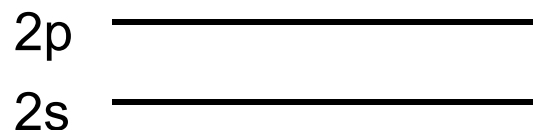# Single bond / double bond / triple bonds

Single bond : Two electrons are shared, sigma bond

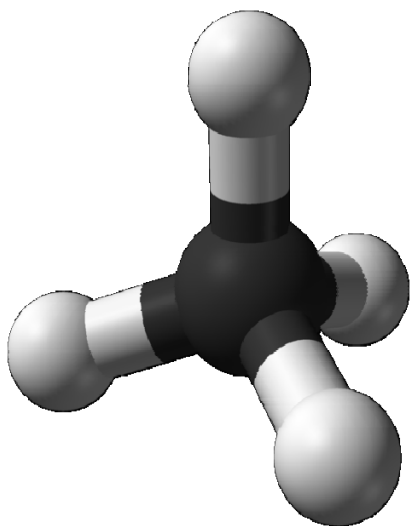Double bond : Four electrons are shared, sigma bond + pi bond

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

Hybrid orbitals

isolated carbon atom

2p ————————————

2s ————————————

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

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

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

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

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

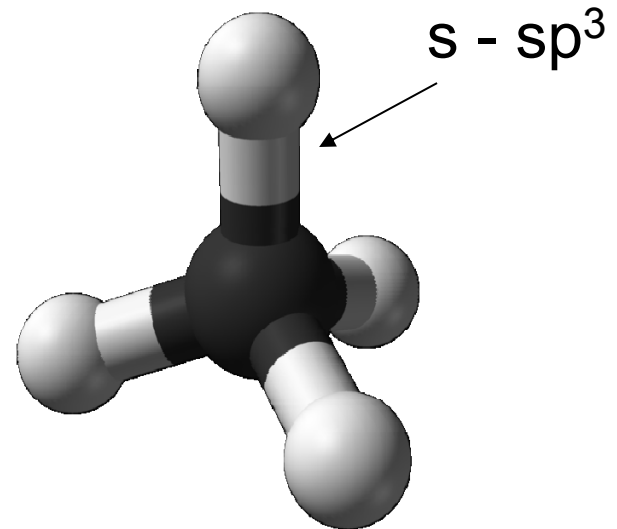# sp^3 hybrid orbitals 109°

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

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

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

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

s - sp^3

In this molecular orbital, the coefficients of these 4 atomic orbitals are about $c_{2s} = 1$, $c_{2px} = -1$, $c_{2py} = -1$, $c_{2pz} = 1$.

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

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

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

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

sp² hybrid orbitals   120º
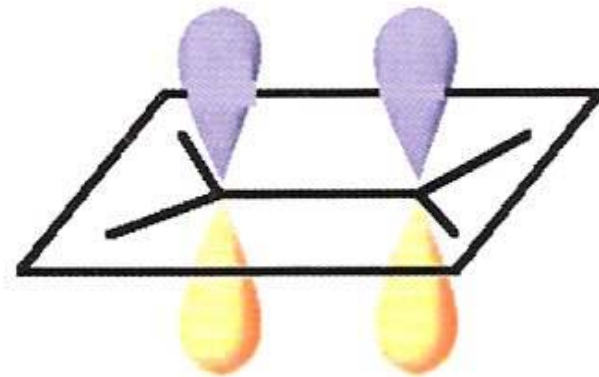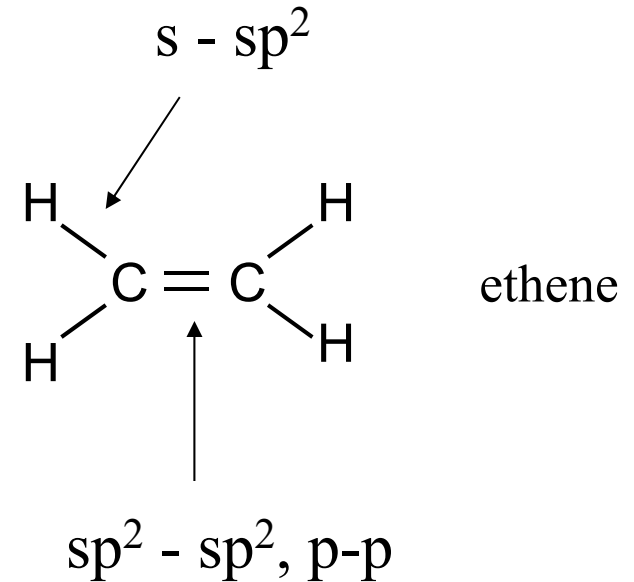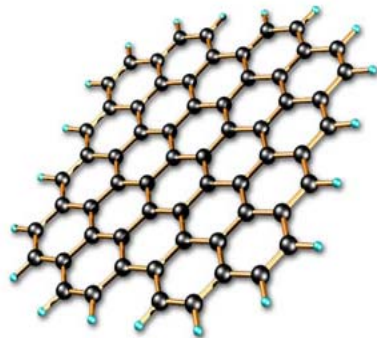
The four orbitals are sp²,sp², sp², p

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

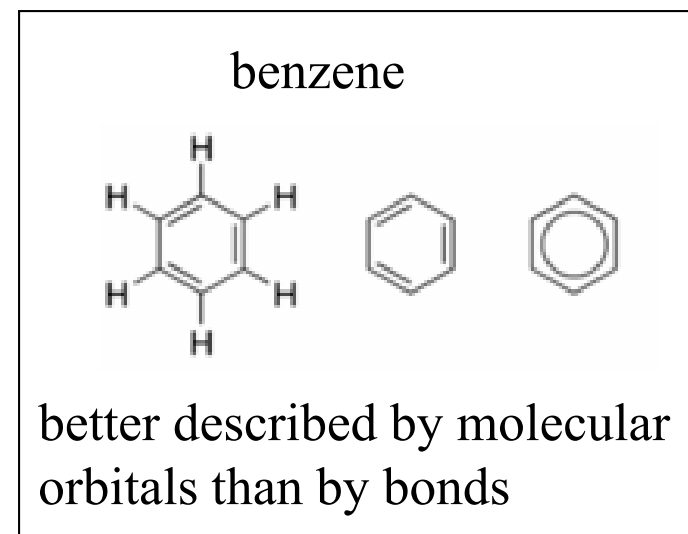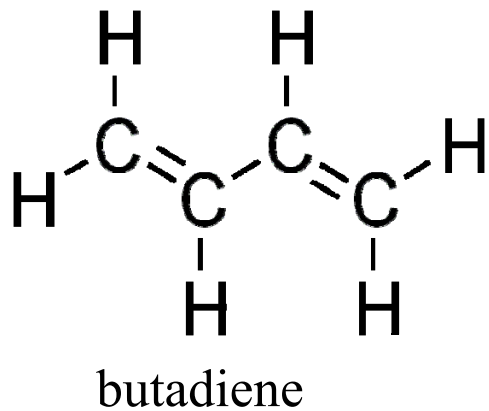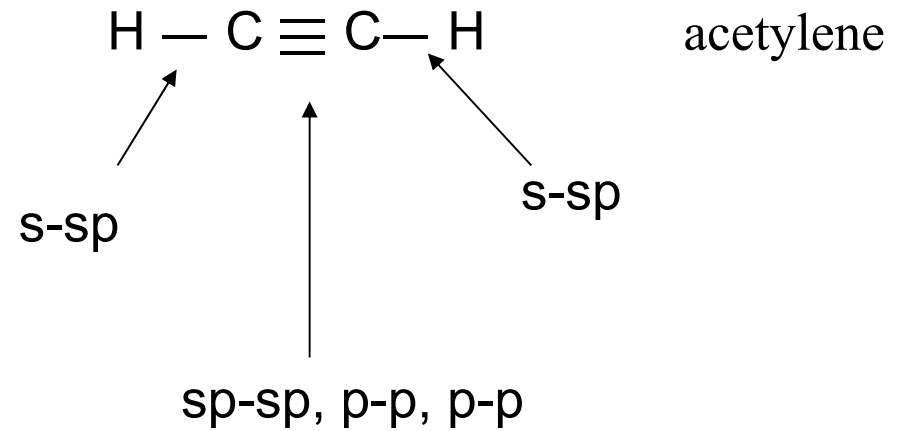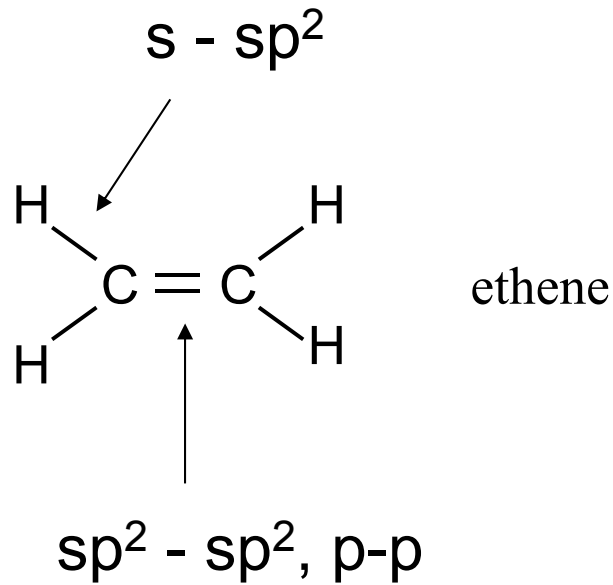$$\psi_2 = \frac{1}{\sqrt{3}}\phi_{2s} - \frac{1}{\sqrt{6}}\phi_{2p_x} + \frac{1}{\sqrt{2}}\phi_{2p_y}$$

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

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

s - sp²

ethene

sp² - sp², p-p

Graphene

sp hybrid orbitals

The four orbitals are sp, sp, p, p

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

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

H — C ≡ C—H   acetylene

s-sp

s-sp

sp-sp, p-p, p-p

Examples of bonds

s - sp^2

H, H
    C = C
H   H
ethene

sp^2 - sp^2, p-p

H — C ≡ C — H   acetylene

s-sp

s-sp

sp-sp, p-p, p-p

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 $A, B \in G, AB \in G$
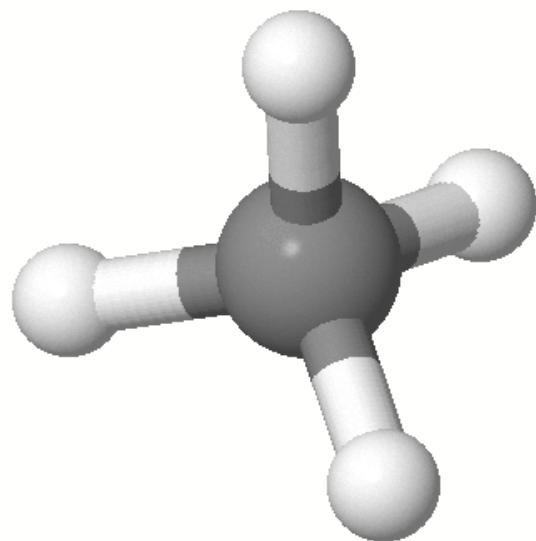
Point symmetries

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:

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

http://symmetry.otterbein.edu/gallery/index.html
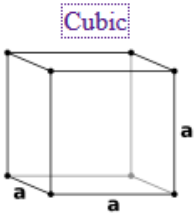
The 32 Crystal Classes

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	$\overline{4}3m$	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