

Review: Molecules I

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

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

Make some approximations.

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

$$H_{\text{red}} = H_{\text{mo}} + H_{\text{mo}} + H_{\text{mo}} + H_{\text{mo}} + \dots$$

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

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

Review: Molecules II

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

The molecular orbitals are constructed using LCAO.

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

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

The many electron wavefunction is constructed as a Slater determinant.

$$\Psi(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \approx |\psi_{\text{mo}1} \uparrow(\vec{r}_1), \psi_{\text{mo}2} \uparrow(\vec{r}_2), \dots, \psi_{\text{mo}N} \uparrow(\vec{r}_N)\rangle.$$

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

The energy is calculated including the electron-electron interactions.

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

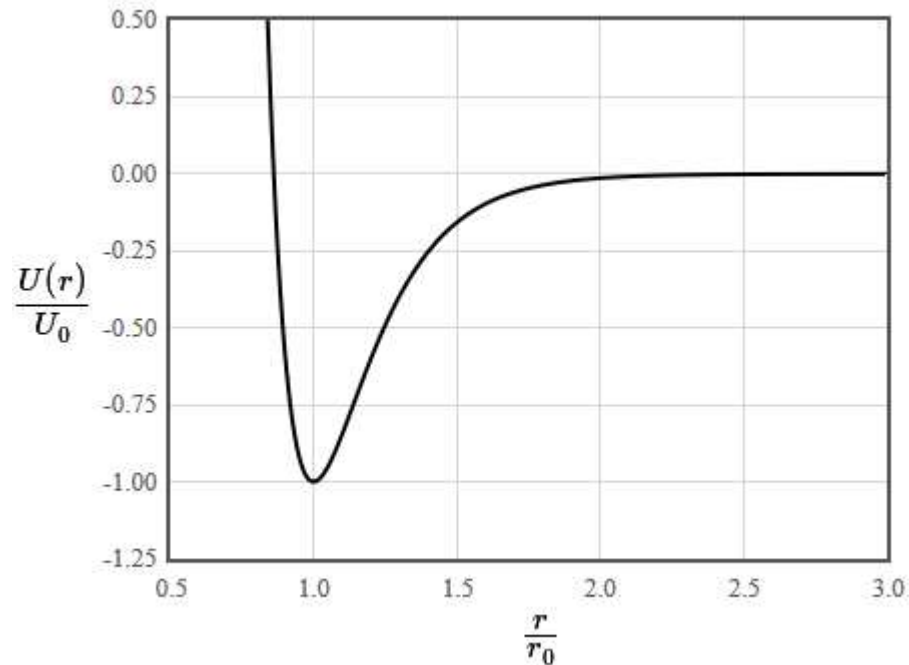
Bond potentials

Morse (covalent)

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

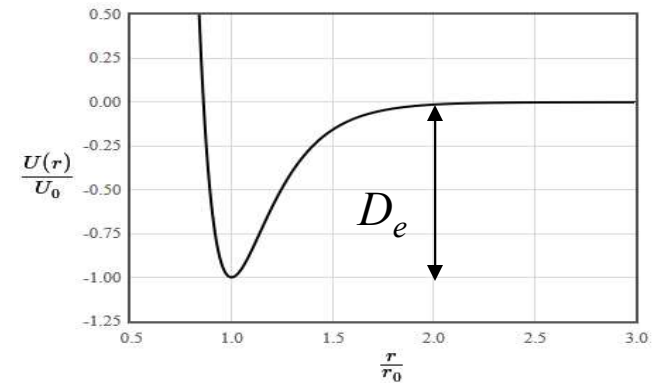
Lennard - Jones (van der Waals)

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



Born-Oppenheimer Approximation (part 2)

Use the electronic energy as the potential for the nuclei



For H_2 , the Hamiltonian for the protons is

$$H\Psi(\vec{r}_A, \vec{r}_B) = \frac{-\hbar^2}{2m_p} (\nabla_A^2 + \nabla_B^2) \Psi(\vec{r}_A, \vec{r}_B) + E_{elec}(r_{AB}) \Psi(\vec{r}_A, \vec{r}_B)$$

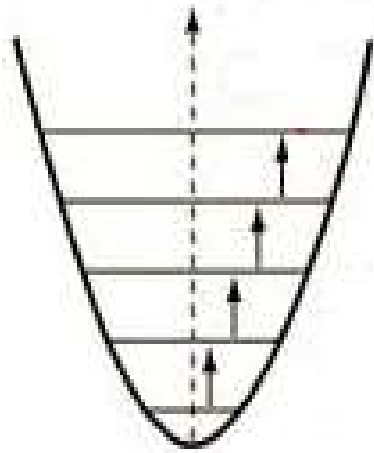
go to center of mass and relative coordinates $\vec{R} = \frac{\vec{R}_A + \vec{R}_B}{2}$ $\vec{r} = \frac{\vec{R}_A - \vec{R}_B}{2}$

$$H = H_R + H_r = -\frac{\hbar^2}{4m_p} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 + E_{elec}(r) \quad \mu = \frac{m_p}{2}$$

Vibrational energy levels

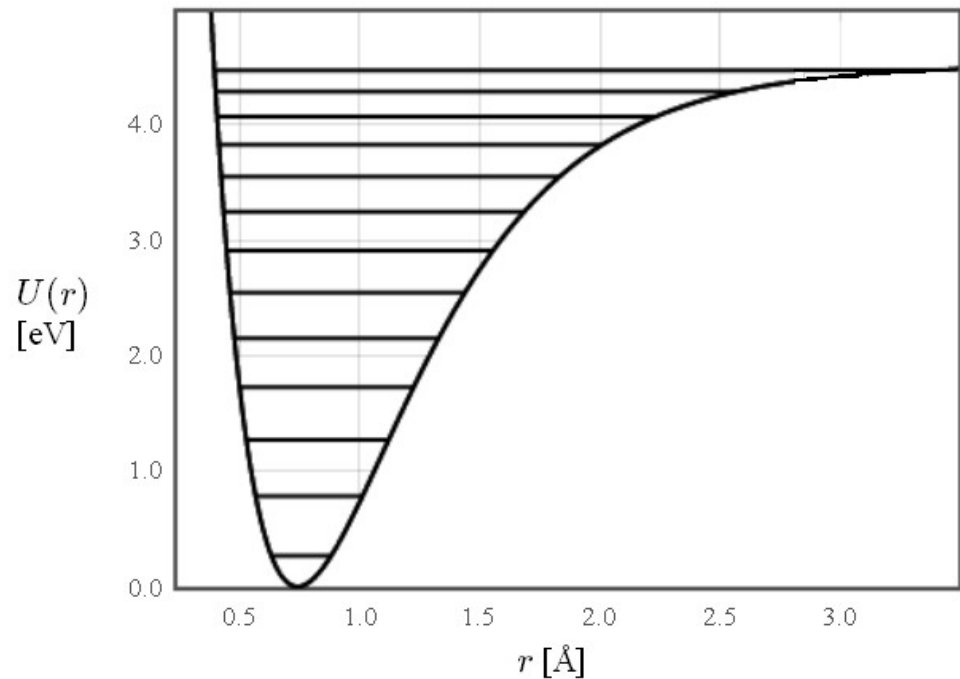
harmonic oscillator

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



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

Morse



$$U(r) \approx U_0 a^2 (r - r_0)^2 + \dots$$

Energy levels of the Morse potential

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

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

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

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

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

Harmonic oscillator
eigen functions

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

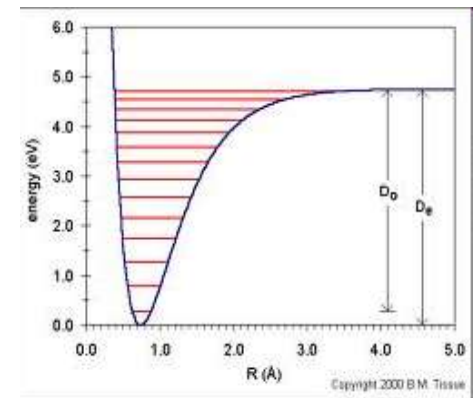
$$c_0 \langle \phi_0 | H_{Morse} | \phi_0 \rangle + c_1 \langle \phi_0 | H_{Morse} | \phi_1 \rangle + \dots = E c_0 \langle \phi_0 | \phi_0 \rangle + E c_1 \langle \phi_0 | \phi_1 \rangle + \dots$$

$$c_0 \langle \phi_j | H_{Morse} | \phi_0 \rangle + c_1 \langle \phi_j | H_{Morse} | \phi_1 \rangle + \dots = E c_j$$

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 $3n$ degrees of freedom

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

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

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

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

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

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

⋮

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

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

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

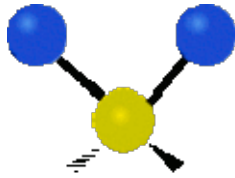
Vibrations, translation, and rotation

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 $p=1,2,\dots,3n$.

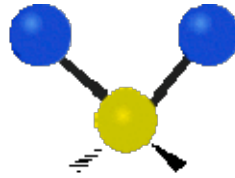
$$\begin{bmatrix}
 \sum_{p \neq 1} \frac{k_{1p}}{m_1} & -\frac{k_{12}}{m_1} & -\frac{k_{13}}{m_1} & \dots & -\frac{k_{1,3n}}{m_1} \\
 -\frac{k_{21}}{m_1} & \sum_{p \neq 2} \frac{k_{2p}}{m_1} & -\frac{k_{23}}{m_1} & \dots & -\frac{k_{2,3n}}{m_1} \\
 -\frac{k_{31}}{m_1} & -\frac{k_{32}}{m_1} & \sum_{p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

$3n$ elements
 \downarrow

The three fundamental vibrations of the water molecule



ν_1 , O-H symmetric stretching
 3657 cm^{-1} ($2.734 \text{ }\mu\text{m}$)



ν_2 , H-O-H bending
 1595 cm^{-1} ($6.269 \text{ }\mu\text{m}$)



ν_3 , O-H asymmetric stretching
 3756 cm^{-1} ($2.662 \text{ }\mu\text{m}$)

$3n - 3$ 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

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

Moment of inertia (Trägheitsmoment)

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

Rotational and vibrational energy levels of diatomic molecules

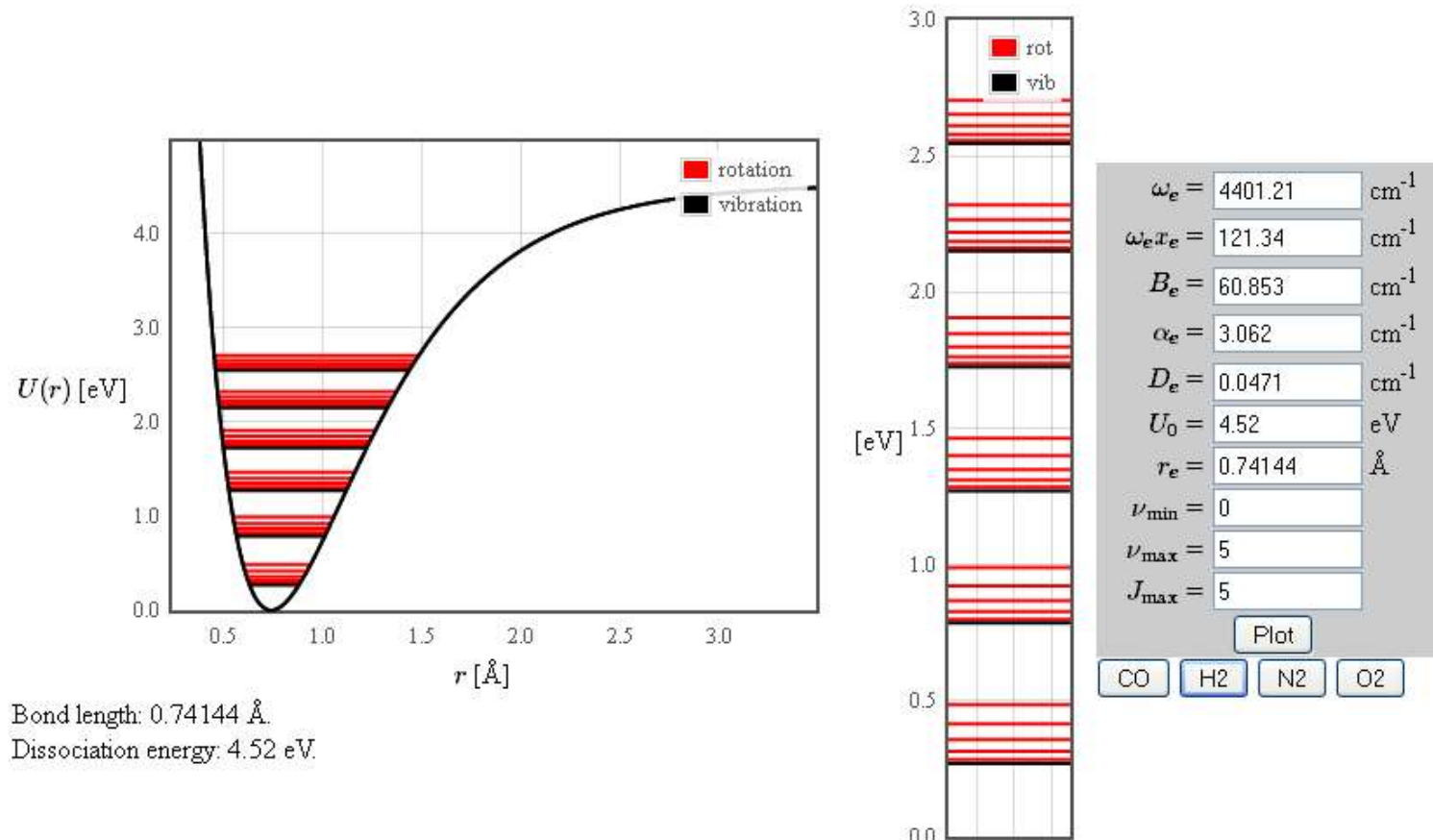
The rotational and vibrational energy levels of diatomic molecules can be approximated as,

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

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

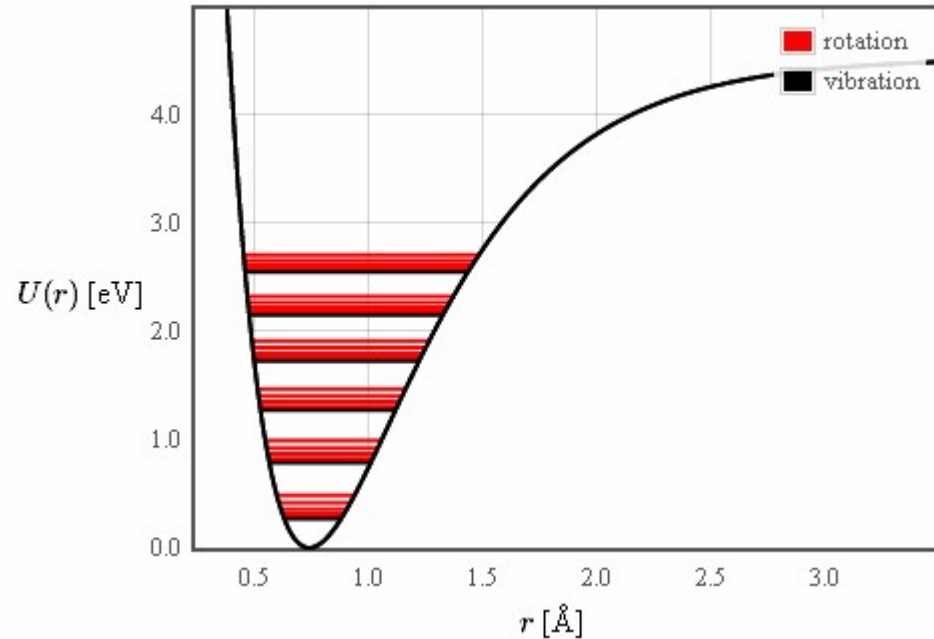
where ω_e , x_e , B_e , α_e , and D_e are spectroscopic constants. The quantum numbers ν and J can take on integer values, $\nu, J = 0, 1, 2, \dots$. Here h is Planck's constant and c is the speed of light in vacuum. The units of all of the spectroscopic constants are cm^{-1} except for x_e which is 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 H₂



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
Jet Propulsion Laboratory
California Institute of Technology

"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/>



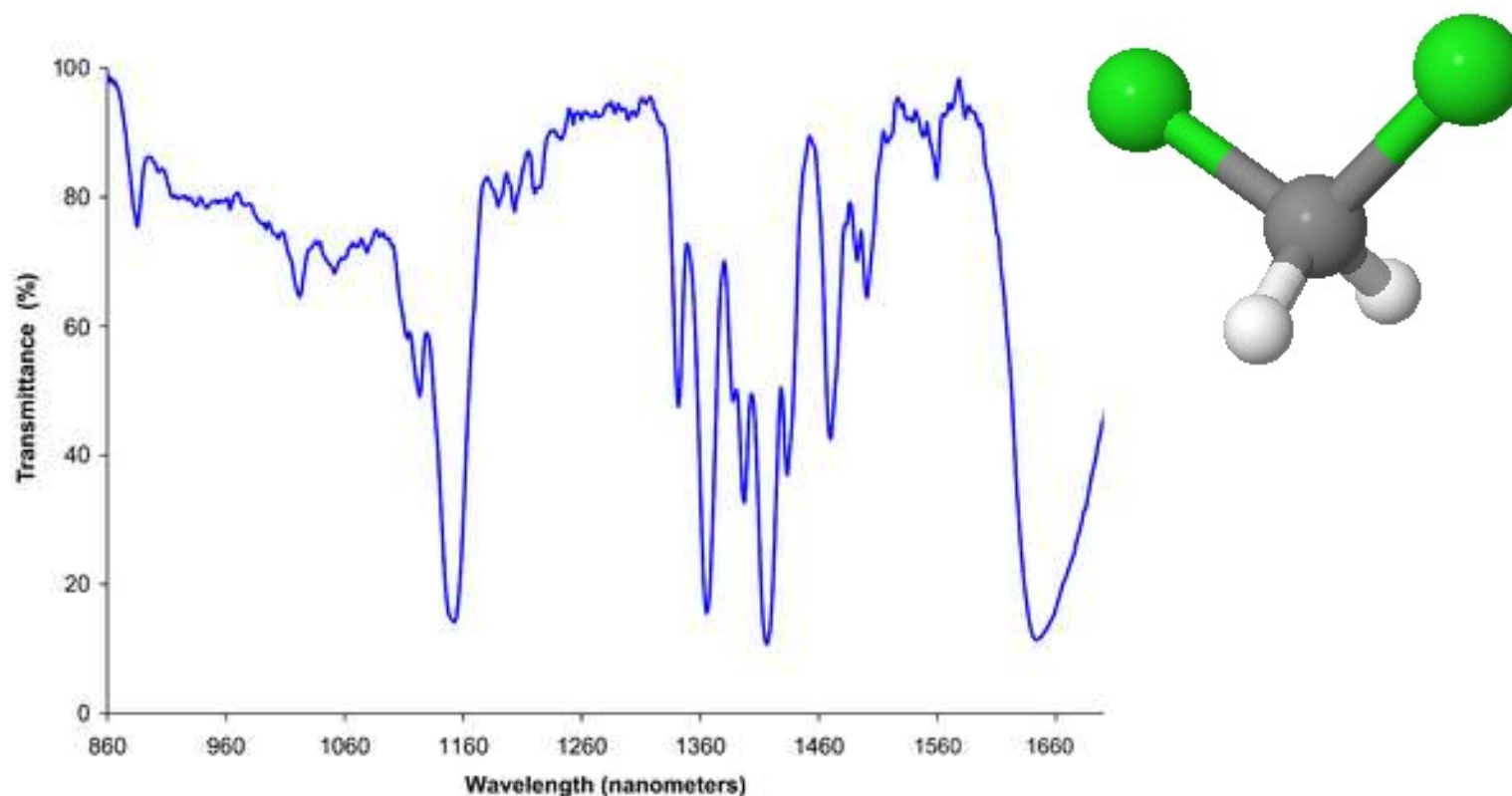


Molecular Spectroscopy
Jet Propulsion Laboratory
California Institute of Technology

Catalog Directory

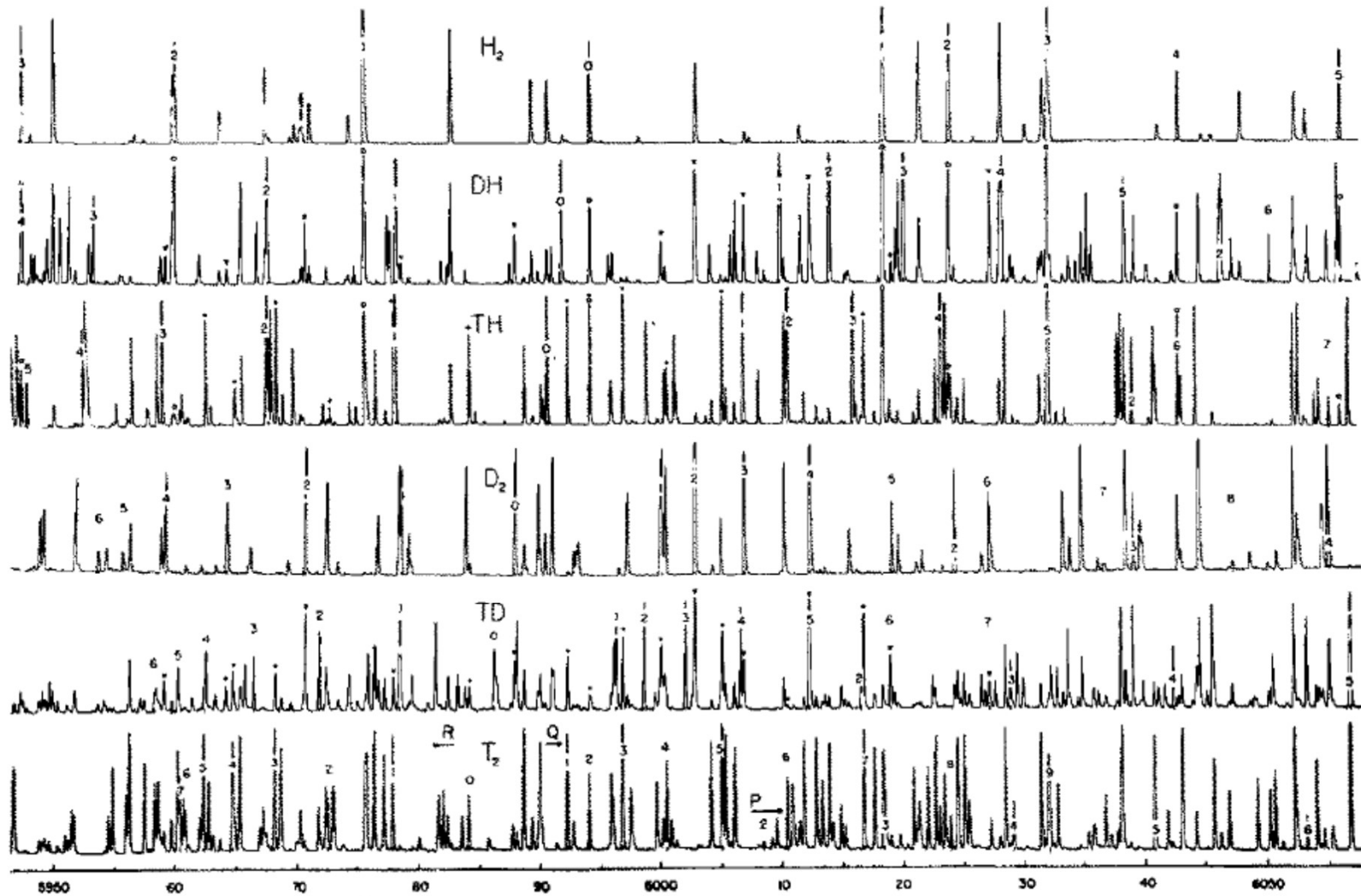
ID	Name	# lines	Ver.	Catalog	Documentation
1001	H-atom	1	1	c001001.cat	pdf or Tex format
2001	D-atom	1	1	c002001.cat	pdf or Tex format
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4001	H2D+	32	2*	c004001.cat	pdf or Tex format
7001	Li-6-H	51	2*	c007001.cat	pdf or Tex format
8001	LiH	53	2*	c008001.cat	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
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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
17002	NH3	1716	5*	c017002.cat	pdf or Tex format
17003	CH3D	143	3*	c017003.cat	pdf or Tex format
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
18005	H2O v2,2v2,v	8608	4*	c018005.cat	pdf or Tex format
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	HD0	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	HD0-18	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

IR absorption spectrum



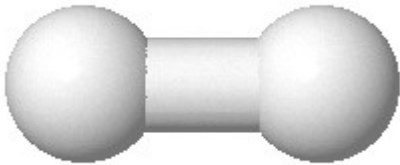
Near IR absorption spectrum of dichloromethane .

Emission spectra



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

Student project: Explain how to calculate the Hamiltonian matrix elements or overlap matrix elements



Molecular orbitals of H₂

The simplest molecule is molecular hydrogen, H₂. The molecular orbital Hamiltonian in this case is,

$$H_{\text{mo}}^{H_2} = -\frac{\hbar^2}{2m_e} \nabla^2 - \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_A|} - \frac{e^2}{4\pi\epsilon_0|\vec{r} - \vec{r}_B|},$$

where \vec{r}_A and \vec{r}_B are the positions of the two protons. If only the two 1s orbitals are used in the linear combination of atomic orbitals, $\psi_{\text{mo}} = c_1\phi_{1s}(\vec{r} - \vec{r}_A) + c_2\phi_{1s}(\vec{r} - \vec{r}_B)$, the associated Roothaan equations are,

$$\begin{bmatrix} H_{11} & H_{12} \\ H_{12} & H_{11} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix} = E \begin{bmatrix} S_{11} & S_{12} \\ S_{12} & S_{11} \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \end{bmatrix},$$

where

$$\begin{aligned} H_{11} &= \langle \phi_{1s}(\vec{r} - \vec{r}_A) | H_{\text{mo}}^{H_2} | \phi_{1s}(\vec{r} - \vec{r}_A) \rangle, \\ H_{12} &= \langle \phi_{1s}(\vec{r} - \vec{r}_A) | H_{\text{mo}}^{H_2} | \phi_{1s}(\vec{r} - \vec{r}_B) \rangle, \\ S_{11} &= \langle \phi_{1s}(\vec{r} - \vec{r}_A) | \phi_{1s}(\vec{r} - \vec{r}_A) \rangle = 1, \\ S_{12} &= \langle \phi_{1s}(\vec{r} - \vec{r}_A) | \phi_{1s}(\vec{r} - \vec{r}_B) \rangle. \end{aligned}$$

Chemical bonds

Ionic bonds

Covalent bonds

Metallic bonds

Bond potentials

Polar bonds

σ - bonds

π - bonds

double bonds

triple bonds

Ionic bond

Coulomb force:

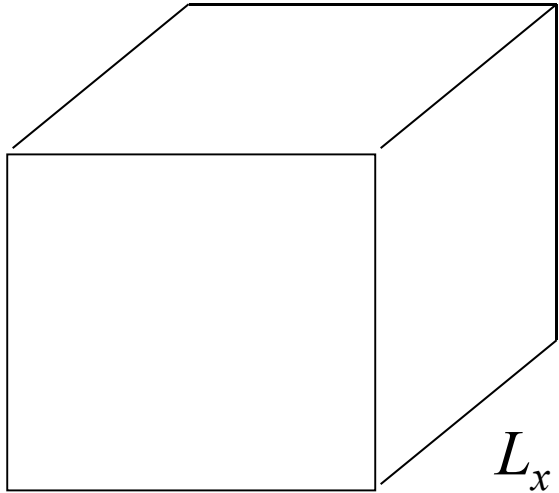
$$F = \frac{e^2}{4\pi\epsilon_0 r^2}$$

Energy needed to separate charges e and $-e$

$$E = \int \vec{F} \cdot d\vec{r} = \int_{0.2 \text{ nm}}^{\infty} \frac{-e^2}{4\pi\epsilon_0 r^2} dr = 7 \text{ eV}$$

Ionic bonds are a few eV

Covalent bond: Square well potential



L_y

L_z

L_x

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

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

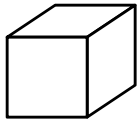
$$\Psi = \frac{2\sqrt{2}}{\sqrt{L_x L_y L_z}} \sin \frac{n_x \pi x}{L_x} \sin \frac{n_y \pi y}{L_y} \sin \frac{n_z \pi z}{L_z}$$

$$n_x, n_y, n_z = 1, 2, 3 \dots$$

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

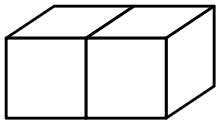
Covalent bond

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



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 $L = 0.2 \text{ nm}$ $\Delta E = 14 \text{ eV}$

Polar bonds

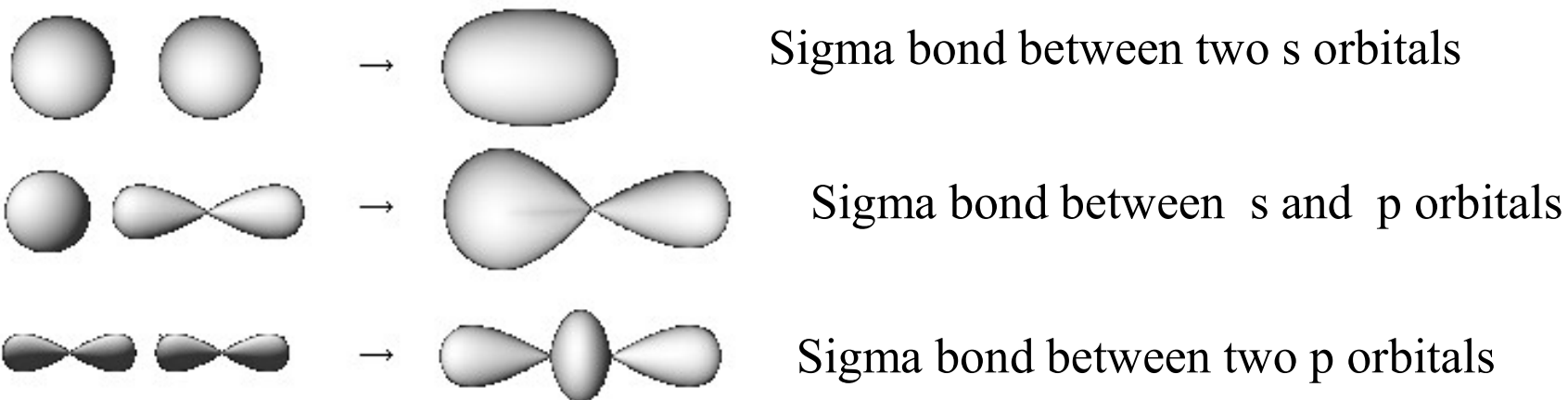
Partly covalent and partly ionic. The more electronegative element will have more negative charge.

0 ————— ————— 4
electronegativity (Pauling's)

Electronegativity

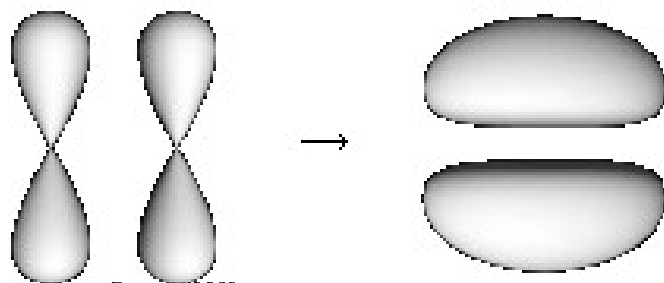
1 H 2.1																	2 He				
3 Li 1	4 Be 1.5															5 B 2	6 C 2.5	7 N 3	8 O 3.5	9 F 4	10 Ne
11 Na 0.9	12 Mg 1.2															13 Al 1.5	14 Si 1.8	15 P 2.1	16 S 2.5	17 Cl 3	18 Ar
19 K 0.8	20 Ca 1	21 Sc 1.3	22 Ti 1.5	23 V 1.6	24 Cr 1.6	25 Mn 1.5	26 Fe 1.8	27 Co 1.8	28 Ni 1.8	29 Cu 1.9	30 Zn 1.6	31 Ga 1.6	32 Ge 1.8	33 As 2	34 Se 2.4	35 Br 2.8	36 Kr 3				
37 Rb 0.8	38 Sr 1	39 Y 1.2	40 Zr 1.4	41 Nb 1.6	42 Mo 1.8	43 Tc 1.9	44 Ru 2.2	45 Rh 2.2	46 Pd 2.2	47 Ag 1.9	48 Cd 1.7	49 In 1.7	50 Sn 1.8	51 Sb 1.9	52 Te 2.1	53 I 2.5	54 Xe 2.6				
55 Cs 0.7	56 Ba 0.9	57 La 1.1	72 Hf 1.3	73 Ta 1.5	74 W 1.7	75 Re 1.9	76 Os 2.2	77 Ir 2.2	78 Pt 2.2	79 Au 2.4	80 Hg 1.9	81 Tl 1.8	82 Pb 1.8	83 Bi 1.9	84 Po 2	85 At 2.2	86 Rn				
87 Fr 0.7	88 Ra 0.9	89 Ac 1.1	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt													
58 Ce 1.1	59 Pr 1.1	60 Nd 1.1	61 Pm 1.1	62 Sm 1.1	63 Eu 1.1	64 Gd 1.1	65 Tb 1.1	66 Dy 1.1	67 Ho 1.1	68 Er 1.1	69 Tm 1.1	70 Yb 1.1	71 Lu 1.2								
90 Th 1.2	91 Pa 1.4	92 U 1.5	93 Np 1.3	94 Pu 1.3	95 Am 1.3	96 Cm 1.3	97 Bk 1.3	98 Cf 1.3	99 Es 1.3	100 Fm 1.3	101 Md 1.3	102 No 1.3	103 Lr								

Sigma bonds



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

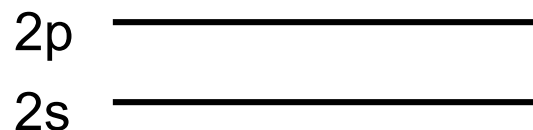
Single bond : Two electrons are shared, sigma bond

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

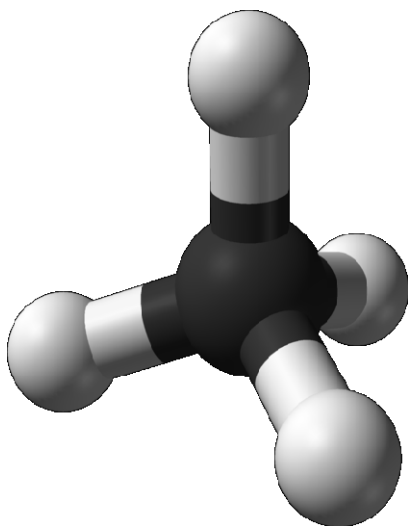
Triple bond : Six electrons are shared, sigma bond + 2 pi bonds

Hybrid orbitals

isolated carbon atom



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



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

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

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

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

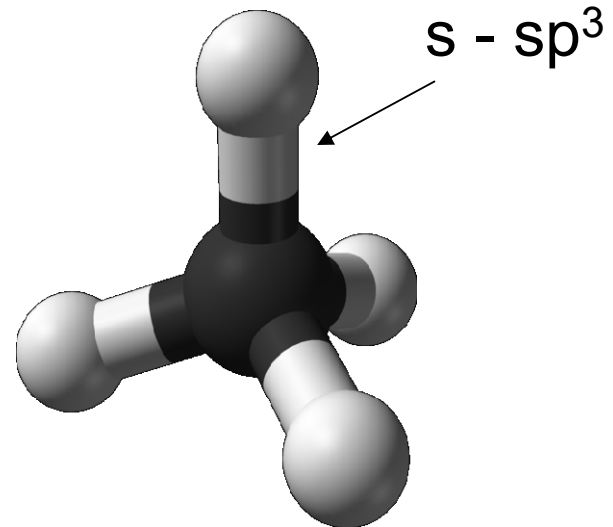
sp^3 hybrid orbitals 109°

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

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

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

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



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

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



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



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



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



sp^2 hybrid orbitals 120°

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

$$\psi_1 = \frac{1}{\sqrt{3}}(\psi_s + \sqrt{2}\psi_{p_x})$$

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

$$\psi_3 = \frac{1}{\sqrt{3}}\psi_s - \frac{1}{\sqrt{6}}\psi_{p_x} - \frac{1}{\sqrt{2}}\psi_{p_y}$$

$$\psi_4 = \psi_{p_z}$$

Graphene

