

Technische Universität Graz

Institute of Solid State Physics

Bonds, Vibrations, Rotation, spectroscopy

Hybrid orbitals

isolated carbon atom



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

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









sp³ hybrid orbitals 109°

$$\psi_{1} = \frac{1}{2} \left(\phi_{2s} + \phi_{2p_{x}} + \phi_{2p_{y}} + \phi_{2p_{z}} \right)$$

$$\psi_{2} = \frac{1}{2} \left(\phi_{2s} + \phi_{2p_{x}} - \phi_{2p_{y}} - \phi_{2p_{z}} \right)$$

$$\psi_{3} = \frac{1}{2} \left(\phi_{2s} - \phi_{2p_{x}} + \phi_{2p_{y}} - \phi_{2p_{z}} \right)$$

$$\psi_{4} = \frac{1}{2} \left(\phi_{2s} - \phi_{2p_{x}} - \phi_{2p_{y}} + \phi_{2p_{z}} \right)$$

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

sp³ hybrid orbitals



sp² hybrid orbitals 120°

The four orbitals are sp², sp², sp², p



sp hybrid orbitals

The four orbitals are sp, sp, p, p

$$\psi_{1} = \frac{1}{\sqrt{2}} \left(\phi_{2s} + \phi_{2p_{z}} \right) \qquad \psi_{2} = \frac{1}{\sqrt{2}} \left(\phi_{2s} - \phi_{2p_{z}} \right)$$
$$\psi_{3} = \phi_{2p_{y}} \qquad \qquad \psi_{4} = \phi_{2p_{z}}$$



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

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

Examples of bonds



Born-Oppenheimer Approximation (part 2)

Use the electronic energy as the potential for the nuclei



For H_2 , the Hamiltonian for the protons is

$$H\Psi(\vec{r}_{A},\vec{r}_{B}) = \frac{-\hbar^{2}}{2m_{p}} (\nabla_{A}^{2} + \nabla_{B}^{2})\Psi(\vec{r}_{A},\vec{r}_{B}) + (E_{elec}(r_{AB}) + \frac{Z_{A}Z_{B}e^{2}}{4\pi\varepsilon r_{AB}})\Psi(\vec{r}_{A},\vec{r}_{B})$$

go to center of mass and relative coordinates

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

1

$$H = H_R + H_r = -\frac{\hbar^2}{4m_p} \nabla_R^2 - \frac{\hbar^2}{2\mu} \nabla_r^2 + E_{elec}(r) + \frac{Z_A Z_B e^2}{4\pi\epsilon |r|} \qquad \mu = \left[\frac{1}{m_A} + \frac{1}{m_B}\right]^{-1}$$

Potential energy surface



$$U=U_0+rac{dU}{dx}x+rac{1}{2}rac{d^2U}{dx^2}x^2+\cdots \qquad \qquad U_{
m spring}=rac{1}{2}kx^2$$

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, 3*n*-6 vibrational degrees of freedom

Vibrations, translation, and rotation

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

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

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

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

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

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

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

$$egin{aligned} &m_nrac{d^2u_{3n-2}}{dt^2} = k_{1,3n-2}(u_1-u_{3n-2})+k_{2,3n-2}(u_2-u_{3n-2})+\dots+k_{3n-2,3n}(u_{3n}-u_{3n-2})\ &m_nrac{d^2u_{3n-1}}{dt^2} = k_{1,3n-1}(u_1-u_{3n-1})+k_{2,3n-1}(u_2-u_{3n-1})+\dots+k_{3n-1,3n}(u_{3n}-u_{3n-1})\ &m_nrac{d^2u_{3n}}{dt^2} = k_{1,3n}(u_1-u_{3n})+k_{2,3n}(u_2-u_{3n})+\dots+k_{3n-1,3n}(u_{3n-1}-u_{3n}) \end{aligned}$$

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Linear differential equations

$$rac{d^2x}{dt^2}+rac{dx}{dt}+x=0.$$

solutions have the form $e^{\lambda t}$

 $\lambda^2 + \lambda + 1 = 0.$

- $\lambda_1 = -0.5 + i0.86603$
- $\lambda_2 = -0.5 i0.86603$

Normal modes

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



Vibrations, translation, and rotation for a diatomic molecule

| | (1 | | $v_1 = \left(-\frac{4}{3}, 1, 0, 0, 0, 0\right)$ | $\lambda_1 = \frac{7}{24}$ |
|--------------|------------|-----------|--|----------------------------|
| eigenvectors | | | $\nu_2 = (0,0,0,0,0,1)$ | $\lambda_2 = 0$ |
| | 8 8 0 0 | | $\nu_3=(0,0,0,0,1,0)$ | $\lambda_3 = 0$ |
| | | 0 0 0 0 0 | $v_4=(0,0,0,1,0,0)$ | $\lambda_4=0$ |
| | | | $\nu_5=(0,0,1,0,0,0)$ | $\lambda_5 = 0$ |
| | | / | $v_6 = (1, 1, 0, 0, 0, 0)$ | $\lambda_6 = 0$ |

Eigen modes for CO

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

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

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,

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

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, $\nu, J = 0, 1, 2, \cdots$. 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 $E_{\nu J} = E_{\nu i b} + E_{rot}$ 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^{*t*} have to be recalculated.



IR absorption spectrum



Near IR absorption spectrum of dichloromethane.

Emission spectra



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

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/



Catalog Directory

| ID | Name ; | ‡ lines | Ver. | . Catalog | Docum | entat | ion |
|-------|--------------|---------|------|-------------|--------|-------|--------|
| 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 | 0-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 | H20 | 1376 | 6* | c018003.cat | pdf or | Tex | format |
| 18004 | NH2D | 5036 | 1 | c018004.cat | pdf or | Tex | format |
| 18005 | H20 v2,2v2,v | 8608 | 4* | c018005.cat | pdf or | Tex | format |
| 18006 | 13CH3D | 143 | 1* | c018006.cat | pdf or | Tex | format |
| 18007 | 170H | 46769 | 1* | c018007.cat | pdf or | Tex | format |
| 19001 | H0-18 | 3159 | з | c019001.cat | pdf or | Tex | format |
| 19002 | HDO | 1401 | з | c019002.cat | pdf or | Tex | format |
| 19003 | H20-17 | 404 | 1 | c019003.cat | pdf or | Tex | format |
| 19004 | H30+ | 304 | 3* | c019004.cat | pdf or | Tex | format |
| 19005 | H30+ v1,v3,v | 1973 | 2* | c019005.cat | pdf or | Tex | format |
| 19006 | 170D | 113226 | 1* | c019006.cat | pdf or | Tex | format |
| 20001 | D20 | 1137 | 2 | c020001.cat | pdf or | Tex | format |
| 20002 | HF | 8 | 1 | c020002.cat | pdf or | Tex | format |
| 20003 | H20-18 | 726 | 1 | c020003.cat | pdf or | Tex | format |
| 20004 | 180D | 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 |

Transition rates

$$H = H_0 + H_1$$

We know the eigenstates of H_0 = molecule + EM waves $|i\rangle$ is the initial state, $|f\rangle$ 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 \implies Forbidden transition

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 :

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



https://symotter.org/tutorial/intro

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 a a | tetrahedral | 23 | Т | 195-199 | 3 | 4 | 12 | 7 | i. | n | | 12 | |
| | diploidal | <i>m</i> 3 | T _h | 200-206 | 3 | 4 | - | 70 | 3 | у | | 24 | |
| | gyroidal | 432 | 0 | 207-214 | 6 | 4 | 3 | 7. | a | n | | 24 | |
| | hextetrahedral | 4 3 <i>m</i> | T _d | 215-220 | 3 | 4 | - | 70 | 6 | n | 216: Zincblende, ZnS, GaAs, GaP, InAs, SiC | 24 | |
| | hexoctahedral | m3m | 0 _h | 221-230 | 6 | 4 | 3 | - | 9 | у | 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