Modelling of Molecular Systems Part II: Nuclear Motion

(VO PHT.105UF)

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The electronic structure part of this lecture (Part I) is mostly based on the book "*Modern Quantum Chemistry*" by A. Szabo and N. Ostlund, Dover 1996.

In Part II of this lecture, dedicated to nuclear motion, several extensions towards molecular spectroscopy will be based on the book "*Symmetry and Spectroscopy*" by D.C. Harris and M.D. Bertolucci, Dover 1989.

Additionally, the book "*Atoms, Molecules and Optical Physics 2*" by I.V. Hertel and C.-P. Schulz, Springer 2015, will be used for the discussion of molecular vibration and symmetry.

The introductive chapter on group theory in the context of molecular physics follows the book "*Molecular Physics and Quantum Chemistry*" by H. Haken and H. C. Wolf, Springer 2006.

The planned introductions to solvent models and QM/MM approaches as well as the chapter on optimization techniques are taken from the book "*Introduction to Computational Chemistry*" by F. Jensen, Wiley 2007.

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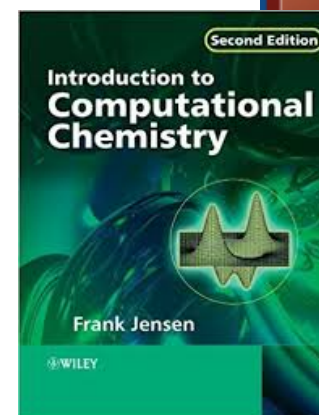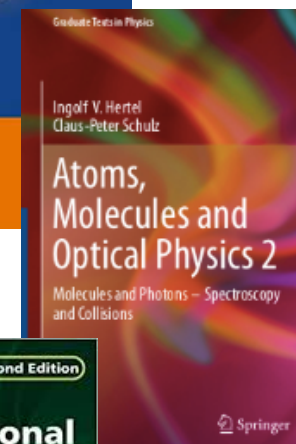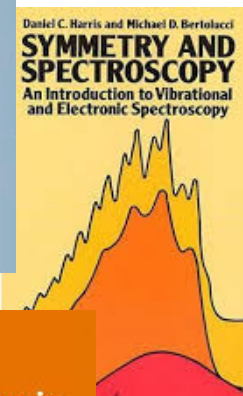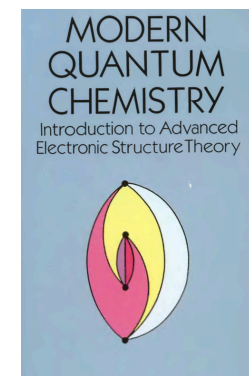
A) **Molecular Rotation and Vibration**
- The Potential Energy Surface
- Optimization techniques (Jensen, chapter 12)
- Molecular Rotation (Hertel/Schulz II, chapter 4.1)
- Vibrational modes of Polyatomic Molecules (Hertel/Schulz II, chapter 4.2)
- Thermochemistry (Jensen, chapter 13.5)

B) **Group Theory in Molecular Physics**
- Introduction to Group Theory (Haken/Wolf II, chapter 6)
- Molecular symmetries (Hertel/Schulz II, chapter 4.3)

C) **Embedding techniques**
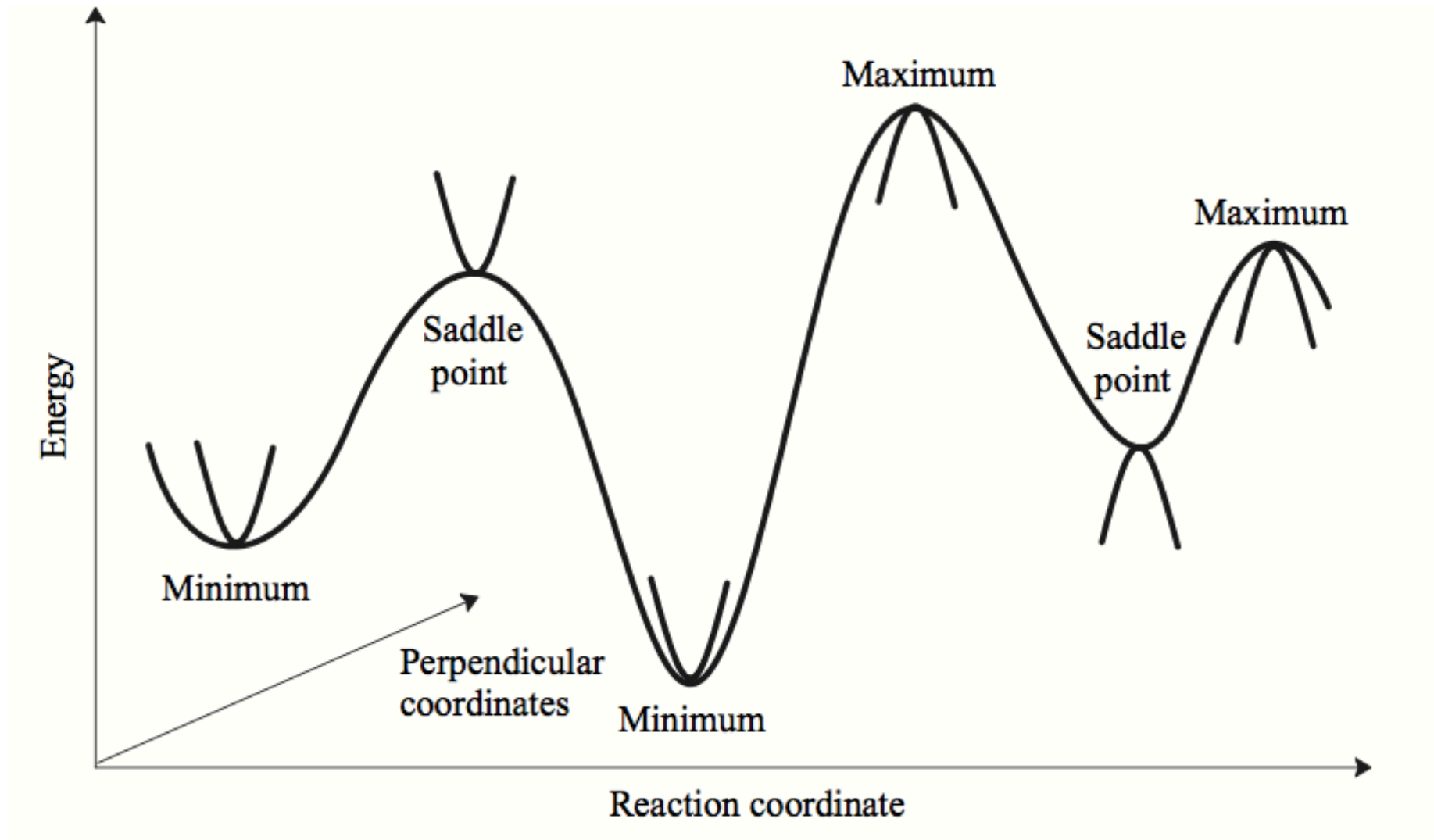- Solvation models (Jensen, chapter 14.6)
- QM/MM techniques

D) **Reaction Dynamics**
- Finding Saddle Points (Jensen, chapter 12.4)
- Intrinsic Reaction Coordinate Methods (Jensen, chapters 12.8 and 14.2.7)
- Transition State Theory (Jensen, chapter 13)
- Bell-Evans-Polanyi Principle (Jensen, chapter 15.5)
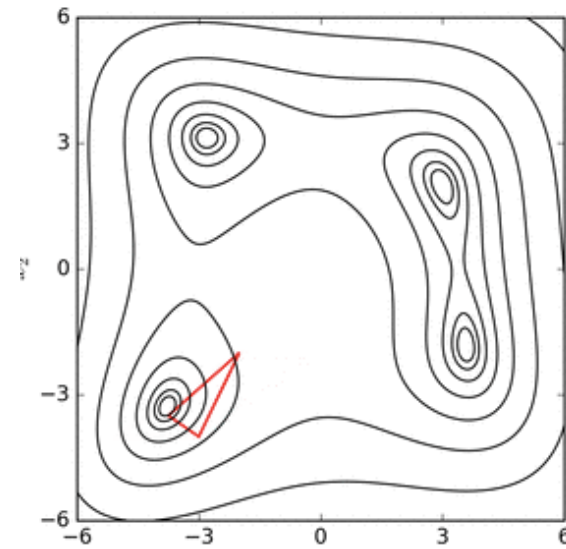
A) Molecular Rotation and Vibration
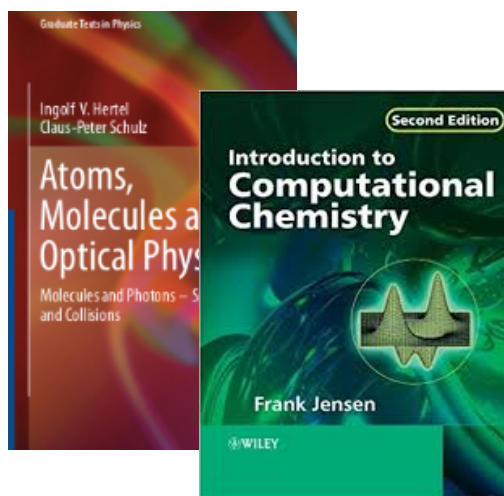
The Potential Energy Surface (PES)

Molecular Rotation and Vibration

General Optimization techniques for <u>Minima</u>

https://en.wikipedia.org/wiki/Nelder–Mead_method

- Independent minimization,
  circulation through variables

- Nelder-Mead or Simplex Method: polytope with N+1 vertices,
  one point changed per step.

- Steepest decent: search direction is
  negative gradient, **d = -g**

- Conjugate gradient method: use information of previous steps:

$$\mathbf{d}_i = -\mathbf{g}_i + \beta_i \mathbf{d}_{i-1} \quad \beta_i^{\mathrm{PR}} = \frac{\mathbf{g}_i^t(\mathbf{g}_i - \mathbf{g}_{i-1})}{\mathbf{g}_{i-1}^t \mathbf{g}_{i-1}} \quad \text{(Polak-Ribiere)}$$
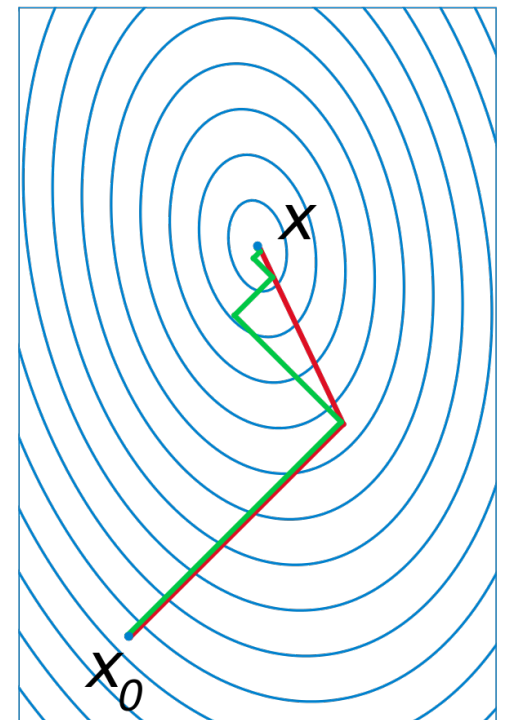
https://en.wikipedia.org/wiki/Conjugate_gradient_method

Molecular Rotation and Vibration

General Optimization techniques for <u>Minima</u>

- Newton-Raphson method applied to find the roots of f: in one dimension we find

$$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)} \qquad \text{from} \qquad 0 \stackrel{!}{=} f'(x_n)\,(x_{n+1} - x_n) + f(x_n)$$
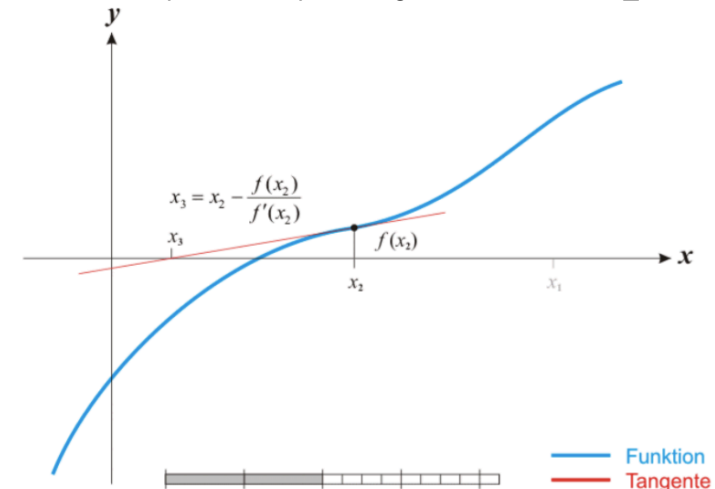
For optimization, we apply this formalism to the derivative:

$$f_T(x) = f_T(x_n + \Delta x) \approx f(x_n) + f'(x_n)\Delta x + \frac{1}{2}f''(x_n)\Delta x^2$$

$$0 \stackrel{!}{=} \frac{d}{d\Delta \mathbf{x}}\left(f(x_n) + f'(x_n)\Delta x + \frac{1}{2}f''(x_n)\Delta x^2 \right) = f'(x_n) + f''(x_n)\Delta x.$$

$$x_{n+1} = x_n - \frac{f'(x_n)}{f''(x_n)}$$

Generalization to higher dimension: $\mathbf{x}_{n+1} = \mathbf{x}_n - [\mathbf{H}f(\mathbf{x}_n)]^{-1}\nabla f(\mathbf{x}_n),\ n \geq 0$

In coordinates where H is diagonal: $\Delta x_i' = -\dfrac{f_i}{\varepsilon_i}$

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General Optimization techniques for <u>Minima</u>

- Problem with Newton-Raphson minimization: Hessian is costly.

  Alternative: approximation via Broyden-Fletcher-Goldfarb-Shanno (BFGS) updating:

$$\mathbf{H}_n = \mathbf{H}_{n-1} + \Delta\mathbf{H}$$

$$\Delta\mathbf{H}_{BFGS} = \frac{\Delta\mathbf{g}\Delta\mathbf{g}^t}{\Delta\mathbf{g}^t\Delta\mathbf{x}} - \frac{\mathbf{H}\Delta\mathbf{x}\Delta\mathbf{x}^t\mathbf{H}}{\Delta\mathbf{x}^t\mathbf{H}\Delta\mathbf{x}}$$

Makes the method a "Pseudo"-Newton Raphson approach.

Note: NR method will converge to any stationary point: can be used for TS search in principle.

The choice of coordinates is important for convergence. It should make the PES as "harmonic as possible". A reasonable choice are symmetry-adapted, internal coordinates.

General Optimization techniques for <u>Transition states</u>

* Newton-Raphson minimization can be used

* Coordinate driving: Pick a coordinate which is approximate reaction coordinate, minimize energy with respect to remaining coordinates, scan over reaction coordinate.

* Methods based on reaction pathway approximations:
  Single-structure-based: Linear Synchronous Transit, Quadratic Synchronous Transit
  Two-structure-based: Saddle, Line-then-plane ...

<u>Multi-structure-based</u>:

Nudged Elastic Band method (NEB):

spring energies

$$T_{\text{NEB}}(\mathbf{R}, \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_M, \mathbf{P}) = \sum_{i=1}^{M} E(\mathbf{x}_i) + \sum_{i=1}^{M-1} \tfrac{1}{2} k (\mathbf{x}_{i+1} - \mathbf{x}_i)^2$$

PES energies

Climbing image–NEB: One point is allowed to move uphill, becoming the saddle point

String method: Redistribution of points at each optimization cycle (no spring forces involved)

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Molecular Rotation

Moments of inertia are described by 2nd rank tensor $\quad I_{ij} = \displaystyle\sum_{k=1}^{\mathcal{N}_{nu}} m_k \left(\mathbf{R}_k^2 \delta_{ij} - R_{k,i} R_{k,j} \right)$

with $\quad R_{k,1} = X_k, \, R_{k,2} = Y_k$ and $R_{k,3} = Z_k$.

For a rotation with angular velocity $\boldsymbol{\omega}$, the angular momentum becomes $\mathbf{N} = \mathbf{I}\boldsymbol{\omega}$
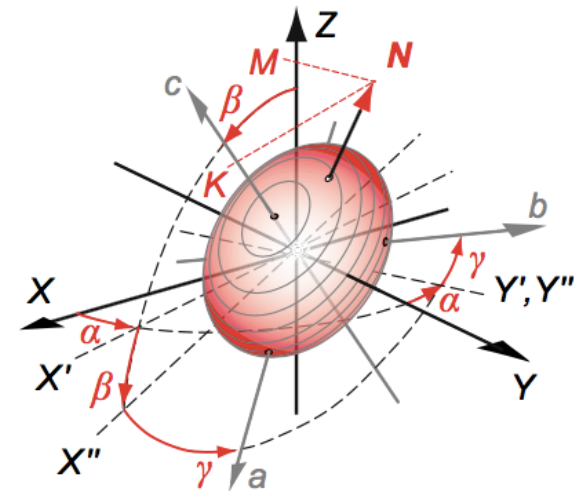
$$I_R = \boldsymbol{e}_R^\top \mathbf{I} \boldsymbol{e}_R = \frac{1}{R^2} \sum_{ij=1}^{3} R_i \, I_{ij} \, R_j$$

unit vector of ω

We define principal axes by diagonalization of **I**: $\quad I_a \leq I_b \leq I_c$

For an arbitrary axis we obtain $\quad I_R = I_a a_1^2 + I_b b_1^2 + I_c c_1^2$

with definitions $\quad a_1/\sqrt{I_R} = a \quad$ we obtain $\quad 1 = I_a a^2 + I_b b^2 + I_c c^2$

Molecular Rotation

The total angular momentum can be expressed as $\widehat{N}^2 = \widehat{N}_X^2 + \widehat{N}_Y^2 + \widehat{N}_Z^2 = \widehat{N}_a^2 + \widehat{N}_b^2 + \widehat{N}_c^2$

space fixed system   body fixed system

$$\widehat{N}^2|NMK\rangle = \hbar^2 N(N+1)|NMK\rangle \quad \text{with } N = 0, 1, 2, \ldots,$$

$$\widehat{N}_Z|NMK\rangle = \hbar M|NMK\rangle, \quad \text{and} \quad \widehat{N}_c|NMK\rangle = \hbar K|NMK\rangle$$

with $M = 0, \pm 1, \pm 2, \ldots, \pm N$ and $K = 0, \pm 1, \pm 2, \ldots, \pm N$.

The total Hamiltonian can be written as $\widehat{H}_{\text{rot}} = \dfrac{1}{2}\left(\dfrac{\widehat{N}_a^2}{I_a} + \dfrac{\widehat{N}_b^2}{I_b} + \dfrac{\widehat{N}_c^2}{I_c} \right)$ with

$$A = \frac{\hbar^2}{2I_a hc}, \qquad B = \frac{\hbar^2}{2I_b hc} \quad \text{and} \quad C = \frac{\hbar^2}{2I_c hc}$$

Molecular Rotation and Vibration

Molecular Rotation

We can distinguish **four** types of molecules:

Linear molecule: $W_N = \dfrac{\hbar^2}{2\bar{M}R^2}N(N+1) = hcBN(N+1)$
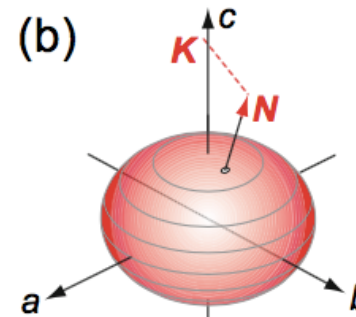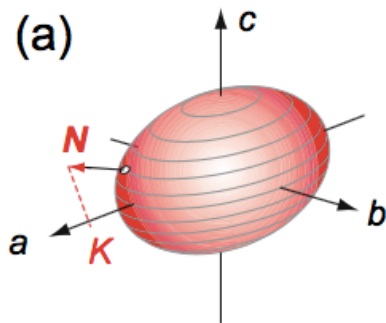
Spherical top: $I_a = I_b = I_c = I$

2N+1 fold degeneracy in K and N gives (2N+1)^2

$$\hat{H}_{\text{rot}}|NMK\rangle = \frac{\hbar^2 N(N+1)}{2I}|NMK\rangle \qquad W_N = \frac{\hbar^2 N(N+1)}{2I} = BhcN(N+1)$$

Symmetric top: Prolate: $I_a < I_b = I_c$ $\qquad$ Oblate: $I_a = I_b < I_c$

(a) $\qquad\qquad\qquad\qquad\qquad$ (b)

introduces extra degeneracy
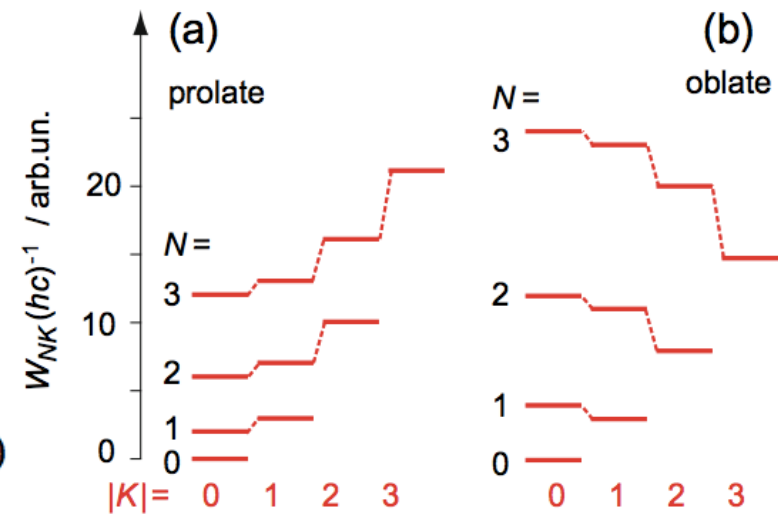for K>0: 2(2N+1)

$$W_{NK} = Bhc\,N(N+1) + (A-B)hc\,K^2 \qquad W_{NK} = Bhc\,N(N+1) + (C-B)hc\,K^2$$

obtained via: $\quad \hat{H}_{\text{rot}} = \dfrac{1}{2I_b}(\hat{N}_b^2 + \hat{N}_c^2) + \dfrac{\hat{N}_a^2}{2I_a} = \dfrac{\hat{N}^2}{2I_b} + \left(\dfrac{1}{2I_a} - \dfrac{1}{2I_b}\right)\hat{N}_a^2, \quad \hat{H}_{\text{rot}}|NMK\rangle = \left[\dfrac{\hbar^2 N(N+1)}{2I_b} + \dfrac{\hbar^2 K^2}{2}\left(\dfrac{1}{I_a} - \dfrac{1}{I_b}\right)\right]|NMK\rangle$
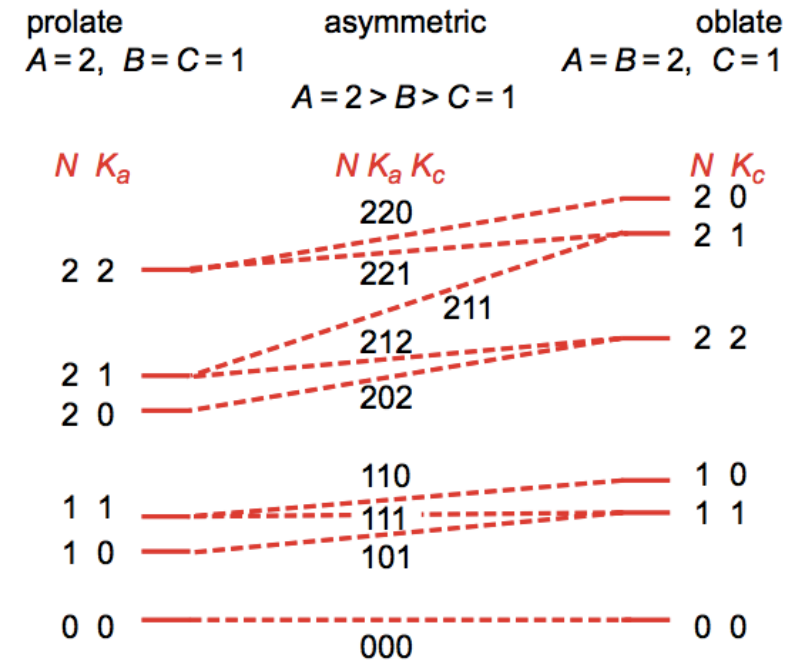
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Molecular Rotation and Vibration

Molecular Rotation

We can dinstinguish four types of molecules:

Asymmetric top: Can not be solved in closed form.

Ansatz 1 – Interpolation between prolate and oblate

prolate	asymmetric	oblate
$A=2$, $B=C=1$	$A=2>B>C=1$	$A=B=2$, $C=1$

Ansatz 2 – Ansatz via eigenfunctions of symmetric top

$$\widehat{H}_{\rm rot} = \alpha \widehat{N}^2 + \beta \widehat{N}_c^2 + \gamma[(\widehat{N}^+)^2 + (\widehat{N}^-)^2]$$

describes deviation from symmetric top

$$|NM\Gamma\rangle = \sum_{K=-N}^{N} f_{NK}|NMK\rangle$$

Molecular Vibration

For nonlinear molecules, we have $3\mathcal{N} - 6$ degrees of vibrational motion.

A series expansion of the PES at the minimum yields

$$V = V_0 + \sum_{i}^{3\mathcal{N}-6} \left.\frac{\partial V}{\partial \xi_i}\right|_{\xi_i=0} \xi_i + \frac{1}{2}\sum_{i,j}^{3\mathcal{N}-6} \left.\frac{\partial^2 V}{\partial \xi_i \partial \xi_j}\right|_0 \xi_i \xi_j$$

The first derivative vanishes, and we can approximate the total nuclear energy as

$$W = \frac{1}{2}\sum_{i}^{3\mathcal{N}-6} m_i \dot{\xi}_i^2 + \frac{1}{2}\sum_{i,j}^{3\mathcal{N}-6} \left.\frac{\partial^2 V}{\partial \xi_i \partial \xi_j}\right|_0 \xi_i \xi_j$$

In a next step, we introduce mass-weighted coordinates $q_i = \sqrt{m_i}\xi_i$

and define the Hessian matrix as $V_{ij} = \left.\frac{\partial^2 V}{\partial q_i \partial q_j}\right|_0$

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Molecular Vibration

We obtain
$$W = \frac{1}{2} \sum_{i}^{3\mathcal{N}-6} \dot{q}_i^2 + \frac{1}{2} \sum_{i,j}^{3\mathcal{N}-6} V_{ij} q_i q_j = \frac{1}{2} \tilde{\dot{q}} \cdot \dot{q} + \frac{1}{2} \tilde{q} \hat{V} q$$

In general, $V_{ij} \neq 0$ so seek new, decoupled coordinates **Q**, which diagonalize V.

$$\hat{A}^{-1} \hat{V} \hat{A} = \hat{\Omega} \qquad Q = \hat{A}^{-1} q$$

With this set of normal coordinates, we can write the total nuclear energy as

$$W = \frac{1}{2} \tilde{\dot{Q}} \dot{Q} + \frac{1}{2} \tilde{Q} \hat{\Omega} Q = \frac{1}{2} \sum_{i} \left(\dot{Q}_i^2 + \omega_i^2 Q_i^2 \right) = T + V$$

The potential energy is now a simple sum over 3N-6 decoupled 1D oscillators.

Molecular Vibration

The Hamiltonian reads: $H = \frac{1}{2} \sum_i \left(P_i^2 + \omega_i^2 Q_i^2 \right) = \sum_i (T_i + V_i)$

$$\dot{P}_i = -\frac{\partial H}{\partial Q_i} = -\omega_i^2 Q_i = \ddot{Q}_i \implies \ddot{Q}_i + \omega_i^2 Q_i = 0$$

Solving these equations of motion we obtain solutions $Q_i(t) = Q_i(0) e^{\pm i \omega_i t}$.

The total energy is given by $W = \sum_i (v_i + 1/2) \hbar \omega_i$.

To visualize the corresponding motion, we transform back into Cartesian coordinates

$$\boldsymbol{q} = \hat{A} \boldsymbol{Q} \quad \text{or} \quad q_j = \sum_k A_{jk} Q_k$$

A normal vibration q_i is characterized by its delocalisation

and the in-phase motion of all atoms of the system with ω_i.

Thermochemistry

The PES obtained from electronic structure calculations is describing the system at T= 0 K.

For finite temperatures, we have to apply corrections to the PES, going from U to G, the Gibbs energy or "Freie Enthalpie".

The partition sum Q for an N-particle system with possible total Energies E_i is given by

$$Q = \sum_{i}^{\infty} e^{-E_i/kT}$$

(In German commonly denoted as F, "freie Energie")

Why is Q interesting? Any thermodynamic function (U,S,H,A,G) can be expressed with it:

$$U = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V$$

$$A = -kT\ln Q$$

$$P = -\left(\frac{\partial A}{\partial V}\right)_T = kT\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

$$H = U + PV = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_V + kTV\left(\frac{\partial \ln Q}{\partial V}\right)_T$$

$$S = \frac{U - A}{T} = kT\left(\frac{\partial \ln Q}{\partial T}\right)_V + k\ln Q$$

$$G = H - TS = kTV\left(\frac{\partial \ln Q}{\partial V}\right)_T - kT\ln Q$$

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Thermochemistry

Assuming that the total energy can be written in separate terms implies that the partition function is a product of contributions.

$$\varepsilon_{tot} = \varepsilon_{trans} + \varepsilon_{rot} + \varepsilon_{vib} + \varepsilon_{elec}$$

$$q_{tot} = q_{trans} q_{rot} q_{vib} q_{elec}$$

$$H_{tot} = H_{trans} + H_{rot} + H_{vib} + H_{elec}$$

$$S_{tot} = S_{trans} + S_{rot} + S_{vib} + S_{elec}$$

Ingredients (see Jensen for details):

$$q_{trans} = \left(\frac{2\pi M k T}{h^2}\right) V$$

$$q_{rot} = \frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 k T}{h^2}\right)^{3/2} \sqrt{I_1 I_2 I_3}$$

$$q_{vib} = \prod_{i=1}^{3N_{atom}-6(7)} \frac{e^{-h v_i/2kT}}{1 - e^{-h v_i/kT}}$$

$$q_{elec} = \sum_{i=0}^{\infty} g_i e^{-\varepsilon_i/kT} \approx g_0 e^{-\varepsilon_0/kT}$$

electronic degeneracy

Thermochemistry

To build the Gibbs energy (or "freie Enthalpie") G = H - TS we need H and S:

$$H_{\text{trans}} = \tfrac{5}{2}RT$$

$$H_{\text{rot}} = \tfrac{3}{2}RT$$

$$H_{\text{vib}} = R \sum_{i=1}^{3N-6(7)} \left(\frac{h\nu_i}{2k} + \frac{h\nu_i}{k} \frac{1}{e^{h\nu_i/kT} - 1} \right)$$

$$H_{\text{elec}}^{\text{reactant}} = 0$$

$$H_{\text{elec}}^{\text{TS}} = \Delta E^{\neq}$$

$$S_{\text{trans}} = \tfrac{5}{2}R + R \ln\left(\frac{V}{N_A} \left(\frac{2\pi M k T}{h^2} \right)^{3/2} \right)$$
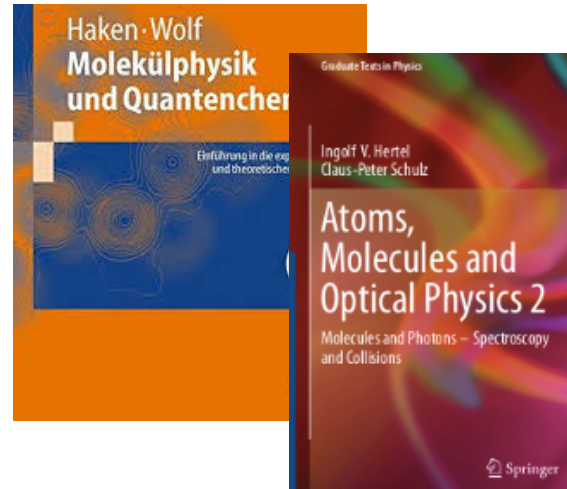
$$S_{\text{rot}} = R \left(\frac{3}{2} + \ln\left(\frac{\sqrt{\pi}}{\sigma} \left(\frac{8\pi^2 k T}{h^2} \right)^{3/2} \sqrt{I_1 I_2 I_3} \right) \right)$$

$$S_{\text{vib}} = R \sum_{i=1}^{3N-6(7)} \left(\frac{h\nu_i}{kT} \frac{1}{e^{h\nu_i/kT} - 1} - \ln(1 - e^{-h\nu_i/kT}) \right)$$

$$S_{\text{elec}}^{\text{reactant}} = S_{\text{elec}}^{\text{TS}} = R \ln g_0$$

As can be seen, in order to calculate G, we need to know the molecular mass, the moment

of inertia, the electronic degeneracy and the Hessian in order to calculate the frequencies.

B) **Group Theory in Molecular Physics**

Symmetry Operations and Elements

E	Identity (no change) or rotation through 360° (E originating from the German word *Einheit* = unit or unity).
C_n	Rotation in respect of a symmetry axis through an angle $2\pi/n$ with $n = 2, 3, \ldots$. Applying this operation k times is denoted by C_n^k. With these definitions the identity becomes $E = C_n^n$.
σ	Reflection at a plane – for which $\sigma\sigma = \sigma^2 = E$ holds.
σ_h	Special reflection at (horizontal) plane perpendicular to the principle axis of symmetry (axis with the highest n).
σ_v	Special reflection at a (vertical) plane containing the principle axis of symmetry.
σ_d	Diagonal or dihedral reflection, a special case of σ_v in which the vertical plane bisects two twofold symmetry axes perpendicular to the principle symmetry axis.
ι	Inversion or point reflection at the origin.
S_n	Rotation-reflection or improper rotation: a rotation through $2\pi/n$ with successive reflection in a plane perpendicular to that rotation axis. Thus $S_n = \sigma_h C_n = C_n \sigma_h$. Also $S_2 = \iota$ as well as $\iota\sigma_h = C_2$ and $\iota C_2 = \sigma_h$ holds.

Point Groups

These symmetry operations may be combined to mathematical groups. They are called *point groups* since each symmetry operation leaves at least one point in space invariant.

Groups of Low Symmetry

C_1 This trivial group contains all molecules which have no symmetries at all; e.g. CHFClBr or 1,2-dibromo-1,1-dichloroethane ($C_2H_2Br_2Cl_2$).

C_i $= S_2$ contains only ι as symmetry operation; e.g. 1,2-dibromo-1,2-dichloroethane ($C_2H_2Br_2Cl_2$).

C_s Only mirror symmetry in respect of a single plane; e.g. nitrosyl chloride (O=N−Cl).

Rotation Groups

C_n Only rotations though an angle $2\pi/n$ around an axis ($C_n^1, C_n^2, \ldots, C_n^k, \ldots$, $C_n^n = E$), i.e. n elements, including E; e.g. hydrogen peroxide (H_2O_2) has C_2 symmetry.

C_{nh} Rotation though $2\pi/n$ and reflection, σ_h, in a plane perpendicular to the rotational axis and in addition inversion (for $n = 2$) or $n - 1$ improper rotations (for $n > 2$), i.e. $2n$ elements; e.g. boric acid (B(OH)$_3$) belongs to the C_{3h} group.

C_{nv} Rotation though $2\pi/n$ as well as n reflections, σ_v, in planes parallel to the rotational axis, i.e. $2n$ elements; e.g. the water molecule (H_2O) has C_{2v}, ammonia (NH$_3$) has C_{3v} symmetry.

Point Groups

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Dihedral Groups

D_n One C_n axis (principle axis) and n C_2 axes perpendicular to the principle axis.

D_{nh} As D_n, with an additional reflection plane, σ_h, perpendicular to the principle axis; e.g ethene (C_2H_4) belongs to the group D_{2h} and benzene, the simplest aromatic ring (C_6H_6) has D_{6h} symmetry.

D_{nd} As D_n, and in addition n reflection planes σ_d parallel to the principle axis; e.g. ethane (C_2H_6) has D_{3d} symmetry.

Special Point Groups

$C_{\infty v}$ Linear molecules without inversion centre; e.g. HCl, N_2O.

$D_{\infty h}$ Linear molecules with inversion centre; e.g. H_2, CO_2.

Improper Rotation Groups

S_n Contains only the symmetry operation S_n. *Note*: S_2 corresponds to C_i, and if n is odd, $S_n = C_{nh}$. Only the groups $S_4, S_6, S_8, \ldots$ are genuine groups; e.g. the somewhat exotic molecule $1,1',1'',1'''$-methanetetrayltetrabenzene (4 benzene rings attached to one carbon atom) belongs to S_4.

Point Groups

These symmetry operations may be combined to mathematical groups. They are called *point groups* since each symmetry operation leaves at least one point in space invariant.

Tetrahedral Groups

T The group of genuine tetrahedral rotations: E, $4C_3$, $4C_3^2$, (axes from corners to the middle of opposite faces), $3C_2$ (axes from the middle of the edges to the middle of the opposite edges), in total 12 symmetry elements.

T_d As T and in addition the $6\sigma_d$ reflections and the respective $6S_4$ operations, in total 24 symmetry elements; e.g. methane (CH_4).

T_h As T and in addition all operations that arise from multiplication the former with inversion ι, in total again 24 symmetry elements; e.g. $C_{60}Br_{24}$.

Octahedral Group

O The group of true cube rotations: E, $8C_3$ (four 3-fold axes through the corners of the cube, with the three elements C_3^1, C_3^2 and $C_3^3 = E$, i.e. two new elements for each axis), $6C_4$ and $3C_2$ elements (3 coinciding C_2 and C_4 axes from the middle of the faces to the opposite faces, with the elements C_2^1 and C_4^1, $C_4^2 = C_2^1$, C_4^2, and $C_4^4 = E$, i.e. one C_2 element and two C_4 elements for each axis), and finally $6C_2'$ (axes from the middle of the edges to the middle of the opposite edges), in total 24 symmetry elements.

O_h Complete octahedral group: O and in addition the operations due to multiplication with inversion ι (improper rotations) lead to 48 symmetry elements; e.g. SF_6.
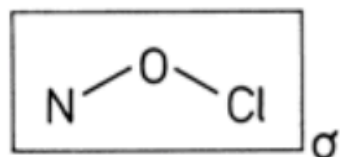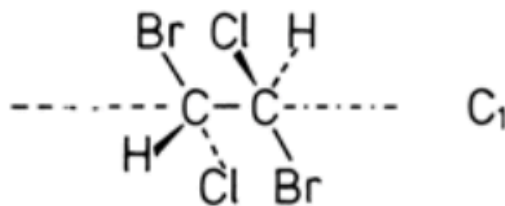
A decision tree for determining molecular symmetry
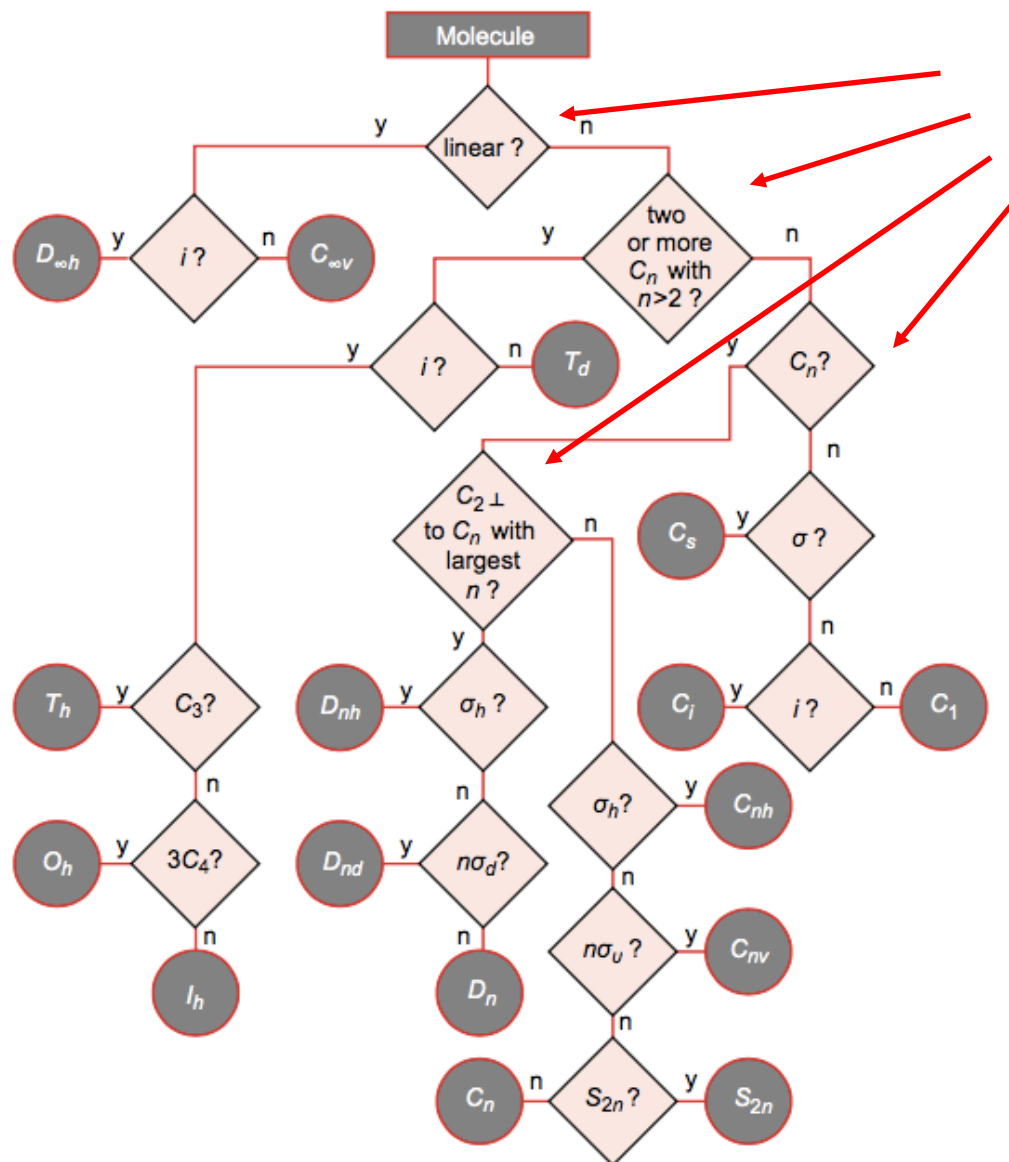
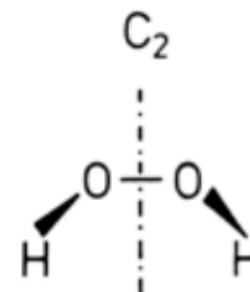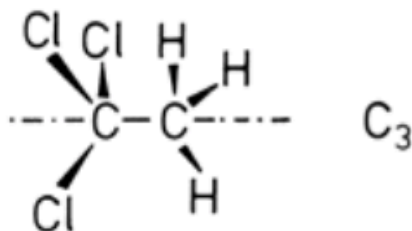looks complicated, but consists of just 4 essential questions!

Some examples

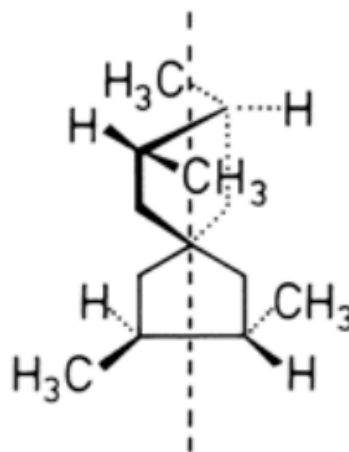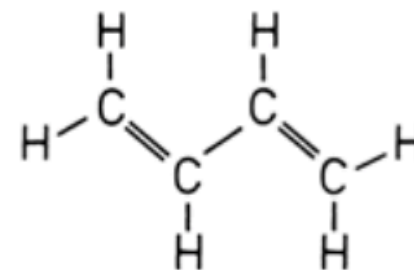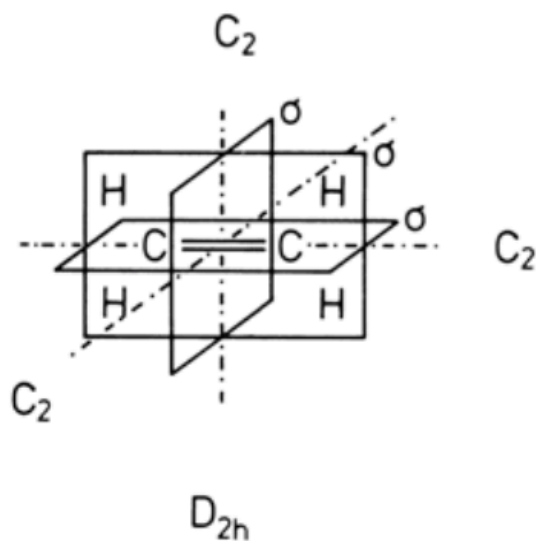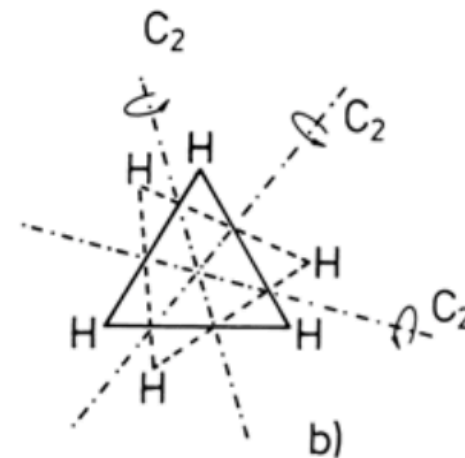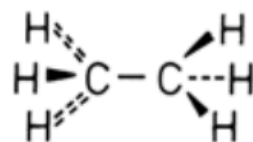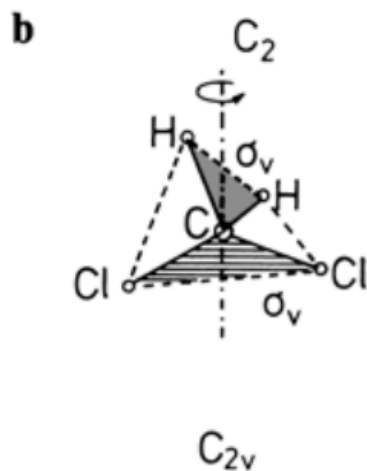Some examples
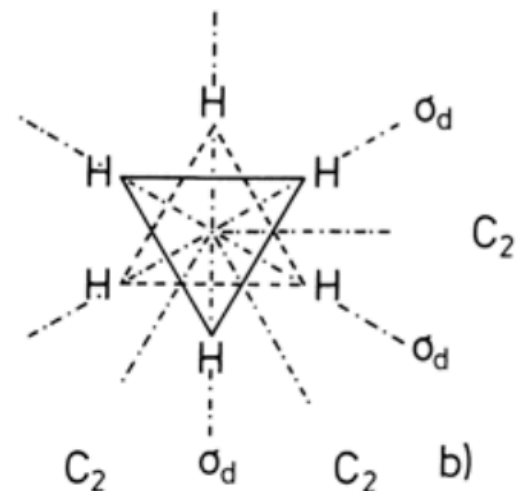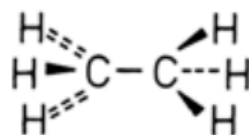
From atoms to molecules

From atomic physics we are familiar with the full three dimensional rotation group called O(3) or SO(3). This symmetry group determines the behaviour of angular momenta of atoms. Obviously, for polyatomic molecules this full freedom of rotation has to be replaced by the symmetry operations of the point groups. Each point group may be represented by a set of irreducible representations Γ_i.

The number of irreducible representations in a point group is equal to its dimension (i.e. to the number of different classes of symmetry operations). The irreducible representations Γ_i replace, so to say, the angular momentum states with quantum numbers LM for states (or lm for orbitals) in atomic physics.

As mentioned above, applying a certain class of symmetry operations onto an irreducible representation (a molecular state, an orbital, a normal mode) corresponds to a linear transformation in space. It turns out, that the entirety of characters for all symmetry operations in a group onto one irreducible representation Γ_i fully characterizes the symmetry properties of this Γ_i.

Hence, the characters of all irreducible representations of a point group are summarized in a so called character table.

Mullikan's name conventions for irreducible representations

Symbol	Degeneracy	Symmetry
A	1	$+$ in respect of C_n
B	1	$-$ in respect of C_n
E	2	
T	3	
G, H	4, 5	in I and I_h

| Indices		Symmetry in respect of				
		ι	σ_h	C_2'	C_2''	σ_v
sub	g, u	$+, -$				
sup	$', ''$		$+, -$			
sub	$1, 2$			$+, -$	or	$+, -$

C_n stands for rotation around the principle axis, C_2' and C_2'' for rotation around one or two axes, respectively, perpendicular to it; the subscripts for A and B symbols depend on the special point group.

Electronic orbitals are written in lower case letters, total states in capital letters. For linear molecules the notation Σ, Π, ... is maintained.

A first example: the water molecule

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz
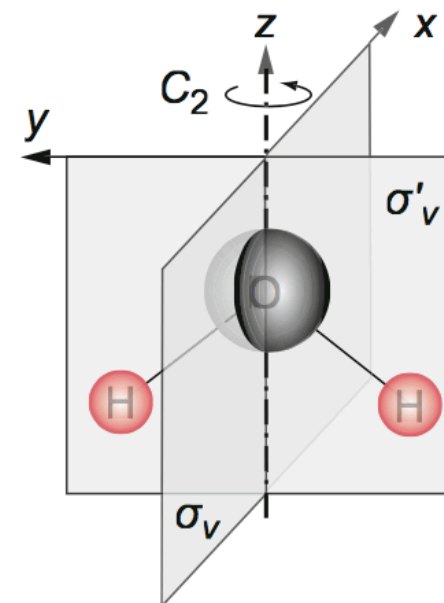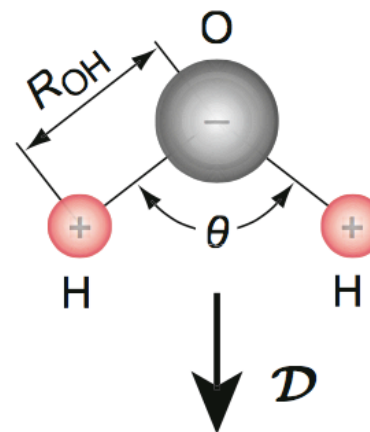
What to do with this information?

Example: We can use this table to check if integrals are nonzero, e.g. $<B_2|\mu_x|A_2>$, the x-component of the dipole transition operator:

The product of the three corresponding representations must contain the highest symmetry representation of the point group.

Here, (B2)*(B1)*(A2) = A1, so it is an allowed transition.