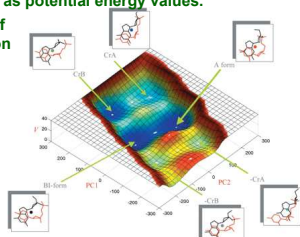


The use of quantum chemistry Definitions

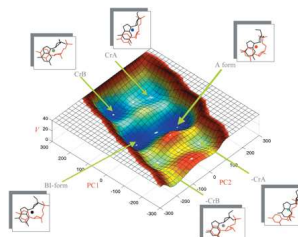
- The purpose of quantum chemistry is to determine the equilibrium geometries of molecules.
- **Born-Oppenheimer approximation:** the assumption that the motion of atomic nuclei and electrons in a molecule can be separated.
- **Potential energy surface (PES):** We can assign the energy of electrons to space coordinates as potential energy values.
- A PES describes the energy of a system (especially a collection of atoms) in terms of certain parameters, normally the positions of the atoms.



The use of quantum chemistry Chemically important points of PES

Minima

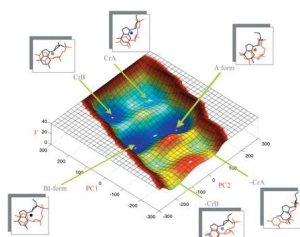
- The individual molecules, stable conformers can be assigned to them.
- First derivatives (gradients) are 0, second derivatives are positive.
- There are global and local minima.
- The "depth" of the minima sets the relative thermodynamic stability of each molecule/conformer.



The use of quantum chemistry Chemically important points of PES

Saddle points

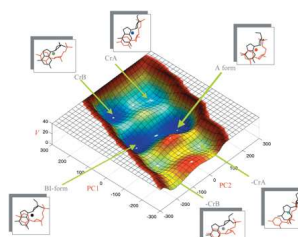
- Gradients are 0, second derivatives are negative except for one.



The use of quantum chemistry Chemically important points of PES

Maxima

- First derivatives (gradients) are 0, second derivatives are negative.



The use of quantum chemistry Calculation methods

Molecular mechanics:

- The interactions between atoms are described with classical mechanical potentials.
- Due to its speed, large systems can be described and it is suitable for large-scale computation (biological systems, molecular dynamics). However, the results provided are relatively inaccurate.
- Unsuitable for examining electronic structure.

Hartree-Fock method:

- A method developed to solve the non-relativistic Schrödinger equation.
- Equations using the Born-Oppenheimer approximation (separation of atomic nuclei and electron movements) and the single electron approximation (separation of single electron movements) are solved by the variational method/principle.

Base: Functions used to decompose the wave function.

(The individual atomic orbital functions of the LCAO series expansion are usually constructed from Gaussian functions. Base 3-21G* denotes the electron orbitals within the core of the atom, it consists of 3 Gaussian functions (with constant coefficients). The electron orbitals on the valence shell are constructed from separate functions composed of 2 or 1 Gaussian functions).

The use of quantum chemistry Calculation methods

Molecular mechanics:

- The interactions between atoms are described with classical mechanical potentials.
- Due to its speed, large systems can be described and it is suitable for large-scale computation (biological systems, molecular dynamics). However, the results provided are relatively inaccurate.
- Unsuitable for examining electronic structure.

Hartree-Fock method:

- A method developed to solve the non-relativistic Schrödinger equation.
- Equations using the Born-Oppenheimer approximation (separation of atomic nuclei and electron movements) and the single electron approximation (separation of single electron movements) are solved by the variational method/principle.

Semiempirical calculations:

• By neglecting and/or substituting some of the integrals that occur during the HF method with experimental values, we can make faster but more inaccurate calculations.

The use of quantum chemistry Calculation methods

Molecular mechanics:

- The interactions between atoms are described with classical mechanical potentials.
- Due to its speed, large systems can be described and it is suitable for large-scale computation (biological systems, molecular dynamics). However, the results provided are relatively inaccurate.
- Unsuitable for examining electronic structure.

Hartree-Fock method:

- A method developed to solve the non-relativistic Schrödinger equation.
- Equations using the Born-Oppenheimer approximation (separation of atomic nuclei and electron movements) and the single electron approximation (separation of single electron movements) are solved by the variational method/principle.

Post-HF calculations:

- These are methods for taking into account the effects neglected by the one-electron approach (such as electron correlation).
- Their calculation costs are significantly higher than those for the HF method.

The use of quantum chemistry Calculation methods

Molecular mechanics:

- The interactions between atoms are described with classical mechanical potentials.
- Due to its speed, large systems can be described and it is suitable for large-scale computation (biological systems, molecular dynamics). However, the results provided are relatively inaccurate.
- Unsuitable for examining electronic structure.

Hartree-Fock method:

- A method developed to solve the non-relativistic Schrödinger equation.
- Equations using the Born-Oppenheimer approximation (separation of atomic nuclei and electron movements) and the single electron approximation (separation of single electron movements) are solved by the variational method/principle.

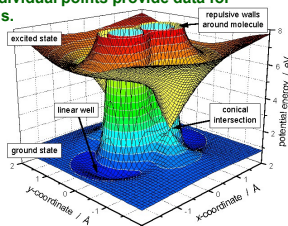
DFT (Density Functional Theory):

- Instead of the wave function, it uses the electron density to calculate the characteristics of the chemical system.
- The cost of DFT calculations (processor time, memory, data storage) is similar to HF calculations but gives better results.

The use of quantum chemistry Some computable properties

Energy:

- Total energy according to the applied method, base, atomic coordinates (geometry) and electron state.
- Its value itself is not useful for many, but when plotted against the coordinates of the atomic nuclei, it is possible to draw the PES where the energy differences between the individual points provide data for modeling chemical transformations.
- Energy differences of PES's of the same atomic nucleus configurations but different electron states give information about the excitation process.



The use of quantum chemistry Some computable properties

Structure:

- Coordinate set for a well-defined point (minimum, saddle, ...) of a given PES (e.g. bond angles, bond distances, di-angular angles).
- Equilibrium geometry: coordinates belonging to a (local or global) minimum. Steps of geometry optimization:

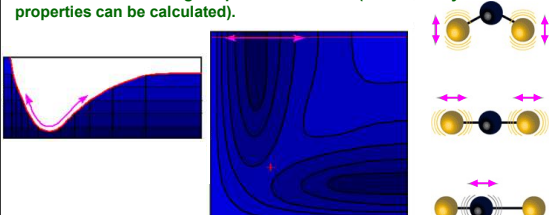
```

    graph TD
      A[choosing a starting geometry] --> B[calculation of energy]
      B --> C[calculation of gradients]
      C --> D[change geometry in the direction of the gradient]
      D --> E[calculation of energy again]
      E --> F[if the change of energy and gradients is small enough, STOP]
      F --> A
  
```

The use of quantum chemistry Some computable properties

Vibrations:

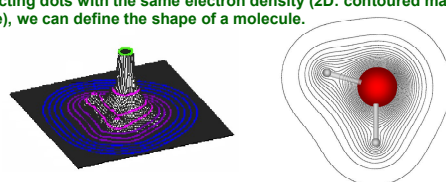
- Assuming harmonic oscillations, the second derivatives of the PES against spatial coordinates (force constants) can be used to calculate the frequencies of the molecular vibrations.
- In addition to characterizing a given point of the PES, they are also suitable for determining the partition function (i.e. thermodynamic properties can be calculated).



The use of quantum chemistry Some computable properties

Electron density:

- The 3D distribution of electrons determined by the wave function (or its square).
- By connecting dots with the same electron density (2D: contoured map, 3D: surface), we can define the shape of a molecule.



The use of quantum chemistry

Some computable properties

Electron density:

- The 3D distribution of electrons determined by the wave function (or its square).
- By connecting dots with the same electron density (2D: contoured map, 3D: surface), we can define the shape of a molecule.

Electron density in water molecule (electron/Å³)

The shape of the molecule depends on the value of electron density!

The use of quantum chemistry

Some computable properties

Electron density:

- The 3D distribution of electrons determined by the wave function (or its square).
- By connecting dots with the same electron density (2D: contoured map, 3D: surface), we can define the shape of a molecule.

Electron density in water molecule (electron/Å³)

The shape of the molecule depends on the value of electron density!

The use of quantum chemistry

Some computable properties

Electron density:

- The 3D distribution of electrons determined by the wave function (or its square).
- By connecting dots with the same electron density (2D: contoured map, 3D: surface), we can define the shape of a molecule.
- The points of such a surface can be colored based on their electrostatic potential values. In such a figure, the positively or negatively charged groups/parts of a molecule can be identified.

The use of quantum chemistry

Some computable properties

Electron density:

- The 3D distribution of electrons determined by the wave function (or its square).
- By connecting dots with the same electron density (2D: contoured map, 3D: surface), we can define the shape of a molecule.
- The points of such a surface can be colored based on their electrostatic potential values. In such a figure, the positively or negatively charged groups/parts of a molecule can be identified.

The use of quantum chemistry

Some computable properties

Atomic charges:

- Determining the values of electron densities (3D distribution) and assigning them to individual atoms (points) by means of an arbitrary method.

Structures of molecules

- Born-Oppenheimer approximation:** the assumption that the motion of atomic nuclei and electrons in a molecule can be separated.
- Potential energy surface (PES):** We can assign the energy of electrons to space coordinates as potential energy values.

The contribution of the vibration energy to E_{tot} is ignored...

↓

The goal is to find the geometric parameters for which the electron energy is minimal.

In addition to the Schrödinger equation for electrons, the Schrödinger equation for the vibrations of the atomic nuclei must also be solved...

↓

Until today, only for molecules containing a few atoms have succeeded.

Structures of molecules

Comparison of calculated and measured geometric parameters:

- All physical methods have their own measurement accuracy/inaccuracy.
- Experimental methods never measure geometric data directly, but can only be calculated/inferred from them.

r_e, α_e : equilibrium geometry (*ab initio* calculations)
 r_0, α_0 : ground state geometry
 r_s, α_s : isotope substituted geometry

$r_e \leq r_s \leq r_0$

MW spectroscopy
 IR spectroscopy
 high resolution electron spectroscopy
 electron diffraction
 X-ray diffraction

Structures of molecules

Comparison of calculated and measured geometric parameters:

- All physical methods have their own measurement accuracy/inaccuracy.
- Experimental methods never measure geometric data directly, but can only be calculated/inferred from them.

r_e, α_e : equilibrium geometry (*ab initio* calculations)
 r_0, α_0 : ground state geometry
 r_s, α_s : isotope substituted geometry

$r_e \leq r_s \leq r_0$

MW spectroscopy
 IR spectroscopy
 high resolution electron spectroscopy
 electron diffraction
 X-ray diffraction

Structures of molecules

Comparison of calculated and measured geometric parameters:

- All physical methods have their own measurement accuracy/inaccuracy.
- Experimental methods never measure geometric data directly, but can only be calculated/inferred from them.

r_e, α_e : equilibrium geometry (*ab initio* calculations)
 r_0, α_0 : ground state geometry
 r_s, α_s : isotope substituted geometry

$r_e \leq r_s \leq r_0$

MW spectroscopy
 IR spectroscopy
 high resolution electron spectroscopy
 electron diffraction
 X-ray diffraction

Structures of molecules

Comparison of calculated and measured geometric parameters:

- All physical methods have their own measurement accuracy/inaccuracy.
- Experimental methods never measure geometric data directly, but can only be calculated/inferred from them.

r_e, α_e : equilibrium geometry (*ab initio* calculations)
 r_0, α_0 : ground state geometry
 r_s, α_s : isotope substituted geometry

$r_e \leq r_s \leq r_0$

MW spectroscopy
 IR spectroscopy
 high resolution electron spectroscopy
 electron diffraction
 X-ray diffraction

r_s : thermal average of atomic distances

Structures of molecules

Comparison of calculated and measured geometric parameters:

- All physical methods have their own measurement accuracy/inaccuracy.
- Experimental methods never measure geometric data directly, but can only be calculated/inferred from them.

r_s : thermal average of atomic distances
 r_0 : in a solid, crystalline material

MW spectroscopy
 IR spectroscopy
 high resolution electron spectroscopy
 electron diffraction
 X-ray diffraction

Structures of molecules

Determination of equilibrium geometry

Fletcher-Powell algorithm:

1. The electron energy for a given starting geometry (i.e. in a given point of the PES, \bullet) is calculated.
2. An arbitrary internal coordinate is selected, and then the energy along this coordinate at two further points (\bullet) is determined.
3. A parabola is fitted to the three points (.....), and then we find the minimum of the parabola.
4. The energy in the minimum point is calculated, then we choose another internal coordinate and steps 2.-4. are repeated.

1. If we find the minimum of the PES according to each coordinate, then we can stop.

- ⊕ general
- ⊕ compatible with all energy calculation methods
- ⊖ slow

Structures of molecules

Determination of equilibrium geometry

Gradient method:
 There are many different algorithms, but they have the same principle:
 • The 1st and 2nd derivatives of the energy coordinates give the gradient vector (the magnitude of the force in a given direction) and the Hess matrix (force constants).

Elements of gradient vector: $F_{ix} = -\left(\frac{dE}{dx}\right)_{x=x_i}$

Elements of Hess matrix: $H_{ixz} = \left(\frac{d^2E}{dxdz}\right)_{x=x_i, z=z_i}$

Structures of molecules

Determination of equilibrium geometry

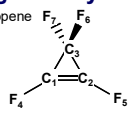
Gradient method:
 There are many different algorithms, but they have the same principle:
 • The 1st and 2nd derivatives of the energy coordinates give the gradient vector (the magnitude of the force in a given direction) and the Hess matrix (force constants).

1. We pick a point near the presumed minimum on PES.
2. We are looking for the steepest slope and take a step in this direction.
3. PES is approximated with parabola toward the gradient. The size of the next step is chosen to reach the minimum of the parabola.
4. E and the gradient is calculated in the new point and we take a step again to F (use of the Hess matrix is advisable).
5. If each element of the gradient vector is less than a predetermined threshold, and when all of the force constants are positive, then we stop.

⊗ fast (analytical differentiation can be used)
 ⊗ for a system with n variables, there are n to 2n steps necessary to calculate the equilibrium geometry with ±0.001Å and ±0.1° accuracy.

Structures of molecules

Determination of equilibrium geometry

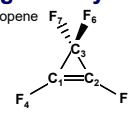
Perfluorinated cyclopropene 

- Molecular formula: C₃F₄
- Toxic
- Flammable and explosive
- There are several sources of experimental results in its structure

	r(C ₂ -C ₃) (pm)	r(C ₁ -C ₂) (pm)	r(C ₁ -F ₄) (pm)	r(C ₃ -F ₆) (pm)	α(C ₁ C ₂ F ₅) (°)	α(F ₆ C ₃ F ₇) (°)
HF/DZP	Consideration of electron correlation:					
HF/TZ2P	• HF (Hartree-Fock): no					
MP2/DZP	• MP2 (second order Møller–Plesset perturbation): yes					
MP2/TZ2P						
ED	Base:					
ED/MW	• DZP: double zeta polarization function (112 base funct.)					
ED/MW/NMR	• TZ2P: triple zeta 2 polarization function (182 base f.)					
RD						

Structures of molecules

Determination of equilibrium geometry

Perfluorinated cyclopropene 

- Molecular formula: C₃F₄
- Toxic
- Flammable and explosive
- There are several sources of experimental results in its structure

	r(C ₂ -C ₃) (pm)	r(C ₁ -C ₂) (pm)	r(C ₁ -F ₄) (pm)	r(C ₃ -F ₆) (pm)	α(C ₁ C ₂ F ₅) (°)	α(F ₆ C ₃ F ₇) (°)
HF/DZP	144.8	128.4	128.5	133.1	150.1	105.8
HF/TZ2P	144.6	128.0	128.3	133.0	149.8	105.7
MP2/DZP	146.9	132.2	131.0	135.7	150.0	105.7
MP2/TZ2P	146.5	131.2	130.8	135.6	149.8	105.8
ED	146.8 (3)	131.4 (8)	131.3 (4)	135.6 (3)		
ED/MW	146.0 (3)	131.0 (8)	131.3 (3)	135.8 (3)		
ED/MW/NMR	146.1 (3)	130.7 (13)	131.5 (3)	136.1 (4)	150.4 (9)	105.4 (5)
RD	145.3 (3)	129.6 (4)	131.2 (2)	137.0 (2)	149.9 (6)	105.4 (5)

Structures of molecules

Determination of equilibrium geometry

Calculating equilibrium binding distances is not enough. The relationship between calculated and measured parameters, possible errors and their causes should be carefully analyzed.

	r(C ₂ -C ₃) (pm)	r(C ₁ -C ₂) (pm)	r(C ₁ -F ₄) (pm)	r(C ₃ -F ₆) (pm)	α(C ₁ C ₂ F ₅) (°)	α(F ₆ C ₃ F ₇) (°)
HF/DZP	144.8	128.4	128.5	133.1	150.1	105.8
HF/TZ2P	144.6	128.0	128.3	133.0	149.8	105.7
MP2/DZP	146.9	132.2	131.0	135.7	150.0	105.7
MP2/TZ2P	146.5	131.2	130.8	135.6	149.8	105.8
ED	146.8 (3)	131.4 (8)	131.3 (4)	135.6 (3)		
ED/MW	146.0 (3)	131.0 (8)	131.3 (3)	135.8 (3)		
ED/MW/NMR	146.1 (3)	130.7 (13)	131.5 (3)	136.1 (4)	150.4 (9)	105.4 (5)
RD	145.3 (3)	129.6 (4)	131.2 (2)	137.0 (2)	149.9 (6)	105.4 (5)


Structures of molecules

Structures and their relative energies

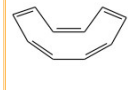
[10] annulenes

- Molecular formula: C₁₀H₁₀
- Olefin (conjugated) or aromatic properties?

Spectroscopic methods indicate the former in both *cis* and *trans* configurations.
 Hückel rule: (4n+2) π-electron system



planar
D_{10h}



„boat“
C₈

Structures of molecules

Structures and their relative energies

[10] annulenes

- Molecular formula: $C_{10}H_{10}$
- Olefin (conjugated) or aromatic properties?

Spectroscopic methods indicate the former in both *cis* and *trans* configurations.

Hückel rule: $(4n+2)$ π -electron system

trans configuration

Structures of molecules

Structures and their relative energies

[10] annulenes

The relative energy of the "heart" conformer compared to the "twisted" structure:

	E_{rel} (kcal/mol)
AM1*	23.95
HF/DZP	10.44
RHF/DZP*	11.47
MP2/DZ	0.56
MP2/DZP	-4.22
MP2/TZ2P	-7.06
MP3/DZP	8.21
MP4/DZP	1.35
B3LYP/DZP	-9.11
BLYP/DZP	-12.76
CCSD/DZP	10.75
UNO-SCF/DZP	11.15

trans configuration

Structures of molecules

Structures and their relative energies

[10] annulenes

The relative energy of the "heart" conformer compared to the "twisted" structure:

	E_{rel} (kcal/mol)
AM1*	23.95
HF/DZP	10.44
RHF/DZP*	11.47
MP2/DZ	0.56
MP2/DZP	-4.22
MP2/TZ2P	-7.06
MP3/DZP	8.21
MP4/DZP	1.35
B3LYP/DZP	-9.11
BLYP/DZP	-12.76
CCSD/DZP	10.75
UNO-SCF/DZP	11.15

trans configuration

Structures of molecules

Structures and their relative energies

[10] annulenes

The relative energy of the "heart" conformer compared to the "twisted" structure:

	E_{rel} (kcal/mol)
AM1*	23.95
HF/DZP	10.44
RHF/DZP*	11.47
MP2/DZ	0.56
MP2/DZP	-4.22
MP2/TZ2P	-7.06
MP3/DZP	8.21
MP4/DZP	1.35
B3LYP/DZP	-9.11
BLYP/DZP	-12.76
CCSD/DZP	10.75
UNO-SCF/DZP	11.15

trans configuration

Thermodynamic calculations

- Calculation of ΔH , ΔS and ΔG .
- Statistical thermodynamics (statistical mechanics): establishes a connection between quantum chemistry and thermodynamics.
- Boltzmann factor:

$$p_j \propto \exp\left(-\frac{\epsilon_j}{kT}\right)$$

probability of state j

The sum of probabilities is 1, so:

$$p_j = \frac{\exp\left(-\frac{\epsilon_j}{kT}\right)}{\sum_j \exp\left(-\frac{\epsilon_j}{kT}\right)} = \frac{\exp\left(-\frac{\epsilon_j}{kT}\right)}{q}$$

Partition function

Thermodynamic calculations

- Using the partition function, the macroscopic properties of the system (energy, molar heat capacity, pressure) can be calculated:

$$q = q_{translation} \cdot q_{rotation} \cdot q_{vibration} \cdot q_{electronic}$$

$$q_{trans} = \left(\frac{2\pi M kT}{h^2}\right)^{3/2} V$$

molar weight, volume

$$q_{rot} = \sum_{j=0}^{\infty} (2J+1) \exp\left(-\frac{E_j}{kT}\right)$$

individual rotational energy levels

$$q_{vib} = \prod_{i=1}^{3N-6} \frac{\exp(-h\nu_i/2kT)}{1 - \exp(-h\nu_i/2kT)}$$

frequency of the i^{th} vibration

$$q_{elec} = g$$

degree of degeneration for the ground state

Thermodynamic calculations

- Using the partition function, the average energy of the system can also be calculated:

$$E_{\text{tot}} = E_{\text{trans}} + E_{\text{rot}} + E_{\text{vib}} + E_{\text{elec}} + E_{\text{nucl. repulsion}}$$

Can be given from quantum chemical calculations

$$E_{\text{vib}} = \sum_{i=1}^{3N-6} \left(\frac{h\nu_i}{2} + \frac{h\nu_i}{\exp(-h\nu_i/kT) - 1} \right)$$

The zero point energy of the molecule

$$E_{\text{rot}} = \frac{3}{2} NkT \text{ (non-linear)}, \quad E_{\text{rot}} = NkT \text{ (linear)}$$

$$E_{\text{trans}} = \frac{3}{2} NkT$$

Sources of error:

- Coupling between different movements
- Managing internal rotation as vibration

Thermodynamic calculations

- Using the gas law:

$$\Delta H = \Delta E + p\Delta V = \Delta E + \Delta nRT$$

- Absolute entropy of the system:

$$S = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{elec}} - nR [\ln(n \cdot N_0) - 1]$$

$$S_{\text{trans}} = nR \left\{ \frac{3}{2} + \ln \left[\left(\frac{2\pi MkT}{h^2} \right)^{3/2} \left(\frac{nRT}{p} \right) \right] \right\}$$

$$S_{\text{rot}} = nR \left\{ \frac{3}{2} + \ln \left[\frac{(\pi V_A V_B V_C)^{1/2}}{\sigma} \right] \right\}$$

Symmetry number (number of non-distinguishable spatial orientations of molecules)

Thermodynamic calculations

- Using the gas law:

$$\Delta H = \Delta E + p\Delta V = \Delta E + \Delta nRT$$

- Absolute entropy of the system:

$$S = S_{\text{trans}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{elec}} - nR [\ln(n \cdot N_0) - 1]$$

$$S_{\text{vib}} = nR \sum_i \left\{ \left[\left(\frac{h\nu_i}{kT} \right) \cdot e^{h\nu_i/kT} - 1 \right] - \ln(1 - e^{-h\nu_i/kT}) \right\}$$

$$S_{\text{elec}} = nR \ln g$$

It is known from classical thermodynamics that:

$$\Delta G = \Delta H - T\Delta S$$

Thermodynamic calculations

Dimerization enthalpy change

Hydrogen bond energy of the water dimer

- In the first approximation, the dimeric bonding energy is the energy difference between the dimer and the two monomers.
- The geometry can be calculated at a low level (e.g.: MP2).
- In the perturbation method, we only take into account the valence electrons, and we "freeze" the inner shells (*frozen core method*).
- Base-superposition error (BSSE, the same base for the monomer is different in "size" than for the dimer)

counterpoise (CP) method can be used to "offset" the effect.

Thermodynamic calculations

Dimerization enthalpy change

Hydrogen bond energy of the water dimer

Calculated: $\Delta E = -4.83$ kcal/mol

Method	DZ	TZ	QZ	5Z
MP2/cc-pVxZ	-7.5	-6.5	-5.5	-5.0
RI-MP2/cc-pVxZ	-7.5	-6.5	-5.5	-5.0
MP2/cc-pVxZ (CP corrected)	-7.5	-6.5	-5.5	-5.0
RI-MP2/cc-pVxZ (CP corrected)	-7.5	-6.5	-5.5	-5.0
MP2/aug-cc-pVxZ	-7.5	-6.5	-5.5	-5.0
MP2/aug-cc-pVxZ (CP corrected)	-7.5	-6.5	-5.5	-5.0
RI-MP2/aug-cc-pVxZ (CP corrected)	-7.5	-6.5	-5.5	-5.0

Thermodynamic calculations

Dimerization enthalpy change

Hydrogen bond energy of the water dimer

- More careful consideration of electron correlation (MP4 instead of MP2) results in an increase of energy only 0.05 kcal/mol.
- Effect of zero point energy
- Temperature increase from 0 K to the T of the measurement (375 K)
- Estimation of vibration anharmonicity

Calculated: $\Delta E = -4.83$ kcal/mol
 $\Delta H = -3.2(1)$ kcal/mol
 Measured: $\Delta H = -3.6(5)$ kcal/mol

- Experimental difficulties increase the inaccuracy of the measurement.
- Careful analysis of calculations, consideration of relevant factors and effects improve the accuracy of the calculation.

Chemical reactions

- There is limited experimental evidence of what is happening in a chemical process
- (products, product ratio, reaction rate, rate constant)

Assumption of reaction mechanism based on electrostatic properties.

Calculation of the total energy (or ΔG) for reagents, products, intermediates, transition states.

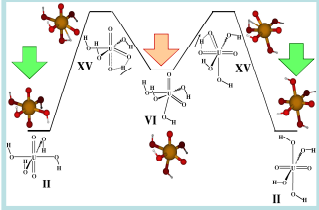
Calculation of the full PES.

Chemical reactions

Chemically important points of PES

Minima

- The individual molecules, stable conformers can be assigned to them.
- First derivatives (gradients) are 0, second derivatives are positive.
- There are global (reactant, product) and local minima (intermediate).
- The "depth" of the minima sets the relative thermodynamic stability of each molecule/conformer.

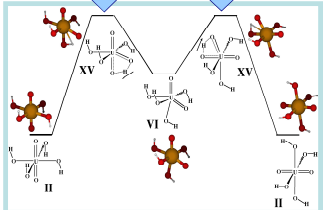


Chemical reactions

Chemically important points of PES

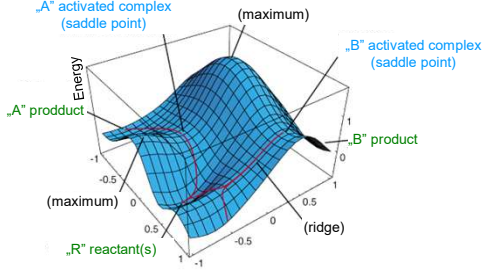
Saddle points

- Saddle points belong to the activated complexes of the reactions (or conformational changes).
- Gradients are 0, second derivatives are negative except for one.
- The „high" of the saddle point sets the rate (kinetics) of the reaction.



Chemical reactions

Chemically important points of PES



„A" product (maximum)

„B" product (maximum)

„R" reactant(s) (ridge)

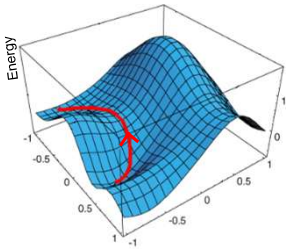
„A" activated complex (saddle point)

„B" activated complex (saddle point)

Chemical reactions

Reaction path:

- It runs along the potential surface
- Each of its points is a 3N dimensional vector



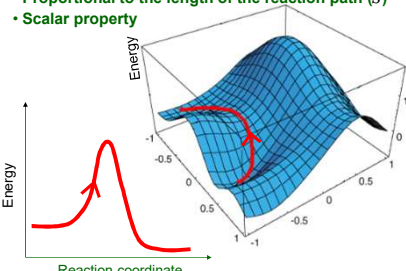
Chemical reactions

Reaction path:

- It runs along the potential surface
- Each of its points is a 3N dimensional vector

Reaction coordinate:

- Proportional to the length of the reaction path (S)
- Scalar property



Chemical reactions

Reaction path:

- It runs along the potential surface
- Each of its points is a 3N dimensional vector

Reaction coordinate:

- Proportional to the length of the reaction path (s)
- Scalar property

• Displacement along the reaction path: $ds^2 = \sum_{i=1}^{3N} (dq_i)^2$

The i^{th} coordinate of a point on the reaction path

• Direction of reaction path: $\eta = \frac{dq(s)}{ds} = \sum_{i=1}^{3N} \left(\frac{dq_i}{ds} \right) \mathbf{e}_i$

unit vector

• „Curvature“ of the reaction path: $\kappa(s) = \frac{d^2q}{ds^2}$

Chemical reactions

Reaction path:

- It runs along the potential surface
- Each of its points is a 3N dimensional vector

- There are many possible reaction pathways.
- *Intrinsic Reaction Coordinate (IRC)*: the path taken by a particle with infinitesimal speed along the energy gradient between the two minima through the saddle point.

• The calculation of IRC is also important if we are not interested in the whole reaction path, only at the critical points of the reaction.

